FINAL REPORT

Treatment of RDX & HMX Plumes Using Mulch Biowalls

ESTCP Project ER-0426

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LIST OF ACRONYMS

ADF	Acid Detergent Fiber
AFCEE	Air Force Center for Engineering and the Environment
BAK	Benzalkonium chloride
BGS	Below Ground Surface
BRAC	Base Realignment and Closure
CHAAP	Cornhusker Army Ammunition Plant
CDPHE	Colorado Department of Public Health and Environment
DNTs	Dinitrotoluenes
DNX	Hexahydro-1,3-dinitrososo-5-nitro-1,3,5-triazine
DoD	Department of Defense
EOS	Emulsified Oil Substrate
EPA	Environmental Protection Agency
ESTCP	Environmental Security and Technology Certification Program
FRTR	Federal Remediation Technologies Roundtable
FUDS	Formerly-Used Defense Sites
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
HSP	Health and Safety Plan
IAAP	Iowa Army Ammunition Plant
IDW	Investigation Derived Waste
LOOW	Lake Ontario Ordnance Works
MNX	Hexahydro-1-nitrososo-3,5-dinitro-1,3,5-triazine
NDF	Neutral Detergent Fiber
ORP	Oxidation-Reduction Potential
PCD	Pueblo Chemical Depot
PI	Principal Investigator
PM	Project Manager
PRB	Permeable Reactive Barrier
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance / Quality Control
RAP	Remediation Action Plan
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RFI	RCRA Facility Investigation
SPE	Solid Phase Extraction

SWMU	Solid Waste Management Unit
SIC	Standard Industrial Classification
TAL	Target Analyte List
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 Agency
VFA	Volatile Fatty Acid
VOC	Volatile Organic Compound
ZVI	Zero-Valent Iron

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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 above-ground 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 PRB 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[5]. Because of their poor soil sorption properties[31] 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[24, 34]. Although there are 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[5]. Hence, there is a need to implement remediation technologies to treat RDX and HMX plumes, especially because some of these plumes have migrated off DoD bases and could threaten public water supplies[17, 35].

The groundwater plume selected for the field demonstration was the eastern-most explosives plume in the 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. A combination of batch sorption tests and column flow-through tests were performed. 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., MNX+DNX+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[17, 38], 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[24, 33] or anaerobic biodegradation[10, 20] 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 zero-valent-iron (ZVI) PRB technology over a 10-year lifecycle. 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.

1. INTRODUCTION

1.1 Background

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[5]. Because of their poor soil sorption properties[31] 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 packaged and handled[24, 34]. Although there are 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 organisms, including hepatic tumors in mice[5]. The 2006 Drinking Water Advisory published by the U.S. Environmental Protection Agency (USEPA), 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 life-time cancer risk[37]. It has been estimated that there are several hundred military sites where groundwater is contaminated with energetics[39]. Hence, there is a widespread 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[17, 35].

Both *ex situ* and *in situ* processes have been proposed for the remediation of RDX- and HMX-contaminated groundwater. *Ex situ* processes include the treatment of pumped groundwater in granular activated carbon units[17, 38], 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[24, 33] or anaerobic biodegradation[10, 20] have demonstrated the potential to reduce RDX and HMX. The disadvantage of zero-valent walls are their high materials expense. Various organic substrates, such as molasses, hydrogen-release compound (HRC®)[20], vegetable oil, etc., have been used as electron donors to generate anaerobic conditions needed for biological reduction of RDX and HMX. However, each of these substances degrades rapidly, requiring multiple applications, and/or requires an above-ground system to supply the substrate to the injection wells.

In this project, an *in situ* mulch permeable reactive barrier (PRB) or biowall was employed as a slow-release source of electron donor. Mulch has several advantages over other electron donors: it is cheaply available, long-lasting, and is naturally present in the environment. The mulch PRB is a passive technology and consequently requires no above-ground injection system, thereby greatly reducing operating and maintenance costs. This field demonstration was the first application of mulch biowall technology for the treatment of a explosives-contaminated groundwater.

1.2 Objectives of the Demonstration

The overall objective of this project was to demonstrate and validate mulch PRB or mulch biowall technology in the field at a pilot-scale. The specific project objectives were to:

1. Test the efficacy of organic mulch as an electron donor that promotes the biological reduction of RDX- and/or HMX-impacted groundwater by:
    a. Implementing a mulch/gravel PRB for the pilot test that seeks to meet the regulatory action levels for the demonstration site.
    b. Determining the extent of RDX and/or HMX removal across the mulch PRB.
    c. Monitoring the accumulation of any primary reduction intermediates (e.g., MNX, DNX, TNX) downgradient of the PRB.
2. Gather sufficient performance and cost data from the pilot test to estimate the cost of implementing the technology at full-scale by:
    a. Monitoring change in total dissolved organic carbon downgradient of the PRB over the course of the demonstration in order to extrapolate the longevity of the implementation.
    b. Determining any fouling characteristics of the mulch/gravel PRB over the course of the demonstration by conducting periodic slug tests in wells located within the PRB.

The pilot-scale field demonstration was performed at the Pueblo Chemical Depot (PCD) in Pueblo, Colorado.

1.3 Regulatory Drivers

Nitro-substituted heterocyclic nitramines such as RDX and HMX are generally regarded as possible human carcinogens. RDX, in particular, is known for its ability to cause adverse effects in a variety of organisms, including hepatic tumors in mice[5]. Hence, RDX is classified as an EPA Class C or possible human carcinogen based on the evidence in animal studies. Very little data are available for assessing the carcinogenicity of HMX towards humans or animals. Therefore, HMX is generally listed as a Class D carcinogen.

The 2006 Drinking Water Advisory published by the 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 life-time cancer risk[36]. 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 end-point.

1.4 Stakeholder/ End-User Issues

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; however, TCLP testing results for the mulch fill in the site-specific treatability phase confirmed no leaching of RDX, HMX, or any primary reduction intermediates. Therefore, post-treatment excavation and disposal are also unlikely.

2. 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[18]. In this project, an *in situ* organic mulch-pea gravel PRB for the treatment of groundwater contaminated with RDX and HMX will be 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, 12, 27, 40]. Therefore, low bioactivity for energetics degradation in an 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 a RDX or HMX plume.

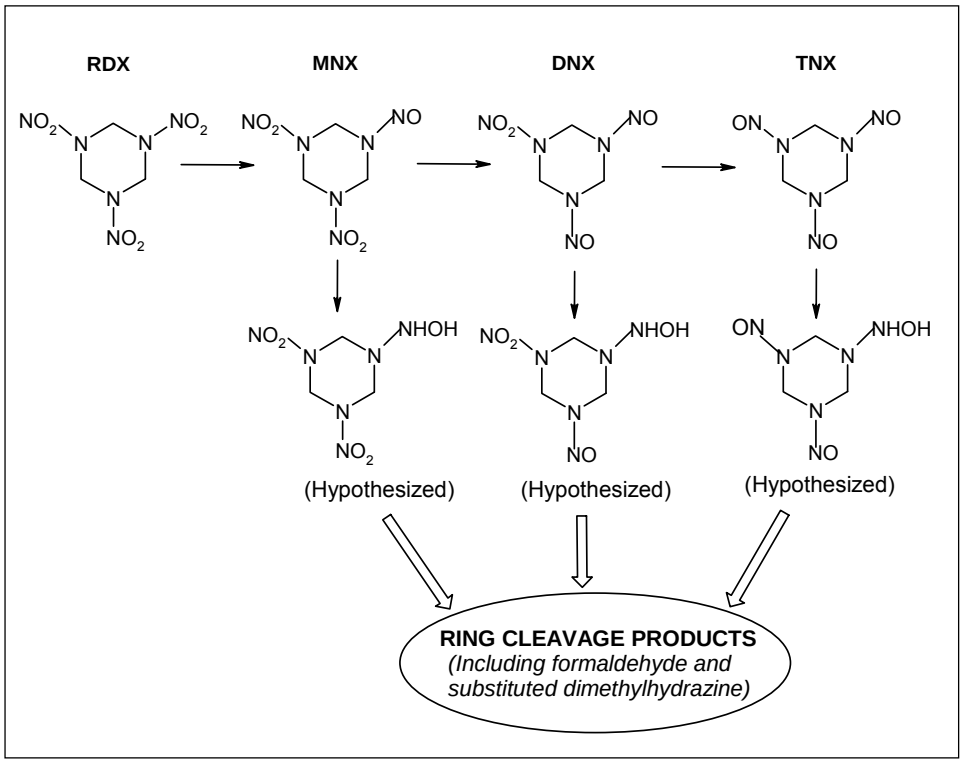


Figure 1. RDX Bioreduction Pathway as Postulated by McCormick et al. (1981).

Anaerobic biodegradation pathways have been employed in multiple studies to establish the mineralization of RDX to innocuous products[7, 13, 16, 19, 20]. These pathways (Figures 1 and 2) tend to be the most cost- 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.[23] using ^{14}C-labeled RDX and anaerobic sludge from a municipal wastewater treatment plant as an inoculum. McCormick et al. 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.[19] 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 (Figure 2), two novel metabolites, methylenedinitramine [$(O_2NNH)_2CH_2$] and bis(hydroxmethyl)nitramine [$(HOCH_2)_2NNO_2$] were produced. 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 [16, 18] (Figure 2).

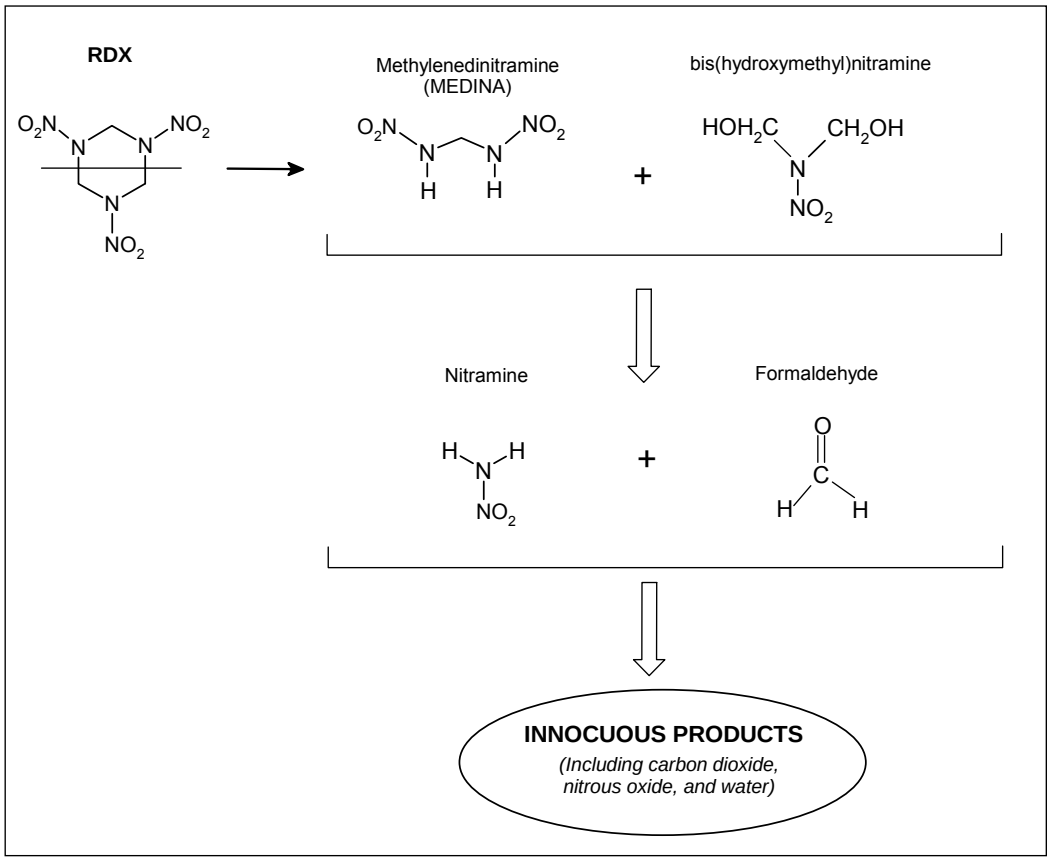


Figure 2. RDX Bioreduction Pathway as Postulated by Hawari et al. (2000).

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, 28]. 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[22] 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.

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 3). Reoxidation of reduced electron carriers can occur through direct or indirect electron shuttling reactions (e.g., indirectly via quinoid moieties in soil natural organic matter and humic substances[22]). 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 sub-class of fermenters) organisms, which can then be utilized as an electron donor by other organisms.

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 4). 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[6], perchlorate[26], and nitrate[29].

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[14] 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, 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).

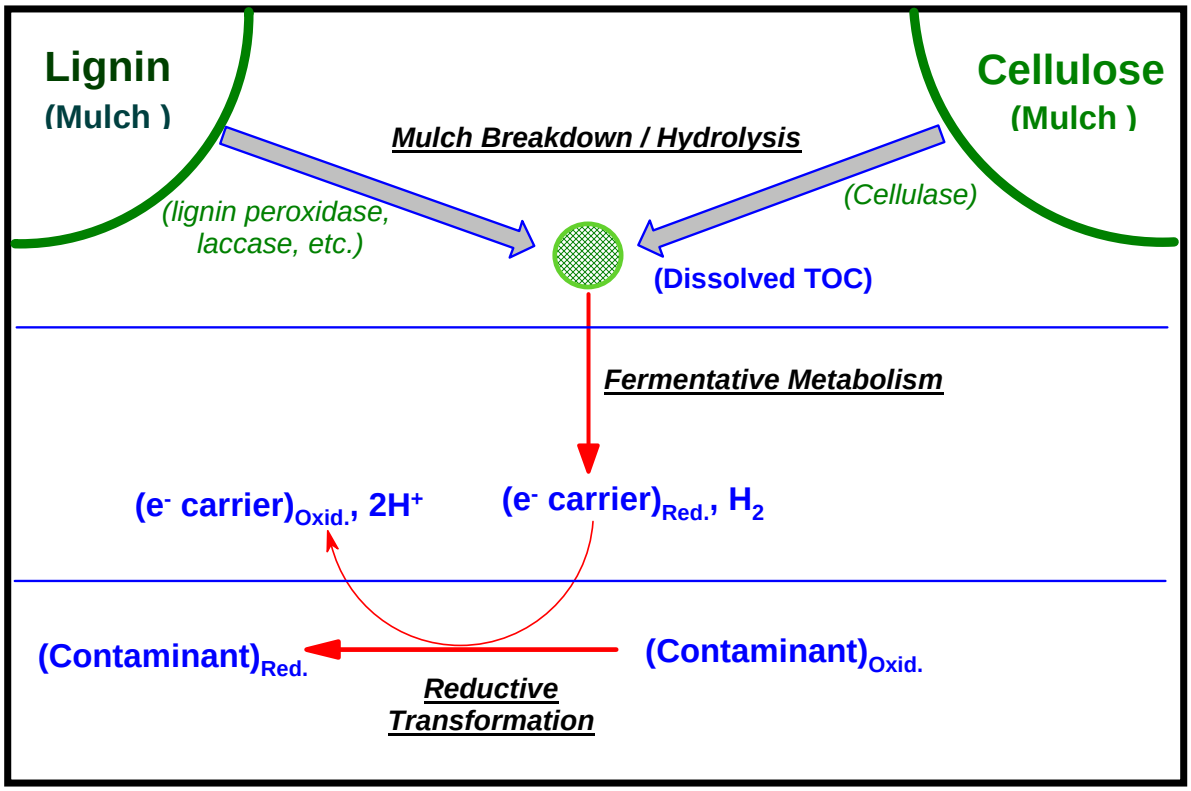


Figure 3. Relationship between Mulch Breakdown via Hydrolytic Reactions, Fermentative Metabolism, and Reductive Transformation of RDX.

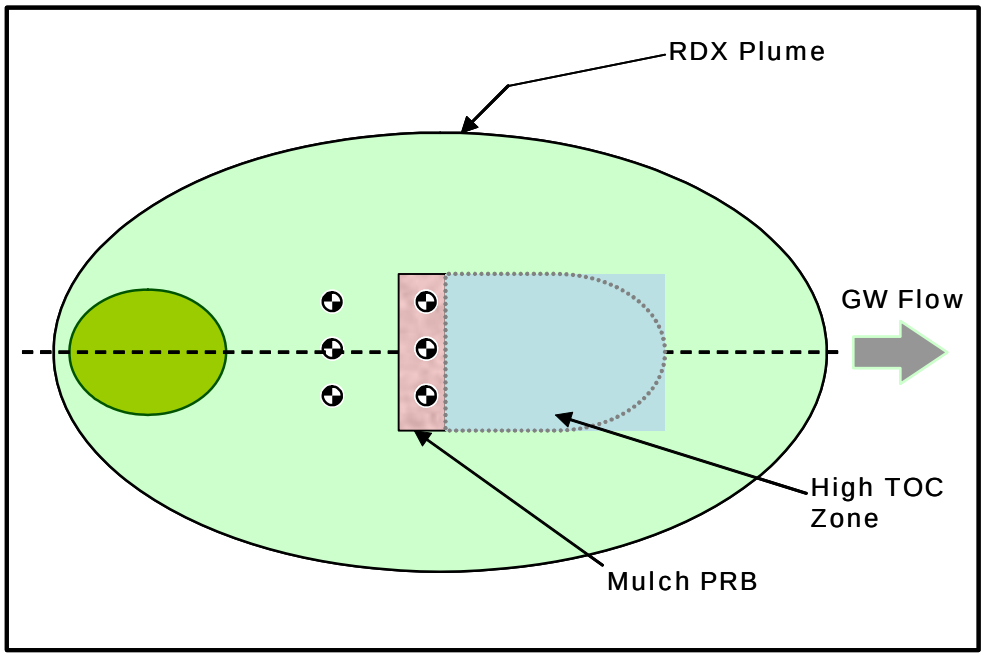


Figure 4. Plan View Schematic of Mulch Wall Implementation Concept.

A brief chronology of work related to the bio-reductive degradation of RDX and mulch biowall technology is presented below:

1980s: Bioreduction pathway of RDX postulated by McCormick[23]. Initial transformation of RDX to partially reduced intermediates, MNX and DNX, confirmed.

1990s: In mixed aqueous energetics contamination 2,4,6-trinitrotoluene (TNT) was shown to be more electrophilic than RDX, resulting in its preferential reduction in a biologically-catalyzed system[13].

2000-Present: (a) Second reductive pathway of RDX leading to mineralization demonstrated using a radiolabeled study by Hawari et al[18, 19]. (b) Mulch and compost PRB implemented to remediate groundwater contaminated with nitrates[29], perchlorate[26], and chlorinated solvents[6].

2.2 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 Engineering and the Environment (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 (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 PRB for the remediation of explosive compounds in groundwater.

2.3 Factors Affecting Cost and Performance

Key factors affecting the implementation cost of this technology at full-scale will be the depth of contamination and wall thickness. The depth of contamination determines the type of trenching procedure needed for PRB implementation. The cheapest and fastest procedure for PRB implementation is the use of a single-pass trencher. Single-pass trenching currently has a depth limitation of approximately 40 ft below-ground-surface (bgs). In some cases, trenching depths have been extended to approximately 50 ft bgs in a "benched-down" implementation. When there is a large difference in depth between the ground surface elevation and the water table, a shallow trench is dug (usually <10 ft bgs) and the trencher is placed within it to extend the one-pass trenching depth. Implementation costs and implementation time rise substantially at deeper contaminant depths, for which more conventional trenching procedures are required, necessitating the need for shoring and trenching of the excavation. For relatively shallow contamination (i.e., <40 ft bgs) that can be accessed using single-pass trenchers, the width of the PRB also affects implementation costs. Single- or one-pass trenchers capable of installing PRB of three different thicknesses are currently available. These thicknesses are 1.5 ft, 2 ft, and 3 ft. The mobilization cost of a 3-ft trencher is almost twice that of the other two machines. In the event that a PRB thickness of greater than 2 ft is needed, it is a more cost-effective strategy to install 2 parallel PRB with the smaller machines. The parallel PRB can be as little as 10 ft apart.

Factors affecting the performance of mulch PRB for treating energetics contamination are the type of co-contaminants present in the groundwater, as well as mulch properties. The electrophilic nature of the target contaminant relative to other contaminants or constituents in groundwater can affect its degree of reduction. In the case of the target energetic RDX, co-contaminants that are preferentially reduced include nitrate and TNT. Both of these have a significant likelihood of co-occurrence with RDX in groundwater at energetic materials handling sites. To ensure a complete conversion of RDX, the PRB design thickness can be increased so that RDX and all its competing co-contaminants are reduced. Mulch properties could also affect the performance of the PRB over the life of its operation. Mulch composition is a key unknown that regulates the rate of release of dissolved TOC into water downgradient of the PRB. Furthermore, studies with several types of mulch beds have demonstrated the varying compacting and settling properties upon mulch breakdown[11]. This can potentially result in the loss of permeability through the barrier in the long term. Hence, to address this concern it becomes essential to use inert media such as sand or gravel in the PRB fill to maintain the structural integrity of the barrier.

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 above-ground 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[8, 19, 21, 39] 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 4).

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 at Offutt AFB for the treatment of a chlorinated solvent plume, there was no decrease in the percent 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 [29, 30]. The lifetime of mulch is expected to be in 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., TNT and DNTs) 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)[29] 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 at Offutt AFB has been observed for over the 4 years of operation. Nevertheless, for this demonstration, monitoring wells will be installed within the mulch wall to monitor reduction in permeability in the event that fouling occurs as a result of the biological growth or other factors, such as inorganic precipitation and mulch compaction.

3. 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			
Determine remediation effectiveness	Contaminant concentrations in groundwater upgradient and downgradient of PRB	*2.4.1 90% removal of RDX across treatment zone*	>90% RDX removal measured in treatment zone once a pseudo-steady-state was established.
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*	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.
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*	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 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 PCD. PRB Performance objective "a" designates a minimum anticipated removal of RDX across the mulch PRB and the treatment zone over an approximate 22-24-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. The threshold is specified for the last row of wells downgradient of the mulch PRB (Row R4A). Concentrations of reduction intermediates were expected to diminish to non-detect levels further downgradient towards the edge of the treatment zone because of the high dissolved TOC levels that will be released from the mulch PRB.

3.2 Selecting Test Site

A short list of facilities with explosives-contaminated sites appropriate for the technology demonstration was created using site information found in Wani et al.[39] and information collected from staff at the USACE in Nebraska (i.e., primarily Mr. Ted Streckfuss and Mr. Al Kam). The most important criterion for selecting facilities for this list was simply the presence of shallow explosives contamination in the groundwater (<30 ft below-ground-surface [bgs] to top of contamination). 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 list of facilities meeting this preliminary criterion is presented in Table 2 below.

Table 2. Facilities with Shallow Groundwater Contaminated with Energetics Material.

Facility Name	Location (State)	Site Name
Cornhusker AAP	Nebraska	-
Holston AAP	Tennessee	-
Iowa AAP (IAAP)	Iowa	Line 800 Area
Fort Meade	Maryland	-
Pueblo Chemical Depot (PCD)	Colorado	SWMU 17
Raritan Arsenal	New Jersey	Area 4
Lake Ontario Ordnance Works	New York	Property E & Vicinity

Following the preliminary selection of facilities, the sites were put through a 2-step selection process. The two steps were: (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 (Table 3). These criteria were:

1. Facility Environmental Project Manager (PM) Support and Interest. PM support and interest is critical to establishing access to the potential site and for acquiring history of site activities, characterization, and remediation. PM interest for conducting the mulch PRB field demonstration was generated at all facilities except for Cornhusker AAP and Ft. Meade. Several indirect issues contributed to the lack of interest at these facilities. Owing to ongoing property transfer activities at the facility, and because of strong natural attenuation conditions (due to the leaching of organic carbon and bioactivity from a massive feedlot overlying the plume), little or no interest was generated at Cornhusker AAP. At Ft. Meade, no clear point of contact could be established in the time designated for site selection. Ft. Meade is a Formerly Used Defense Site (FUDS) with an unclear chain of responsibility to outside parties. The responsibility for site activities is likely to be shared among 4 entities, namely, facility personnel, USACE FUDS Office in Kansas City, University of Nebraska, and environmental contractors.

Table 3. Site Screening Criteria.

Screening Criteria	Sites Eliminated from Consideration
1. Facility PM Support	Cornhusker AAP, Ft. Meade
2. Level of Site Characterization	Holston AAP, Lake Ontario OW
3. Contaminant Concentration	Raritan Arsenal

2. Level of Site Characterization. A sufficient level of site characterization is important to the success of the mulch PRB field demonstration. The reason for this constraint is budgetary because extensive site characterization activities were neither anticipated nor funded as part of this project. The project assumed the presence of several well characterized RDX and/or HMX shallow groundwater plumes. Pertinent site characterization activities include the delineation of the RDX and/or HMX plume, determining groundwater flow characteristics (e.g., direction of flow, gradient), and establishing the levels of competing electron acceptors. Holston AAP and Lake Ontario Ordnance Works (OW) were ruled out because of the lack of site characterization at the time of site screening.

3. Contaminant Concentration. Of the two heterocyclic nitramines (i.e., RDX and HMX) that are the target of this project, RDX is predominantly used in secondary explosive formulations. Because of this fact and because of its physical properties that render it more mobile in an aqueous environment, RDX is more likely to occur in the groundwater of facilities where ordnance has been handled. Moreover, RDX is the COC that controls groundwater remediation end-points when both contaminants are present; RDX has a significantly lower cleanup level when compared to that of HMX (e.g., 0.55 ppb for RDX

versus 602 ppb for HMX at PCD). Newer analytical methods that combine solid phase extraction (SPE) with HPLC are capable of detecting RDX concentrations well below 1 ppb. As a result of these factors, only a small amount of RDX needs to be present in the groundwater to conduct a field demonstration. For this project, a minimum threshold of 30 ppb (approx. 50x cleanup level) was set in the source area so that removal could be clearly observed. All sites, with the exception of the Raritan Arsenal in New Jersey, met this criterion. Raritan Arsenal has no history of RDX handling, and consequently no RDX has been detected in its groundwater to date. Energetic compound detections in groundwater at the Raritan Arsenal are comprised solely of nitroaromatics.

The two sites remaining after the screening, PCD and IAAP, were contacted for additional information on the selection criteria listed below and presented in Table 4.

a. Maximum RDX Levels in Source Area: A 50 ppb or higher value was preferred for this parameter so that a clear removal of RDX can be demonstrated. The maximum RDX levels at IAAP are unusually high and are indicative of the persistence of RDX at that site.

b. Competing Electron Acceptor Presence: Unlike PCD, a considerable number of competing electron acceptors were found to be present in the groundwater at IAAP. Most of these are nitroaromatic explosives and their transformation products. These compounds are preferentially reduced before RDX.

c. Maximum Concentration of Competing Electron Acceptors: A mulch PRB can be over-designed to handle electron acceptors that are preferentially reduced, provided their concentrations are not so high that an over-design becomes impractical.

d. Depth to Bedrock: A maximum value for this parameter represents a depth limitation for the single-pass-trencher installation method for the PRB. A PRB that extends to the bedrock is less likely to demonstrate groundwater bypass problems.

e. GWBU Geology: This parameter is not a critical factor provided optimal seepage velocities exist at the site. Slow contaminant transport through fine grained materials such as the glacial till at IAAP could pose a problem for demonstrating a steady-state removal over the 24-month time frame of the field demonstration.

f. Optimal Seepage Velocity: An optimal seepage velocity could help balance the needs of attaining steady-state with contaminant removal extent. Neither facility's average seepage velocity fell in the optimal range.

g. Minimum Redox Potential: A minimum threshold value of -50 mV was chosen for this parameter to ensure that conditions were not already strongly anaerobic in the site groundwater. The mulch in the PRB helps drive down the redox level and provides a slow-release supply of electron donor for the biologically-mediated reduction of RDX and HMX. Redox values lower than -50 mV exist in several wells at IAAP, indicating that the mulch PRB is unlikely to promote further reduction of RDX at the site.

h. Dissolved Total Organic Carbon (TOC) Levels in Groundwater: This parameter indicates whether the system is limited in organic carbon. An addition of organic carbon (e.g., from mulch) to such a system is likely to promote contaminant reduction. IAAP is reported to have high levels of TOC in the groundwater, indicating that it is not limited by this parameter.

i. Presence of Other Remediation Technologies Upgradient of Mulch PRB Installation Area: This parameter poses a problem when there are downgradient residual effects from the remediation technology. At IAAP, there is an active phytoremediation process in the source area (i.e., the former Pink Water pond area) that might already be contributing dissolved TOC downgradient of this area.

Table 4. 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. Max. RDX concentration	> 50 ppb	2	> 50 ppb	> 13000 ppb
b. Presence of competing electron acceptors (Nitrate, Nitroaromatics, etc.)	No	1	No	Yes (Nitroaromatics)
c. Max. concentration of competing electron acceptors (if present)	< 10% RDX Conc.	1	N/A	80 – 100% RDX Conc.
d. Depth to Bedrock	< 35 ft	2	20 ft (approx.)	40 ft (approx.)
e. GW-Bearing Unit (GWBU) Geology	Fine Sand	3	Sand, fine to medium	Glacial Till
f. GW Seepage Velocity	0.01 – <1 ft/day	1	1 ft/day	0.00001 – 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.
N/A = Not Applicable

3.3 Test Site History/Characteristics

Using the site selection criteria described in the previous section, Pueblo Chemical Depot (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 5). 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.

The munitions contamination in groundwater at PCD emanates from the SWMU-17 area (Figure 6), 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, TNB, RDX, and HMX. Some munitions contamination has migrated off-base to Ciruli Springs southwest of PCD, prompting the Colorado Department of Public Health and Environment (CDPHE) to issue a compliance order (Compliance Order No. 99-10-06-01) that requires PCD to delineate the nature and extent of onsite and related offsite munitions-contaminated groundwater, and sets cleanup levels for munition COCs in groundwater. The RDX and HMX cleanup levels set by CDPHE are 0.55 ppb and 602 ppb, respectively.

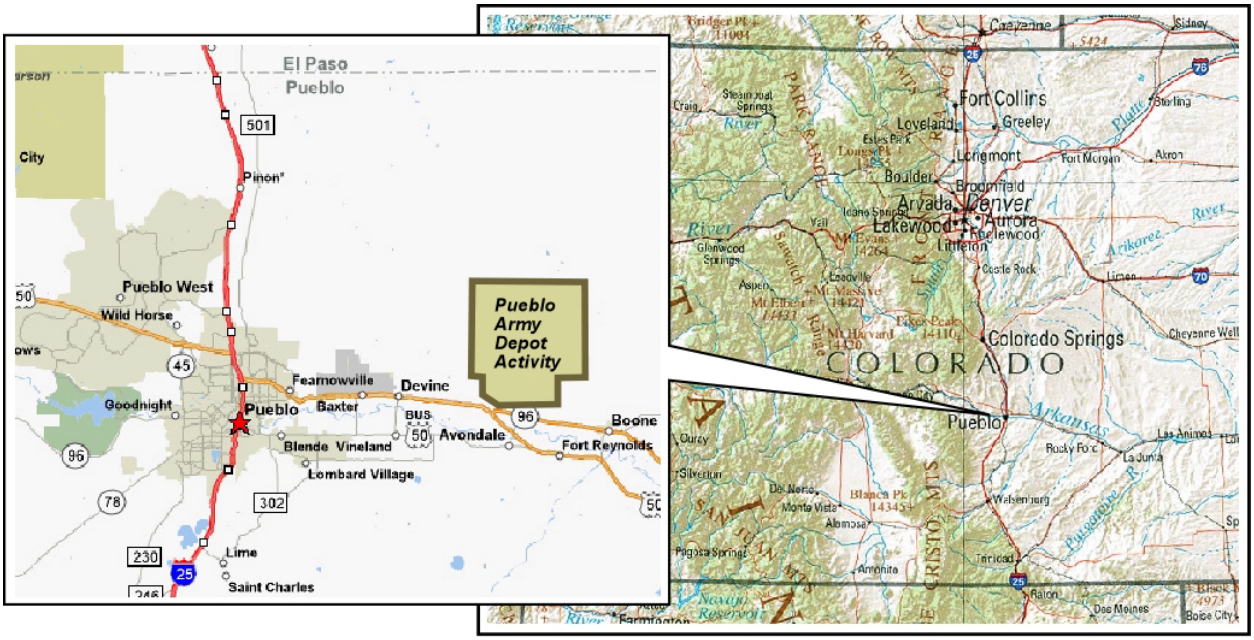
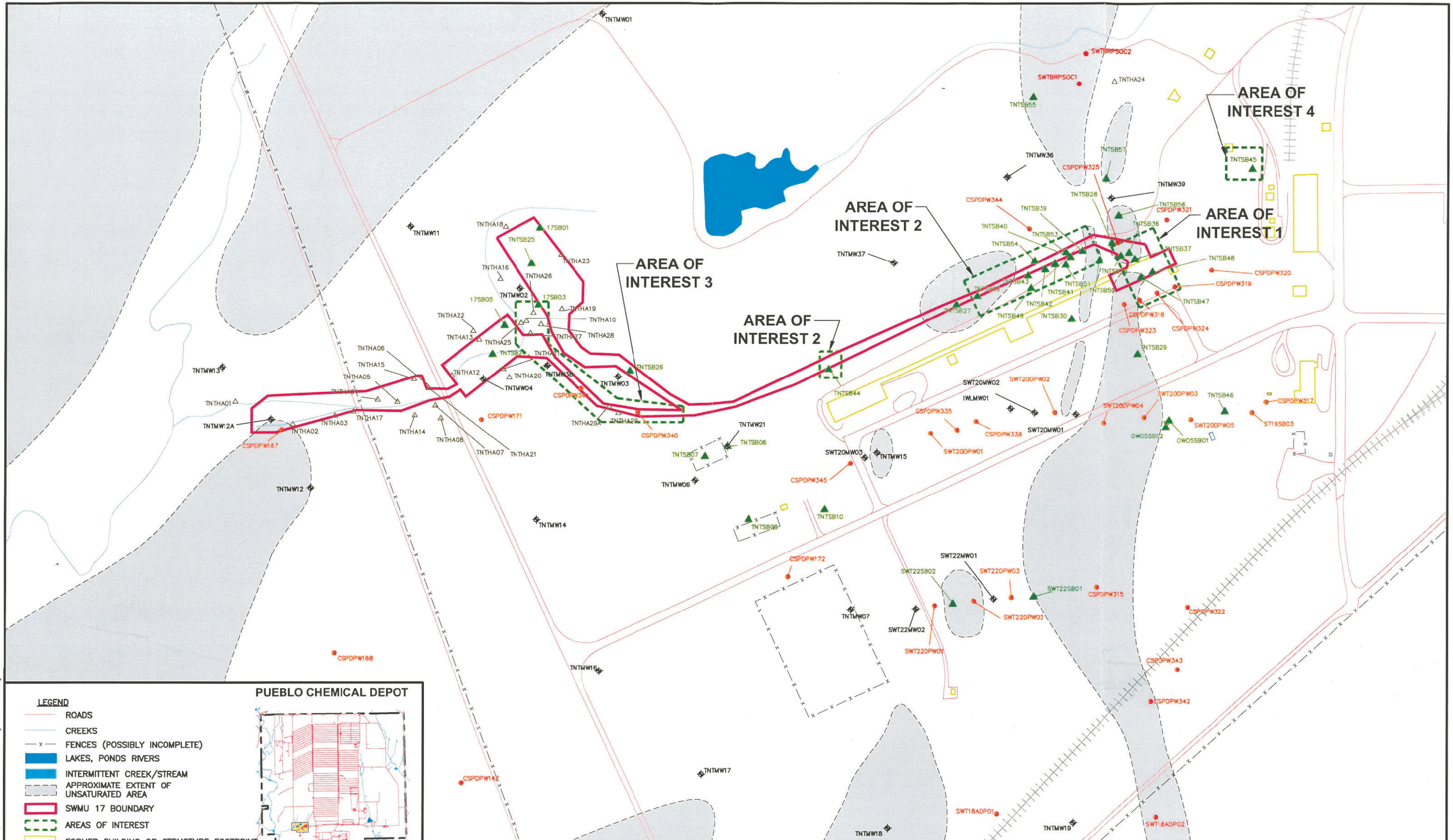


Figure 5. Location of Selected Facility (Pueblo Chemical / Army Depot Activity).

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 (Figure 7) 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. This physical setting is easier to visualize in the east-to-west cross sections for the SWMU-17 area presented in Figure 8. The general decline in the surface elevation in the westward direction is also visible in the cross sections.


AREA OF INTEREST 1
AREA OF INTEREST 2
AREA OF INTEREST 2
AREA OF INTEREST 3
AREA OF INTEREST 4
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SWT22MW02
IWLMW01
SWTBRPSOC1
SWTBRPSOC2
CSPDPW167
CSPDPW168
CSPDPW171
CSPDPW172
CSPDPW142
CSPDPW340
CSPDPW345
CSPDPW344
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TNTHA29
TNTHA29A
TNTHA30
TNTHA31
TNTHA32
TNTHA33
TNTHA34
TNTHA35
TNTHA38
PUEBLO CHEMICAL DEPOT
LEGEND
ROADS
CREEKS
FENCES (POSSIBLY INCOMPLETE)
LAKES, PONDS RIVERS
INTERMITTENT CREEK/STREAM
APPROXIMATE EXTENT OF UNSATURATED AREA
SWMU 17 BOUNDARY
AREAS OF INTEREST
FORMER BUILDING OR STRUCTURE FOOTPRINT
OIL WATER SEPARATORS/SEPTIC TANK
UNDERGROUND TANK
MONITORING WELL
DIRECT PUSH/MONITORING WELL
SOIL BORING
HAND AUGER BORING
NOTES:
ALL ELEVATIONS ARE IN FEET ABOVE MEAN SEA LEVEL.
CONTOURS ARE DASHED WHERE INFERRED.
COORDINATE SYSTEM:
STATE PLANE COORDINATE SYSTEM (NAD 83)
N
EARTH TECH
FIGURE 6
AREAS OF INTEREST LOCATION MAP
SWMU 17 SUPPLEMENTAL RFI
PUEBLO CHEMICAL DEPOT
PUEBLO, COLORADO
DEC. 2004
62317
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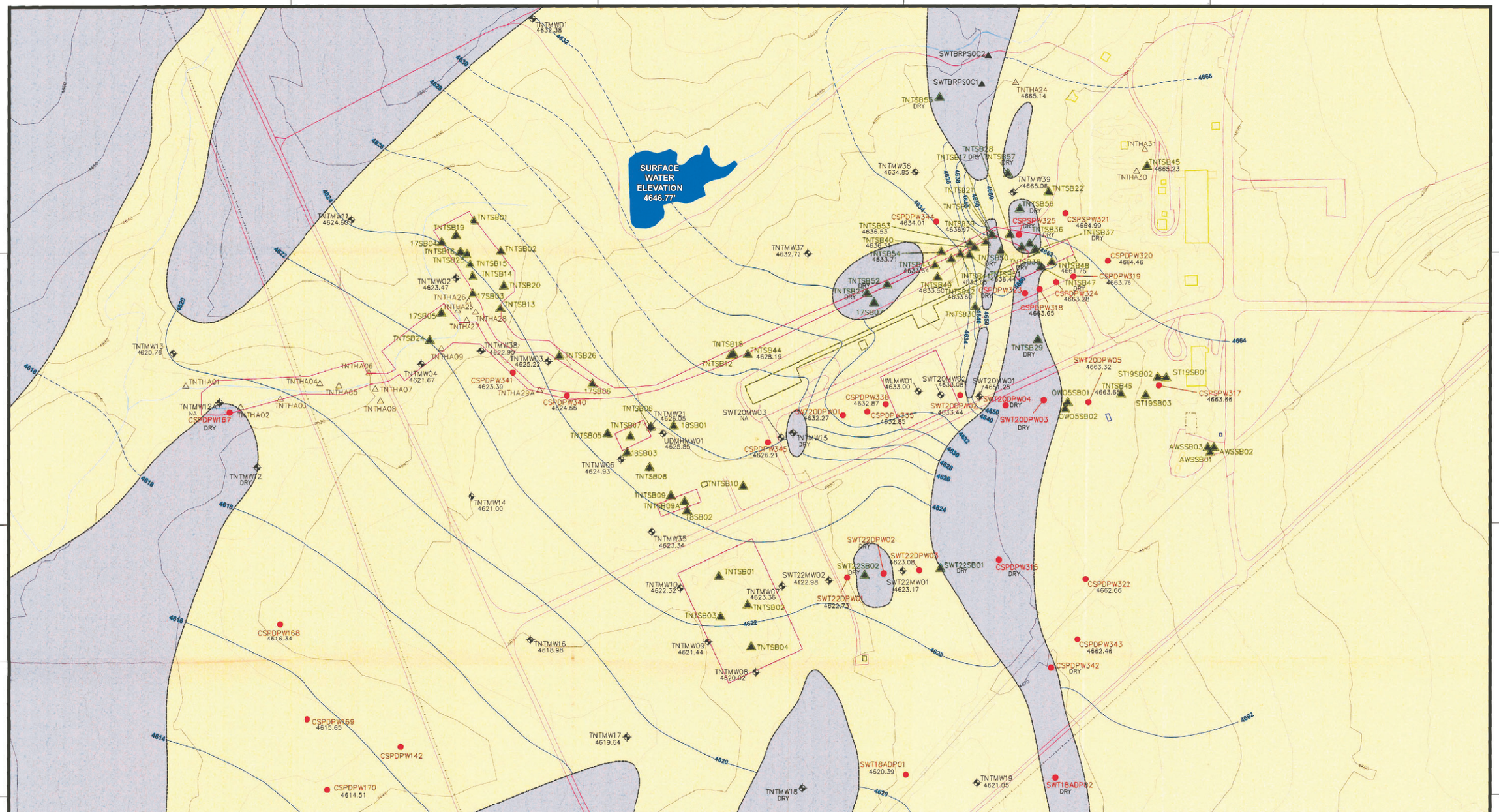
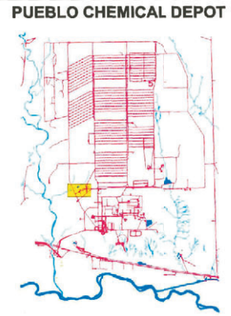


LEGEND

- GROUND SURFACE ELEVATION CONTOUR (INTERVAL 10 FT)
- GROUND SURFACE INTERMEDIATE ELEVATION CONTOUR (INTERVAL 5 FT)
- 4663 WATER LEVEL ELEVATION CONTOUR (DASHED WH
- ROADS
- CREEKS
- FENCES (POSSIBLY INCOMPLETE)
- LAKES, PONDS, RIVERS
- INTERMITTENT CREEK/STREAM
- APPROXIMATE EXTENT OF UNSATURATED AREA
- SWMU BOUNDARY (SWMU 17/44)
- FORMER BUILDING OR STRUCTURE FOOTPRINT
- OIL/WATER SEPARATOR/SEPTIC TANK
- UNDERGROUND TANK
- TNTMW16 MONITORING WELL
- CSPSB017 SOIL BORING
- TNTHA03 HAND AUGER BORING
- CSPDPW323 DIRECT PUSH/MONITORING WELL
- BEDROCK OUTCROP

PUEBLO CHEMICAL DEPOT



NOTES:

ALL ELEVATIONS ARE IN FEET ABOVE MEAN SEA LEVEL. CONTOURS ARE DASHED WHERE INFERRED. ALL WATER LEVELS WERE MEASURED DURING JULY 2004.

SURFACE WATER ELEVATION AT THE POND MEASURED DURING DECEMBER 2004.

COORDINATE SYSTEM:

STATE PLANE COORDINATE SYSTEM (NAD 83)

N

Revisions				
Symbol	Descriptions	Date	Rev	App

EARTH TECH

U.S. ARMY
CORPS OF ENGINEERS
OMAHA, NEBRASKA

Designed by: MMW
Drawn by: SR
Checked by: LP
Approved by:
Submitted by: Architect-Engineer

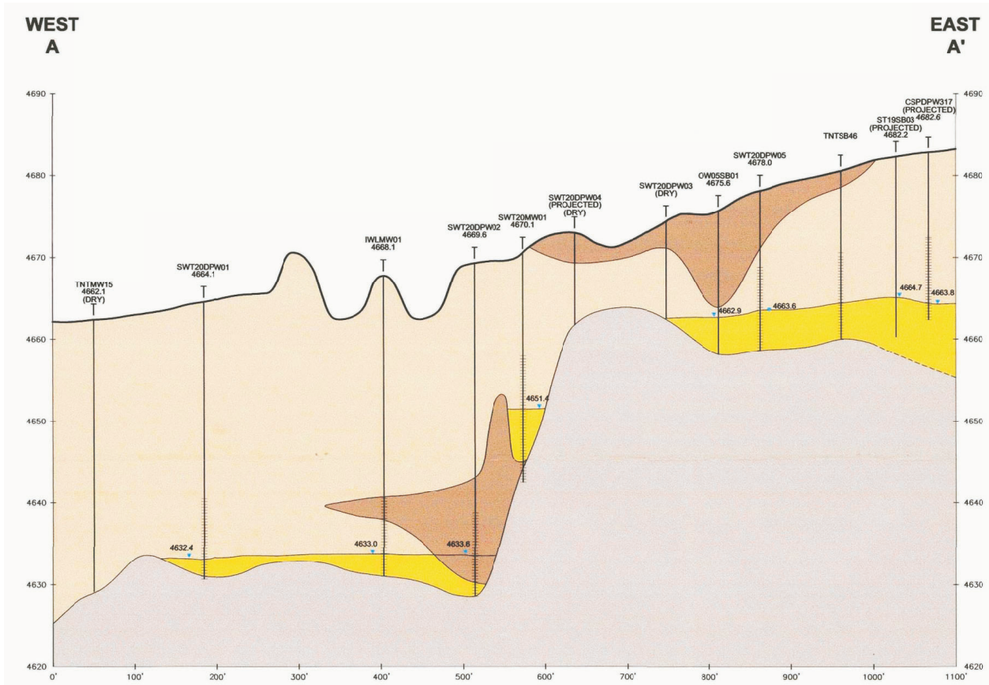
PUEBLO CHEMICAL DEPOT — PUEBLO, COLORADO

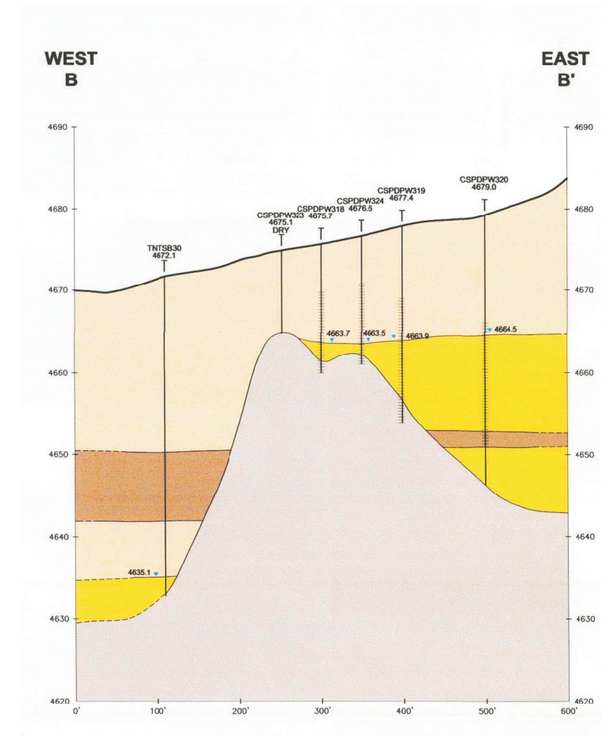
FIGURE 7

ALLUVIAL GROUNDWATER ELEVATION CONTOUR MAP SWMU 17 SUPPLEMENTAL RFI

Scale: AS SHOWN
FIG 3-1.DWG [layout 1 100']
Contract No:
Sheet reference number:
Date: FEB. 2005
Drawing Code:

WORK\62517\CAD\FEB05\FIG 3-1.DWG [layout 1 100']





SILTY FINE SAND WELL AND POORLY GRADED SAND WITH GRAVEL

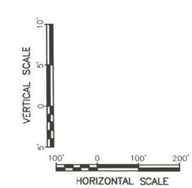
SATURATED SAND AND GRAVEL

CLAY, SILT AND SILTY OR SANDY CLAY

SHALE/CLAYSTONE (BEDROCK)

CSPDPW277 — WELL DESIGNATION
4580.53 — GROUND SURFACE ELEVATION

WATER LEVEL
4580.53 — WATER ELEVATION
SCREEN INTERVAL
POTENTIOMETRIC SURFACE



Revisions

Symbol	Descriptions	Date	Rev	App

EARTH TECH

U.S. ARMY
CORPS OF ENGINEERS
OMAHA, NEBRASKA

Designed by: MMW

Drawn by: SR

Checked by: MMW

Approved by:

Submitted by: Architect–Engineer

PUEBLO CHEMICAL DEPOT — PUEBLO, COLORADO

FIGURE 8

CROSS-SECTIONS A-A' AND B-B'
SOUTHWEST TERRACE
EXIT INVESTIGATION

Scale:

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Contract No:

Sheet reference number:

Date: FEB. 2004

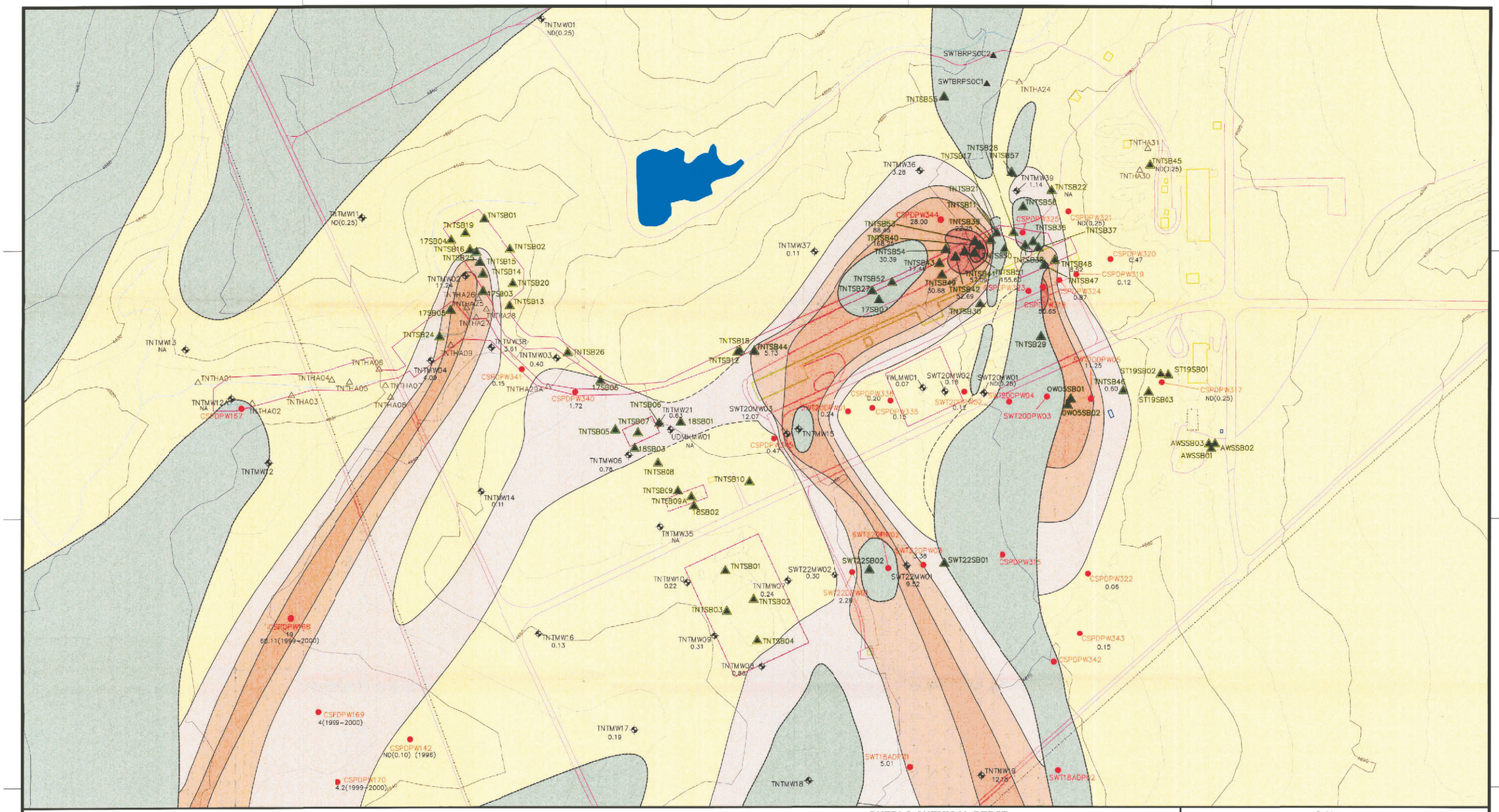
Drawing Code:

The RDX contamination in the groundwater in the SWMU-17 area occurs in the form of two distinct plumes (Figure 9) that are separated by a large dry or unsaturated area depicted in the cross-sections of Figure 8. The chemical characteristics of these two adjacent plumes suggest that these plumes might have resulted from different contamination events. The longer plume in the western portion of SWMU-17 is the result of the commingling of two separate plumes that have emanated from the munitions washwater leachbeds, and one that has originated from the conveyance system that transported the washwater to the leachbeds. This ommingled plume possesses a variety of munitions-related electron acceptors such as TNT, TNB, DNT, HMX, and nitrates. In contrast, the smaller eastern plume of RDX, located south of CSPDPW-318 and running along the unsaturated area, only has trace levels of HMX and substantially lower levels of nitrate. Both plumes have high levels of sulfate, but this is unlikely to interfere in the remediation of RDX because of the lower electrophilic nature of the sulfate ion. Complete removal of RDX in the presence of sulfate has already been demonstrated in the site groundwater as part of the treatability study. This finding is supported by RDX remediation literature as well[10]. As mentioned earlier, the source of the smaller eastern plume at SWMU-17 lies near well CSPDPW-318, where RDX concentrations have historically been recorded in excess of 50 ppb. The eastern RDX plume is the shallower of the two plumes at SWMU-17, and is the one chosen for the field demonstration (Figure 10). Based on slug tests conducted at a nearby well (i.e., CSPDPW-324) and area hydraulic heads, the seepage velocity near the selected location is in the range of 2.2 cm/hr (1.7 ft/d) to 2.8 cm/hr (2.2 ft/d). Complete removal of up to 90 ppb of RDX was demonstrated in mulch column treatability tests performed at similar seepage velocities.

Pilot-scale tests for two other groundwater remediation technologies are currently underway at PCD. Both of these technologies are being demonstrated for mixed munitions contamination comprising of both nitroaromatics (e.g., TNT and DNTs) and heterocyclic nitramines (e.g., RDX and HMX). Field tests have already been completed for hydrogen-release-compound (HRC®) injection. HRC is lactic acid polymer that, like mulch, also induces biologically mediated reduction of electrophilic compounds. The disadvantage of this technology is that it can require repeated injections, especially in a fast flowing regime. The other technology demonstration to be conducted at PCD involves Electronic Barriers (E-Barriers). Disadvantages of this technology include power costs and adverse geochemical effects. In addition to demonstrations of new remediation technologies, PCD has an elaborate groundwater pump-and-treat system located in the Southwest Terrace near the facility boundary; the pump-and-treat system serves to limit contaminant transport south of the facility.

3.4 Pre-Demonstration Testing and Analysis

Four types of activities were completed prior to field mobilization for the technology implementation at PCD. These activities were:



PUEBLO CHEMICAL DEPOT

LEGEND

- GROUND SURFACE ELEVATION CONTOUR (INTERVAL 10 FT)
- GROUND SURFACE INTERMEDIATE ELEVATION CONTOUR (INTERVAL 5 FT)
- ROADS
- CREEKS
- FENCES (POSSIBLY INCOMPLETE)
- LAKES, PONDS, RIVERS
- INTERMITTENT CREEK/STREAM
- APPROXIMATE EXTENT OF UNSATURATED AREA
- SWMU BOUNDARY (SWMU 17/44)
- FORMER BUILDING OR STRUCTURE FOOTP
- OIL/WATER SEPARATOR/SEPTIC TANK
- UNDERGROUND TANK
- TNTMW16 MONITORING WELL
- CSPSB017 SOIL BORING
- TNTHA03 HAND AUGER BORING
- SPDPW323 DIRECT PUSH/MONITORING WELL
- BEDROCK OUTCROP

RDX CONCENTRATIONS (µg/L)

- 0.55–5
- 5–10
- 10–35
- 35–75
- >75

NOTES:

GROUNDWATER CLEANUP LEVEL FOR RDX IS 0.55 µg/L. RDX CONCENTRATIONS PRESENTED ON THIS MAP ARE FROM SAMPLES COLLECTED BETWEEN OCTOBER 2002 AND JULY 2004. WHERE WELLS WERE SAMPLED MORE THAN ONCE, THE HIGHEST CONCENTRATION FOR THE ANALYTE IS PRESENTED.

DUE TO THE LACK OF RECENT CHEMICAL DATA IN THE SOUTHWESTERN PORTION OF THE MAP, HISTORICAL SAMPLE RESULTS HAVE BEEN INCLUDED AT SELECTED WELLS TO AID IN DETERMING CONCENTRATION ISOPLETHS. THE HIGHEST CONCENTRATION FOR THE ANALYTE IS PRESENTED WITH THE SAMPLING TIME FRAME OF HISTORICAL DATA

GROUND SURFACE ELEVATIONS ARE IN FEET ABOVE MEAN SEA LEVEL.

NA – NO DATA AVAILABLE

LOCATIONS SHOWING INITIAL SAMPLE AND SUBSEQUENT SAMPLING RESULTS FOR MAPPED CONTAMINANT

WELL ID	AREA OF INTEREST	DATE SAMPLED	RDX RESULT (ug/L)
CSPDPW340	AOI 3	3/8/04 3/25/04 4/21/04 7/29/04	1.72 ND (0.25) 0.20 ND (0.25)
CSPDPW318	AOI 1	7/24/03 10/30/06 1/28/04 4/21/04	56.65 35 37.49 26.37
SWT20MW05	AOI 1	7/24/03 1/28/04 4/21/04	1.25 0.41 0.37

COORDINATE SYSTEM:
STATE PLANE COORDINATE SYSTEM (NAD 83)

N

Revisions

Symbol	Descriptions	Date	Rev	App

EARTH TECH

U.S. ARMY
CORPS OF ENGINEERS
OMAHA, NEBRASKA

Designed by: MMW
Drawn by: SR
Checked by: LP
Approved by:
Submitted by: Architect–Engineer

PUEBLO CHEMICAL DEPOT — PUEBLO, COLORADO

FIGURE 9

RDX CONCENTRATIONS IN GROUNDWATER
SWMU 17 SUPPLEMENTAL RFI

Scale: AS SHOWN
FIG 3-3.DWG (LAYOUT 1 100')
Contract No:
Sheet reference number:
Date: FEB. 2005
Drawing Code:

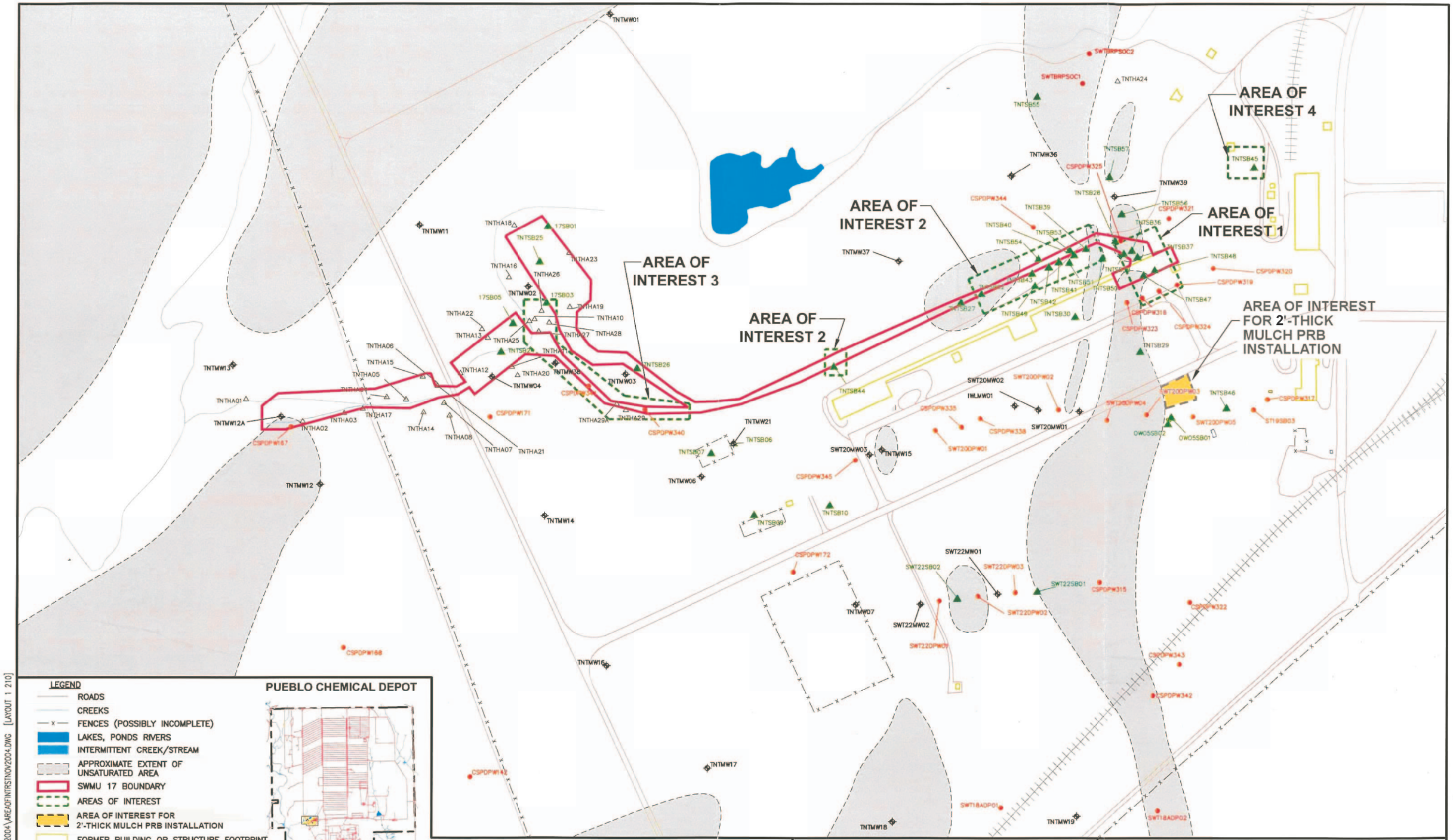


FIGURE 10

LOCATION OF MULCH PRB

a. Monitoring and Analysis of Area Wells: The SWMU-17 and surrounding area at PCD had undergone extensive site investigation and groundwater characterization as part of a RCRA Facility Investigation (RFI; 1999-2000) and a supplemental RFI (2004-2005). The most recent groundwater RDX contamination and potentiometric surface data prior to mulch PRB installation were reviewed. This information is presented in Figures 7 (potentiometric surface) and 9 (groundwater RDX contamination). Additional groundwater data collected as part of regular monitoring at PCD were also reviewed before mobilization. These data served as a preliminary baseline prior to the implementation. Furthermore, the implementation was completed in a phased fashion, where the first phase involved installing, developing, and sampling 6 monitoring wells, 3 upgradient (Row 1-A) and 3 downgradient (Row 3-A) of the PRB. Data from these wells was collected to serve as the true baseline prior to the emplacement of the PRB.

b. Treatability Testing to Evaluate Technology Feasibility: A bench-scale treatability study[4, 15] with pine bark mulch was conducted for the treatment of RDX- and HMX-contaminated groundwater obtained from the selected plume at PCD in Pueblo, Colorado. The treatability study constituted an early phase of this ESTCP- project ER-0426, in which an organic mulch/gravel PRB technology is to be demonstrated in the field. The site-specific cleanup criteria of 0.55 ppb RDX and 602 ppb HMX were used as the logical cleanup goals for the study. A combination of batch sorption tests and column flow-through tests were performed. 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 treatability study 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 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 k values obtained from the study corresponded to a maximum steady-state design wall thickness of 64.5 cm for the field-scale implementation (for a conversion of 90 ppb influent RDX to <0.55 ppb effluent RDX). In addition, the pine bark mulch used was found to stabilize RDX in aqueous solution, possibly via complexation effects, instead of exhibiting RDX sorption. Moreover, no RDX, HMX, or reduced metabolites were detected in TCLP test extracts of the column packing material at the end of the flow-through tests. A preliminary PRB design thickness of 3 ft was determined based on a >99% removal of 90 ppb of influent RDX from the treatability test results. The preliminary PRB design thickness incorporated a safety factor of 40% over the worst performing column's data.

c. Limited Groundwater Flow Modeling in the Area of the PRB Installation: A limited groundwater flow modeling exercise was conducted for the area of the PRB implementation. The object of the exercise was to hone in on a location for

mulch PRB installation south of the plume source well, CSPDPW318, while ensuring that adequate groundwater flow occurs across the PRB upon its implementation. Concern about unfavorable flow conditions across the PRB arose from three factors: (1) Based on the treatability testing, only about half the hydraulic conductivity of the formation (formation K = 0.006 cm/s) could be achieved in a constructed mulch/gravel PRB; (2) a groundwater divide was found to exist at, or just north of the source well for the plume, CSPDPW318; and, (3) the hydraulic gradient between the north and south boundaries of the area being considered for implementation (i.e., the two cross-sections shown in Figure 8) is very small. Points (1) and (3) combined indicate that preferential flow through the PRB would be difficult to attain. Points (1) and (2) together imply that placing a lower permeability PRB at or near the groundwater divide could further impede groundwater flow across the PRB. Details of the modeling exercise and its findings were presented in Appendix A of the Field Demonstration Plan. In summary, it was found that emplacement of the barrier just south of the source well (Case 1), CSPDPW318, will indeed cause flow problems across the PRB by shifting the groundwater divide further south of the PRB, in effect reversing the flow direction across the PRB. Placement of the PRB south of boring TNTSB29 was found to result in favorable plume capture conditions (Case 3), with the best location being the farthest south, near the cross-section A-A' shown in Figure 8 (Case 2). The emplacement location of the PRB would also impact the PRB thickness required because the influent RDX concentrations to the PRB would be on the order of 20 ppb (based on the concentrations determined in the RFIs). The lower influent concentration would require only a 97% reduction of the influent RDX to attain cleanup levels. Taking this information into consideration and the previously-used 40% or higher safety factor, a PRB thickness of 2 ft was required for the PRB.

d. Testing of Available Mulch and Selection of a Supplier: Five different types of pine-based mulch samples were collected from mulch vendors in the Pueblo area and were shipped for forage analyses at the University of Wisconsin Soil and Forage Analysis Labs in Marshfield, Wisconsin. Analyses conducted included elemental analyses (Total C, N, P, K, Ca, Mg, and S), Crude Protein, Acid Detergent Fiber (ADF), Neutral Detergent Fiber (NDF), lignin, nitrogen speciation (ammonium vs. nitrate), and particle size distribution. The cellulose and hemicellulose content of the mulch were calculated from the ADF, NDF, and lignin results. Key analytical results are presented in Table 5 for the final two selections of mulch for the PRB from local vendors, as well as the mulch used in the treatability study. Results were compared to results of the mulch used in the treatability study to select a similar or better (i.e., higher crude protein, higher cellulose/lignin ratio, other) mulch in the PRB.

Both local mulches selected had a far superior cellulose-to-lignin than the mulch used in the treatability study. This ratio gives an idea about the usable portion of the mulch to its inert fraction. Both local mulches showed higher hemicellulose content, indicating the likelihood of a more sustained release of dissolved TOC[3]. For the final selection, the Donley Chipper Mulch was chosen over the Demmler

Trash Pine Mulch because the Donley mulch (1) indicated a higher inoculum load (higher crude protein and sulfur), (2) displayed a better Nitrogen-to-Phosphorus ratio (this should approach 5), and (3) was known to contain a significant component of local shrubs and trees. For the PRB installation the mulch-to-pea gravel ratio was mixed in at 2:1 (by volume), or 2/3 mulch and 1/3 pea gravel.

Table 5. Comparison of Forage Analysis Parameters of Mulches Selected for the PRB.

Parameter	Treat. Study: Pine + Pine Bark	Mulch PRB: Donley Chipper Mulch	Demmler Trash Pine (Alternate for PRB)	Units
Total Nitrogen	0.16	0.64	0.47	% Dry Weight
Total Phosphorus	0.022	0.088	0.040	% Dry Weight
Total Sulfur	0.028	0.112	0.053	% Dry Weight
Crude Protein	1.81	4.02	2.95	% Dry Weight
Acid Detergent Fiber (ADF)	85.91	69.99	72.97	% Dry Weight
Neutral Detergent Fiber (NDF)	89.67	84.84	84.99	% Dry Weight
Lignin	52.56	25.03	25.31	% Dry Weight
Cellulose	33.35	44.96	47.66	% Dry Weight
Hemicellulose	3.76	14.85	12.02	% Dry Weight

3.5 Testing and Evaluation Plan

The following sub-sections provide information on field activities that were conducted as part of the demonstration/validation effort.

3.5.1 Demonstration Installation and Start-Up

Implementation of the mulch/gravel PRB and the associated performance monitoring wells shown in plan view in Figure 11 was completed in three phases. In the first phase, two rows of 3 monitoring wells each were installed, developed, and sampled. The northern-most row of wells installed in this phase eventually served as the row upgradient of the PRB (Row R1A, Figure 11). Prior to the installation of these wells, 10 pilot soil borings were completed along the trace of the mulch PRB in order to fix its position on the East-West axis by determining the edge of the saturated zone. This exercise also served to determine the depth to bedrock at the eastern or distal end of the PRB (Figure 12). Once the PRB's location was fixed, the Row R1A wells were installed 15 feet upgradient of the PRB trace. Then, Row R3A monitoring wells were installed roughly 42 ft south of row R1A. Prior to the mulch/gravel PRB installation, groundwater was collected from the 6 wells installed in the first phase. These samples established the baseline distribution of target contaminants in the field demonstration area.

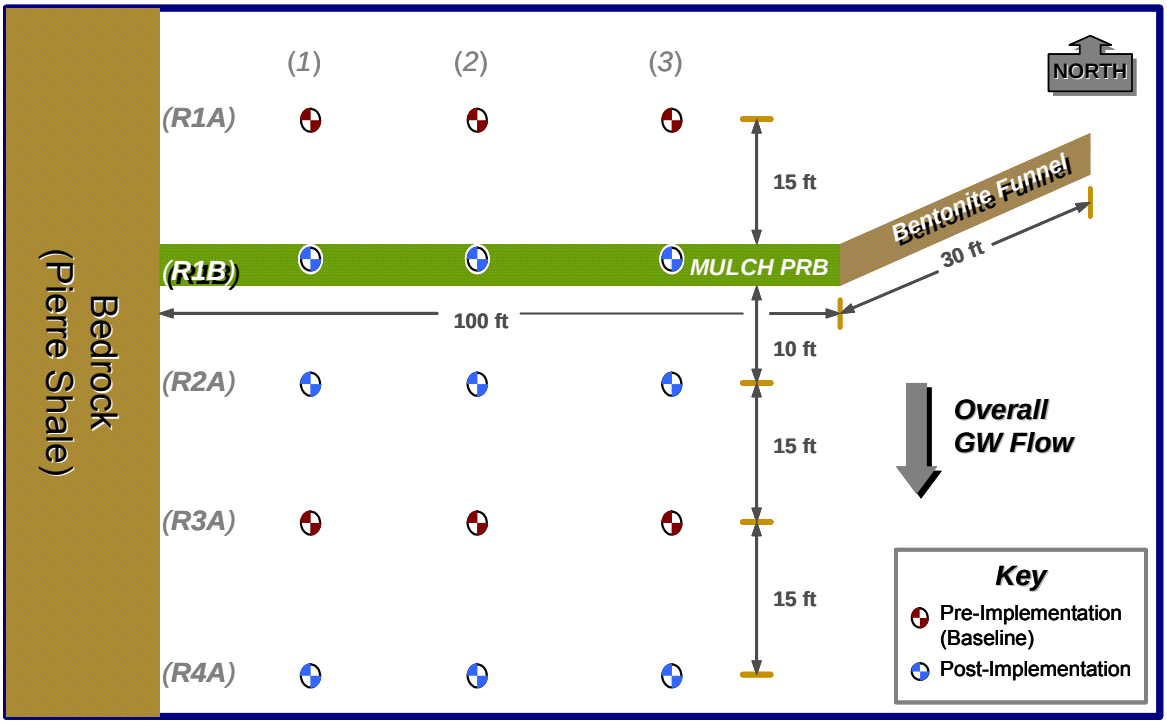


Figure 11. PRB and Well Network Plan View Implementation Schematic (not to scale). Well Row Designations are Shown; Row R1A and R3A Wells (red color symbols) **Were Installed Prior to the PRB Installation, and Row R1B, R2A, and R4A Wells** (blue color symbols) **Were Installed After the PRB Installation. The PRB and Funnel Trench Installation Began at the Eastern-most 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. The soil-bentonite funnel/or impermeable wall was approximately 30 ft long (Figure 11). Trenching depth varied between 14 bgs and 24 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, in order to account for any drop in the bedrock elevation below the saturated alluvium. 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 3 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 these second row 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. Further details on mulch/gravel PRB installation and monitoring well installation is provided below:

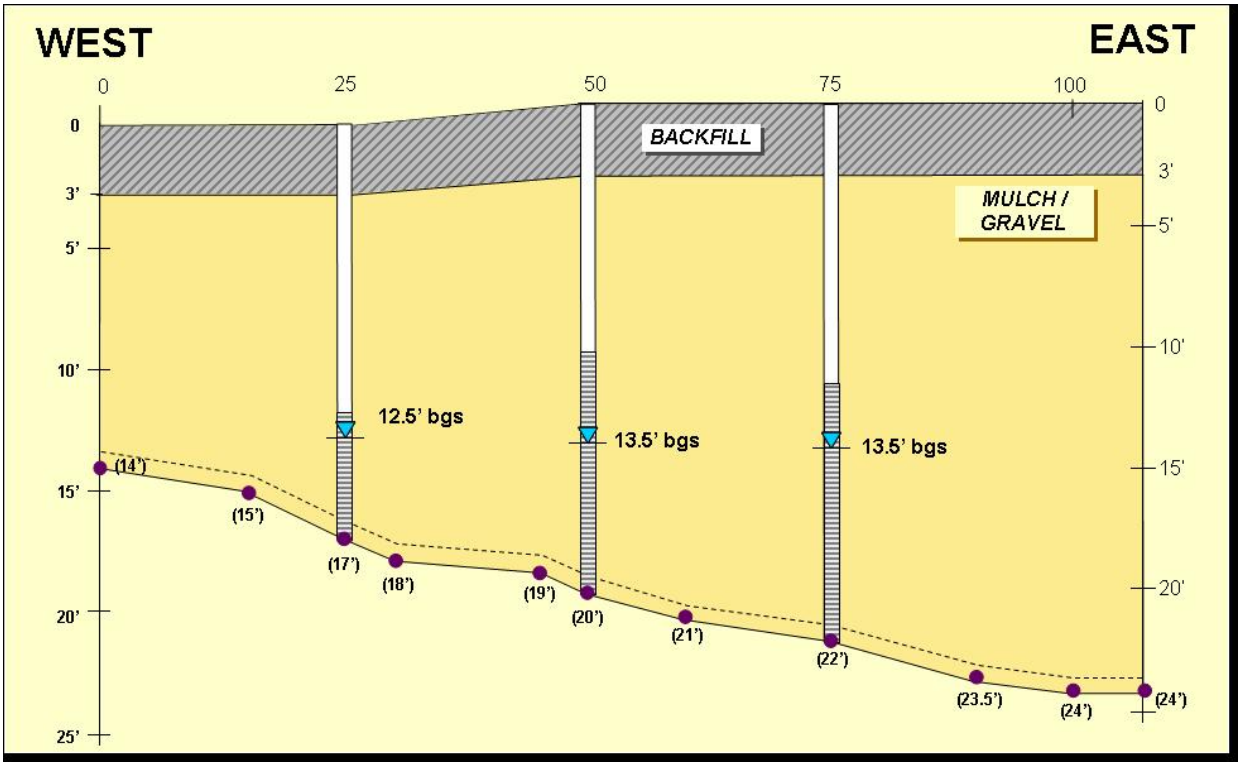


Figure 12. Cross-section of the Pilot Scale Mulch PRB at the PCD SWMU-17 Area.
Note that the bentonite funnel wall intersects the mulch PRB between the 100-ft and 105-ft mark at an approximate angle of 35 degrees (not shown)**. The dotted line near the base of the PRB indicates the original location of the Pierre shale bedrock; the PRB was keyed-in approximately 1 foot into the bedrock.**

Mulch-Gravel Biowall Installation: The mulch/gravel PRB or biowall was installed using the DeWind 800 hp one-pass trencher. The biowall was constructed to be keyed-into the Pierre Shale bedrock confining layer and, hence, varied in its depth from 14 ft bgs on the western end of the PRB to 24 ft bgs at the western end (Figure 12). The variable trenching depth of the PRB was accomplished by relying on pilot boring data during installation phase 1, and by monitoring the resistance of the trencher's cutting blade. The mulch PRB was approximately 105 ft long and 2 ft thick. Prior to trenching, a 33%:67% (volume:volume) pea gravel:mulch fill mixture was created on-site using a front-end loader. The cutting boom of the trencher was set to 20 ft or the maximum depth-to-bedrock encountered during the pilot borings. Starting from the eastern end of the biowall, the cutting chain of the trencher cut into the ground to the designated depth. When the trenching boom became perpendicular to the ground surface, the hopper for the fill delivery system was filled with the gravel/mulch mixture. The trencher then began moving westward while simultaneously cutting the trench and installing the gravel/mulch backfill from the bottom of the trench to near land surface. The gravel/mulch mixture was continuously fed into the delivery system using a front-end loader. Biowall installation proceeded until the unsaturated zone was encountered, which marked the western end of the wall. An approximately one foot cap was created over the biowall using native soils present at the site as fill material.

Soil-Bentonite Impermeable Wall Installation: A 30-ft long and 2-ft thick soil-bentonite impermeable wall was tied into the eastern end of the biowall. The impermeable wall served as a hydraulic control for the eastern end of the mulch biowall and helps funnel groundwater through the biowall. The impermeable wall was oriented approximately 30-35 degrees north of the biowall orientation (See Figure 11). The design depth of the soil-bentonite wall was 24 ft bgs to account for the grade of the shale bedrock confining the bottom of the saturated alluvium. Three-percent bentonite by weight was added to the formation, resulting in a mixture that sufficiently lowered the hydraulic conductivity to create an effective impermeable funnel wall. Initially, a 2-ft deep and 2-ft wide trench was excavated along the trace of the impermeable wall and the specified amount of bentonite was placed inside the excavation. The trencher was then introduced to cut vertically into the ground to the desired depth. The trenching activity homogenized the dry bentonite with the native soils. Water was then added to hydrate the mixture and create the impermeable funnel wall.

Groundwater Monitoring Wells: As discussed above, groundwater monitoring wells around the mulch biowall were installed in two phases, one initiated before the PRB installation and one after installation. Six monitoring wells were installed prior to the mulch PRB / soil-bentonite wall installation, and the remaining 6 monitoring wells, Row R2A (10-ft downgradient of the biowall) and Row R4A wells (40-ft downgradient of the biowall) were installed after the PRB emplacement. The location of the wells in relation to each other and the PRB are shown in Figure 11.

During each monitoring well installation, drill cuttings were logged to provide a description of the stratigraphy until the Pierre Shale bedrock was encountered. The sampling tool was decontaminated between each sampling interval. There was no historical evidence of VOC release at SWMU-17 and no VOC had been detected in earlier drilling operations in the area; therefore, no VOC screening was performed on the soil cuttings. Boreholes were drilled with 6-inch diameter hollow stem augers with a minimum 2-inch annular space provided between the monitoring well casing and the borehole.

Each monitoring well was constructed with 2-inch diameter schedule 40 PVC (Figure 12) and extended in depth to the alluvium/bedrock interface. A 10-foot length of 0.01-inch slot PVC screen was installed from the base of the water-bearing alluvium. In locations where the bedrock was encountered at a shallow depth (approximately 15 feet bgs) and the saturated thickness was less than 5 feet, a 5-ft screen was used. A sand pack consisting of 20-40 mesh interval silica sand was installed opposite the screened section. The well annulus above the sand pack was sealed with bentonite pellets and topped with cement bentonite grout to within 3 to 4 feet of the surface. Wells will be completed with above-ground (stick-up) completions consisting of concrete pads and locking steel well covers installed to a minimum depth of 2 feet below grade in concrete which extended a minimum 3 feet below grade, to prevent frost heaving of the well and well pad. The well covers and locks were painted to make the wells clearly visible from a distance.

Biowall Monitoring Wells: Hollow stem augers were used to install the 2-inch diameter monitoring wells within the biowall. The boreholes in the biowall material were drilled with slow rotation and with a drilling plug in the lead auger. Each borehole was advanced one to two feet into the natural formation beneath the bottom of the biowall to seat the augers and prevent the flow of sand and mulch into the hollow stem augers when the drilling plug is removed. After the

well was installed inside the augers, the augers were slowly pulled to allow the biowall backfill material to collapse around the well screen. A gravel/mulch mixture was added as necessary to bring the biowall backfill level above the top of the well screen. The well annulus above the top-of-screen depth was sealed and topped with bentonite pellets to within 3 to 4 feet of the surface.

Biowall monitoring wells were constructed with two-inch diameter PVC with the screened section (0.02-inch slot well screen) installed in the same depth interval as the groundwater monitoring wells (i.e., approximately 10-20 feet below grade). The surface completion of the biowall wells was above grade with concrete well pads and locking steel well covers set in concrete that extended to a minimum 3 foot depth below grade.

Monitoring Well Development: Monitoring wells were developed by extended pumping with an electric submersible pump or using an equivalent pumping method. A minimum of three casing volumes of fluid was removed from each monitoring well. Development continued until the pH and electrical conductivity of the discharged fluid did not vary more than 5% between successive casing evacuations. Fluid purged from the monitoring wells during development and groundwater sampling was containerized and scanned with a PID meter for the presence of volatile organic compounds. Arrangements were made for the proper disposal of the fluid at PCD.

3.5.2 Period of Operation

The first phase of the technology implementation began with the installation, development, and sampling of the baseline monitoring wells (Rows R1A and R3A) 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. Work through the second phase is anticipated to last 2 weeks from the start of implementation activities. The remaining well installation activities were completed in the week of November 28, 2005, the week after Thanksgiving holiday. 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.

3.5.3 Amount / Treatment Rate of Material Treated

For the pilot-scale demonstration, an estimated 17.2 gal/hr (2.3 ft^3/hr) of contaminated groundwater was treated, reducing the peak influent RDX concentration of 2-3 ppb to less than the analytical reporting limit of 0.2 ppb (below the regulatory threshold of 0.55 ppb) in the effluent. Peak groundwater influent concentrations were found to be significantly lower than those measured as part of the site investigation activities. The mass removal rate corresponding to these mass loadings was approximately 8.3E-6 lb/day or 3.0E-3 lb/year. Additional 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 12.

3.5.4 Residuals Handling

Trench cuttings, especially those containing saturated zone soils, were loaded onto dump trucks and transported off-site to the Southside Landfill in Pueblo for disposal as a non-hazardous waste. Explosives-contaminated groundwater from well development and purging activities was drummed and labeled for processing as investigation-derived waste (IDW) through the GETI system at PCD. Over the course of monitoring, purge water collected from treatment zone wells

that was found to be above the 10 ppb threshold of the Arsenic Rule was collected separately from the December 2005 monitoring event, and was disposed offsite at a cost of approximately $200 per 55-gallon barrel. The GETI system at PCD was not permitted to treat water with arsenic levels above 10 ppb.

3.5.5 Operating Parameters for the Technology

The mulch biowall technology is a passive continuous treatment technology whose operating parameters cannot be manipulated once it is implemented. Therefore, no variability in operating parameters was expected during the field demonstration.

3.5.2 Experimental Design

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 11), 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 RDX and HMX.
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 method selected for this analysis (See Section 3.6) 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.

3.5.7 Sampling Plan

A flow-through cell was used to obtain field measurements of dissolved oxygen, redox potential, temperature, pH, and specific conductance at all monitoring wells. In addition, the ferrous iron field method, HACH 8146, was initially performed on groundwater from wells in rows R1A, R2A, R3A, and R4A, and correlated to off-site analysis of dissolved iron. Field analysis of ferrous iron was discontinued because a good correlation was obtained in the first groundwater monitoring round between the field ferrous iron results and the dissolved iron results using laboratory results. Monitoring wells were purged, monitored, and sampled under low-flow (300 ml/min.) using a peristaltic pump. Prior to monitoring and sampling, wells were purged until field parameters (i.e., pH, temperature, and specific conductivity) stabilized. The types of analyses, number of samples, and other related information are summarized in Table 6.

3.5.8 Demobilization

Four solid samples, 2 from the PRB and 2 from the treatment zone, will be collected in the saturated zone using direct-push methods, once the demonstration/validation effort has been completed. At present, the period of operation of the pilot test has been extended by ESTCP to monitor for TOC depletion and contaminant breakthrough. Once collected, these samples will be subjected to TCLP analysis, following pore water removal, to confirm that the mulch PRB can be left in-place after the completion of the field demonstration. Similar post-steady-state testing of mulch/gravel packed columns from the treatability study demonstrated that no RDX, HMX, or RDX intermediates leach from the PRB fill material. Additional analyses involving the forage properties of the spent mulch will also be conducted, and the results will be compared to the initial fresh mulch/gravel mixture readings.

3.6 Selection of Analytical/Testing Methods

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 is a modification of SW-846 SW-8330 Method, developed by USACE Labs. The sample preparation modification by USACE uses solid-phase extraction (SPE) to enhance the sensitivity of the SW-846 SW-8330 Method. A copy of this method is included in Appendix A. 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/ERDC Omaha, Nebraska, 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 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 GC/ECD method (SW846 Method 8095) and the previously-mentioned variation of the USACE SW-8330 method. The GC method is 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-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 ion chromatography method selected for volatile fatty acid analysis (AM-23G) is far more sensitive than the gas chromatography method. Method AM-23G was developed by Microseeps and was offered exclusively by this lab.

Table 6. 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)	1000 mL	Amber-colored Glass; None	SW-8330M SW-8095M	USACE Labs, Omaha, Nebraska
Inorganic Anions (Sulfate and Nitrate)	Aqueous	12 / sampling event (R1A, R2A, R3A, R4A)	500 mL	Plastic or Glass; None	SW-9056	Severn-Trent Labs, Houston or Austin, Texas
Total (dissolved) Organic Carbon	Aqueous	12-15 / sampling event (R1A, R2A, R3A, R4A)	>100 mL	Plastic or Glass; pH<2	SW-9060	Severn-Trent Labs, Houston or Austin, Texas
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 Labs, Houston or Austin, Texas
Volatile Fatty Acids	Aqueous	6 / sampling event (R1A, R2A)	40 mL x 2	40 mL Glass VOA vials; BAK	AM23G	Microseeps, Pittsburgh, Pennsylvania
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 Labs, Omaha, Nebraska

3.5.3 QA/QC Samples not listed; Field duplicates at a 10% frequency of sampling.
** In addition to the samples listed in the table for the 5 sampling events after the PRB installation, 6 groundwater samples will be collected prior to the PRB installation, 3 from well row R1A and 3 from R3A. These baseline samples will be analyzed using Method SW-8330 listed above (explosive COCs and RDX nitroso intermediates).
***Further details listed in the Demobilization section below.

3.7 Selection of Analytical/Testing Laboratory

Reasons for the selection of USACE Labs and Microseeps Labs were outlined in the previous section. Severn-Trent Labs (STL, now TestAmerica) in Austin was chosen for its competitive rates and prior performance during the treatability testing. Note that all analyses for the base-wide quarterly groundwater monitoring program at PCD are currently performed at an onsite fixed-based laboratory run by the facility environmental contractor, EartTech, Inc. To summarize, USACE/ERDC Labs performed all explosives and explosive intermediates analyses, whereas STL and Microseeps performed analyses for inorganics and volatile fatty acids, respectively.

4. PERFORMANCE ASSESSMENT

4.1 Performance Criteria

The primary and secondary performance criteria that address the project objectives for the technology demonstration are summarized in Table 7 below.

Table 7. Performance Criteria.

Performance Criteria	Description	Primary or Secondary
Contaminant Removal	Determine the removal of RDX and HMX across the PRB and over the entire measured treatment zone by the end of the demonstration or by the time steady-state is reached.	Primary
Compliance with Regulatory Concentration	Determine whether the downgradient RDX concentration approaches the 0.55 ppb level set by the CDPHE by the edge of the measured treatment zone.	Primary
Accumulation of Intermediates	Determine the level of accumulation of nitroso intermediates from the partial reductive transformation of RDX; values in the treatment zone will be adjusted for background levels (i.e., intermediates observed upgradient of the PRB).	Primary
PRB Longevity	Evaluate the change in TOC levels downgradient of the PRB; assess loss in permeability of PRB from time of implementation and over the period of steady-state operation.	Secondary
Change in Groundwater Geochemistry	Document changes in geochemistry across the barrier and over the treatment zone.	Secondary
Analytical Matrix Effects	Document any problematic matrix effects encountered in samples downgradient of the PRB.	Secondary

4.2 Performance Confirmation Methods

Performance metrics and confirmation methods for primary and secondary criteria listed in the previous section are summarized in Table 8 below.

Table 8. 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 were 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 after 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 were detected downgradient of the PRB.
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 is 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.

Performance Criteria	*Expected Performance Metric*	*Performance Confirmation Method*	Actual (Post-Demonstration)
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 were 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 spectral analysis was not available.

The collection of site data that is representative of actual site conditions was achieved mostly through compliance with the Quality Assurance Project Plan (QAPP), included as Appendix B. The QAPP details the sampling and analysis procedures that were utilized for each type of sample during for the data collection portion of the project. In addition, the QAPP defined quality assurance objectives for precision, accuracy, completeness, representativeness, and comparability used to quantitatively evaluate the quality of the data obtained. The Health and Safety Plan that was followed during data collection is included as Appendix C.

4.3 Data Analysis, Interpretation, and Evaluation

Complete summaries of all analytical and field data are provided in Appendix D and E, respectively of this report.

4.3.1 System Startup

Installation activities for the mulch PRB and the impermeable funnel wall were conducted from November 14th through the 16th, 2005. The mulch PRB became functional immediately upon installation as it was installed using one-pass trenching. As mentioned earlier, one of the primary concerns in selecting the location for the PRB installation within the eastern RDX plume at SWMU-17 was the direction of groundwater flow. The groundwater modeling effort presented in the Field Demonstration Plan indicated the existence of a groundwater divide at, or immediately upgradient of, the source well. Placing a PRB of a permeability lower than the surrounding formation could have an effect on the location of the groundwater divide, leading to possibility of the groundwater flow direction reversal. Based on these findings, a location in the plume farther downgradient from the source was selected in order to have minimum impact on the flow regime. Hence, upon technology implementation and startup, the primary concern was to confirm that groundwater flow was occurring across the PRB from the source. The potentiometric surface interpolated from hydraulic heads measured during the first post-implementation groundwater monitoring event on December 2nd, 2005 (Figure 13) confirmed that groundwater flow continues to occur across the PRB in a south to south-westerly direction.

The second key concern upon system startup was to confirm that the plume was not bypassing the mulch PRB at its western end, where the saturated zone pinches out into an unsaturated

zone because of a rise in the bedrock elevation (Figures 8 and 12). The RDX concentrations in the plume are highest along the interface with the unsaturated zone (Figure 14).

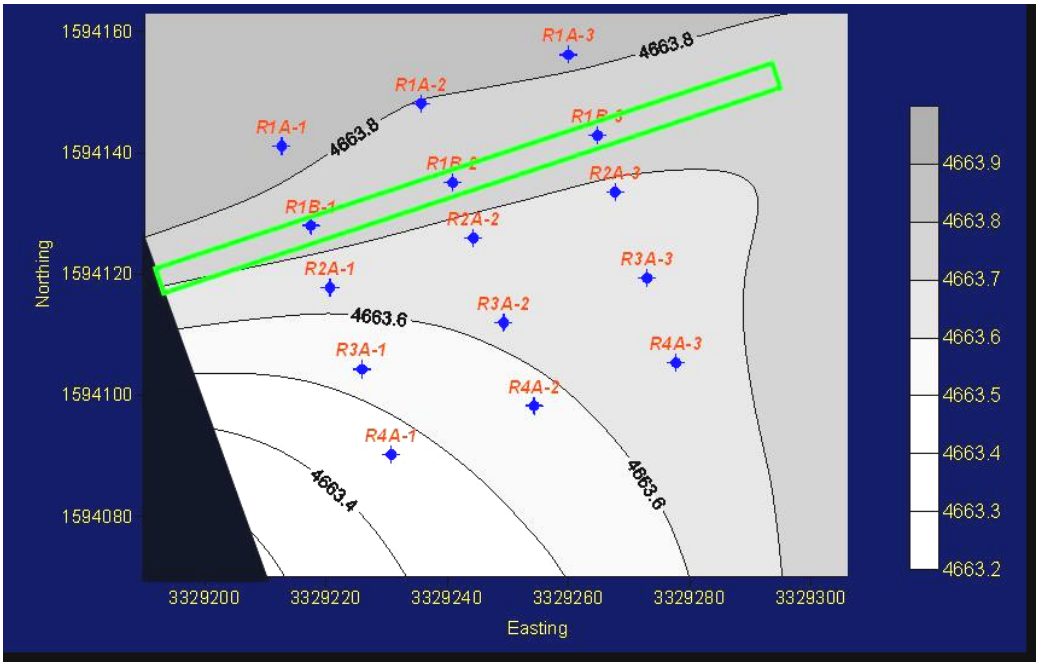


Figure 13. Potentiometric Surface Based on Hydraulic Heads Measured on December 2, 2005, 2.5 Weeks after Technology Implementation.

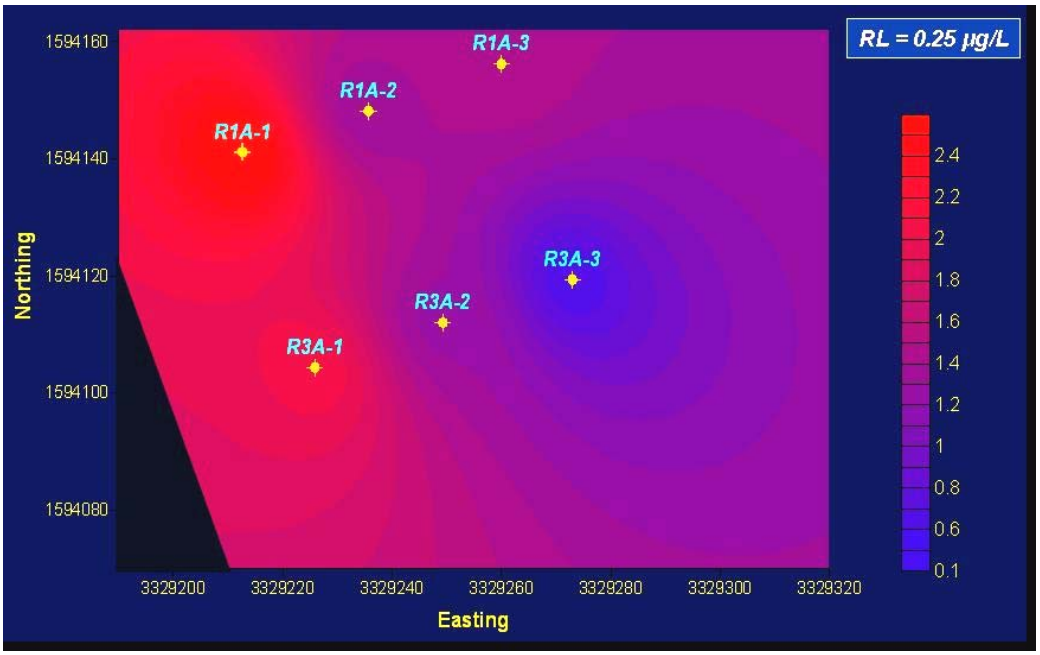


Figure 14. Baseline RDX Concentration Measured on November 10, 2005 Prior to Technology Implementation.

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.

Precautionary measures were taken prior to mulch PRB installation to ensure that the western end of the PRB would be keyed-into the unsaturated zone, precluding the possibility of contaminant bypass. These measures included drilling several pilot soil borings along the trace of the PRB to fix its location on the axis perpendicular to the anticipated groundwater flow direction. The final location of the installed mulch PRB was approximately 40 feet further east along this axis away from the unsaturated zone boundary shown adjacent to the proposed PRB installation area in Figure 10.

Plume bypass along the western end of the mulch PRB was evaluated by reviewing RDX data downgradient of the PRB until the system approached steady state. The duration of system evaluation corresponded to two monitoring events, one in December 2005 and the other in June 2006. The December 2, 2005, monitoring event (Figure 15) provided a glimpse into the startup behavior and the transient response of the system. The monitoring event occurred roughly 2.5 weeks after the mulch PRB installation, an interval that corresponded to half the estimated contaminant travel time from Row R1A wells to Row R4A wells. In other words, only about half the system pore volume had been displaced by the time of the December 2005 sampling event. This is clear in Figure 15, which shows RDX persisting in R3A and R4A wells located 25 and 40 feet downgradient of the mulch PRB, respectively. By the December 2005 event, no RDX was detected immediately downgradient of the PRB. These findings are further corroborated by the inverse correlation of RDX concentrations TOC concentrations (Table 9) observed in the monitoring data from the first two monitoring events after PRB installation.

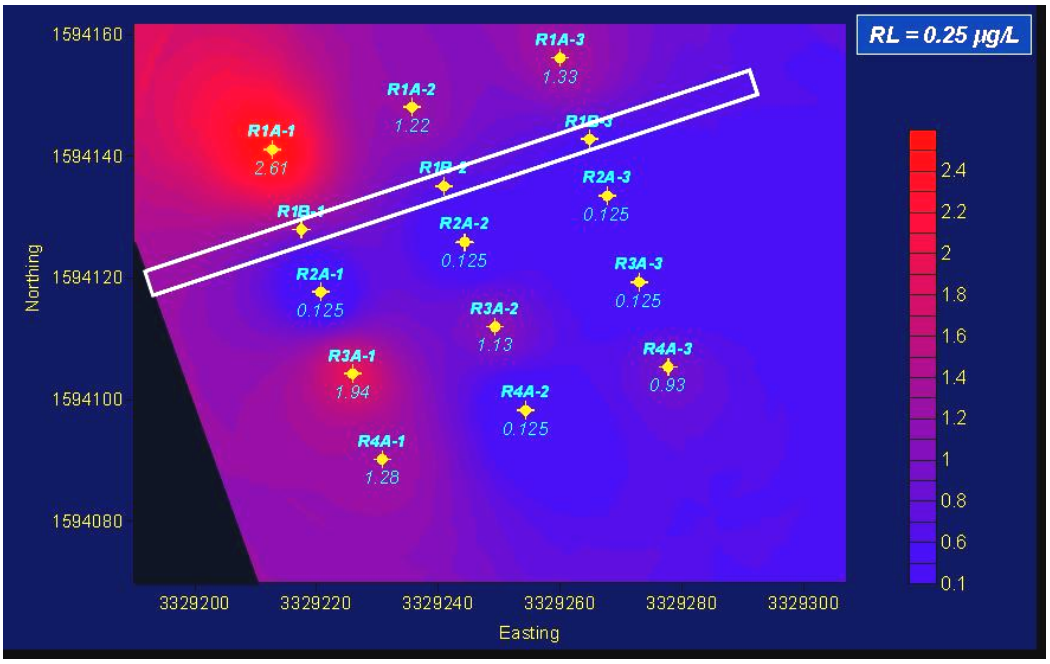


Figure 15. RDX Concentrations Measured on December 2, 2005, 2.5 Weeks After Mulch PRB Installation.

The Highest RDX Concentrations Downgradient of the PRB Generally Corresponded to the Lowest Measured TOC Concentrations, and Vice Versa. The System Exhibits Transient Behavior with a Displacement of Only Half the System Pore Volume (travel time between R1A wells and R4A wells was approximately 5 weeks, and wells were monitored only 2.5 weeks after PRB installation)**.**

Table 9. 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 ug/L	**TOC, RL = 1 mg/L**	**RDX, RL = 0.25 ug/L**	**TOC, RL = 1 mg/L**	**RDX, RL = 0.20 ug/L**	**TOC, RL = 1 mg/L**	**RDX, RL = 0.20 ug/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*	2.60	*0.100*	1.80
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	0.570	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.

By the second post-installation monitoring event on June 20, 2006, almost 31 weeks after the PRB installation, approximately 6 system pore volumes had been displaced. By this time, the system appeared to be approaching a steady state, 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 (Fig. 16).

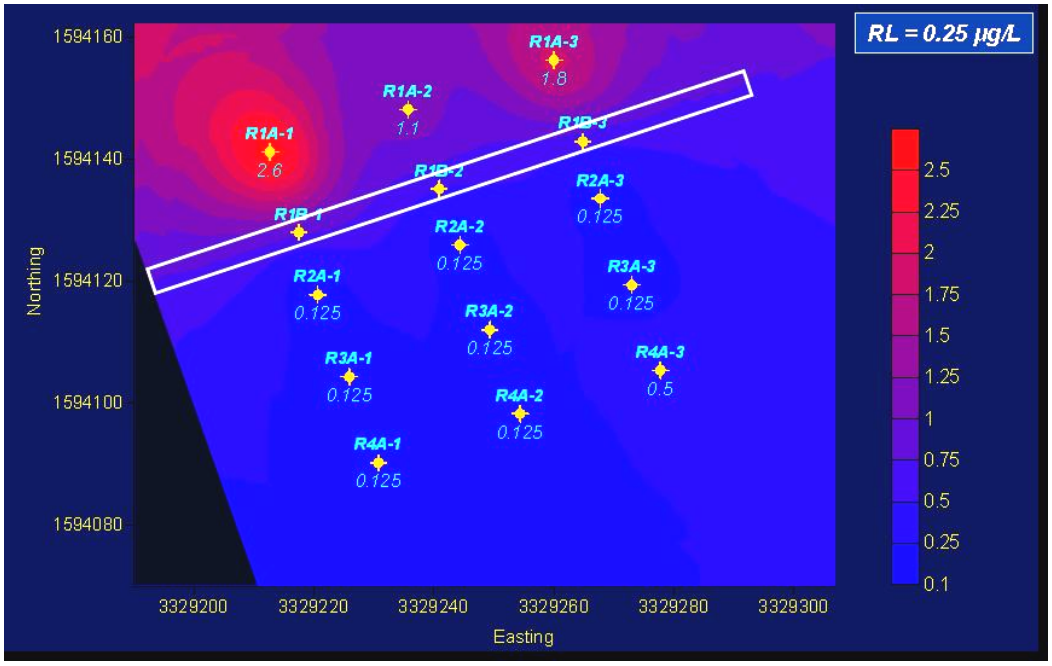


Figure 16. RDX Concentrations Measured on June 20, 2006, 7 Months After Mulch PRB Installation. RDX detected in only one downgradient well (R4A-3) at a concentration less than the regulated level.

4.3.2 Geochemistry & the Establishment of the Treatment Zone

Several of the performance criteria listed in Tables 3 and 4 mention conditions that need to be met for a "treatment zone" downgradient of the mulch PRB. Earlier in Section 3.1, a 3-part decision rationale was defined to establish the downgradient edge of the treatment zone. The 3 criteria that the downgradient wells in Rows R3A and R4A needed to satisfy were:

1. ORP less than +50 mV
2. TOC concentration of greater than or equal to 20% of the TOC concentrations in Row R2A wells.
3. Ability to consistently reduce inorganic electron acceptors, especially those that are less-preferred over RDX (e.g., sulfate).

The first criterion was easily satisfied by all field demonstration monitoring wells downgradient of the mulch PRB (Figure 17), after the first post-installation (non-steady-state) monitoring event in December 2005. The +50 mV value has been listed in literature as a threshold value for aerobic activity of facultative organisms[32].

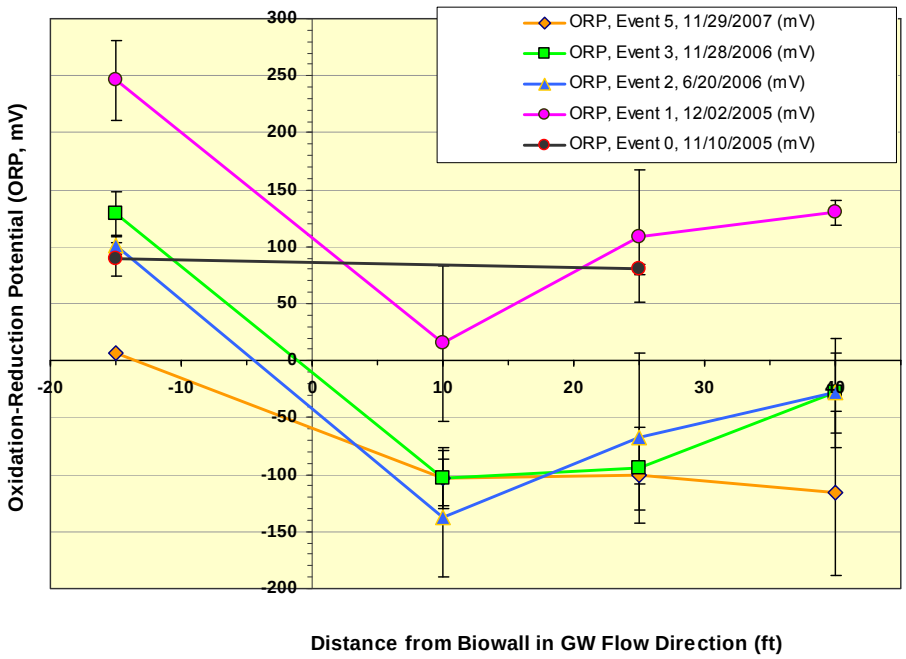


Figure 17. Oxidation-reduction Potential (ORP) Measurement Averaged Over Different Well-rows. Data is Presented as Transects Along the Direction of Groundwater Flow, Tangential to the Mulch PRB axis. Error Bars (Figures 17-21) Represent ±standard Deviation from the Average Value at Each Row. Wells Downgradient of the Mulch PRB Met the <+50 mV Limit Listed Earlier as One of the Criteria Defining the "treatment zone". Note that Data from the July 18, 2007 Event is Not Shown Because of a Systematic Calibration Error that Resulted in ORP Readings 100 mV Lower Than Expected. Instead, the Figure Shows Data from a 5th Monitoring Event Conducted in November 2007 to Ensure That System Breakthrough Was not Occurring.

For the second criterion, TOC concentrations in R3A and R4A wells were measured at values greater than 20% the value in R2A wells for all but the first post-installation monitoring event in December 2005 (Table 10). For the December 2005 monitoring event, the mean TOC concentration in R4A wells was only 0.2% of the mean R2A concentrations well below the 20% threshold listed earlier. This occurred mainly because the system was in a transient phase when it was starting up, well before it had reached pseudo-steady-state conditions.

Table 10. Post-Installation TOC Concentrations in mg/L.

Well Row ID	Distance from Biowall (ft)	Row-Averaged TOC (RL = 1 mg/L))			
		Event 1 (12/02/2005)	Event 2 (06/20/2006)	Event 3 (11/28/2006)	Event 4 (07/18/2007)
R1A	-15	*0.5 (ND)*	*0.5 (ND)*	*0.5 (ND)*	*0.5 (ND)*
R2A	10	536.63	7.37	4.20	5.33
R3A	25	188.27	5.17	2.93	2.60
R4A	40	1.13	2.43	2.03	2.03

Notes:
Non-detects shown as half their respective reporting limits.
*Blue-shaded cells indicate well-rows meeting the TOC treatment zone criterion of 20%*R2A TOC concentration.*
Orange-shaded cells indicate well-rows not meeting the TOC criterion, primarily because of non-steady-state conditions.

Geochemical indicators of reducing conditions were evident in the treatment zone downgradient of the mulch PRB. Background nitrate levels of approximately 4-6 mg/L were found to fall below detection levels downgradient of the PRB (Figure 18) in all wells except for R4A-3, which appeared to be influenced a more lateral (East-to-West) direction of groundwater flow. The reduction reaction of nitrate to nitrite is known to have a higher mid-point redox than RDX reduction, indicating that nitrate is preferentially reduced compared to RDX. Sulfate reducing conditions were also present downgradient of the PRB (Figure 19) after the December 2005 monitoring event, when the freshly installed mulch PRB appeared to temporarily release sulfate into the groundwater; however, strong sulfate reducing conditions for the 106 mg/L background sulfate in the groundwater at SWMU-17 existed only in Rows R2A and R3A. Concentrations approached background levels by Row R4A. Since RDX reduction occurs somewhere between nitrate and sulfate reducing conditions, it is best to select the less preferred electron acceptor for setting the edge of the treatment zone. Using this approach, RDX reduction is ensured within the defined treatment zone. Hence, the treatment zone was defined as the area that included Row R2A and R3A wells, but not R4A wells.

Metals mobilized by a reduction from their insoluble oxidized form to their reduced soluble form corroborated the extent of the treatment zone defined by sulfate reduction. Both total iron (Figure 20) and total arsenic (Figure 21) were observed to rise sharply above their background levels immediately downgradient of the mulch PRB in Row R2A wells. These elevated concentrations subsided by the time they reached the farthest downgradient Row R4A wells via re-oxidation and precipitation back into the aquifer matrix. These findings further indicated that the edge of the treatment zone existed between the Row R3A and R4A wells. Release of naturally-occurring arsenic above the Arsenic Rule threshold of 10 ppb proved to be problematic, as purge water generated from sampling Row R2A and R3A wells could not be treated using the GETI treatment system at PCD.

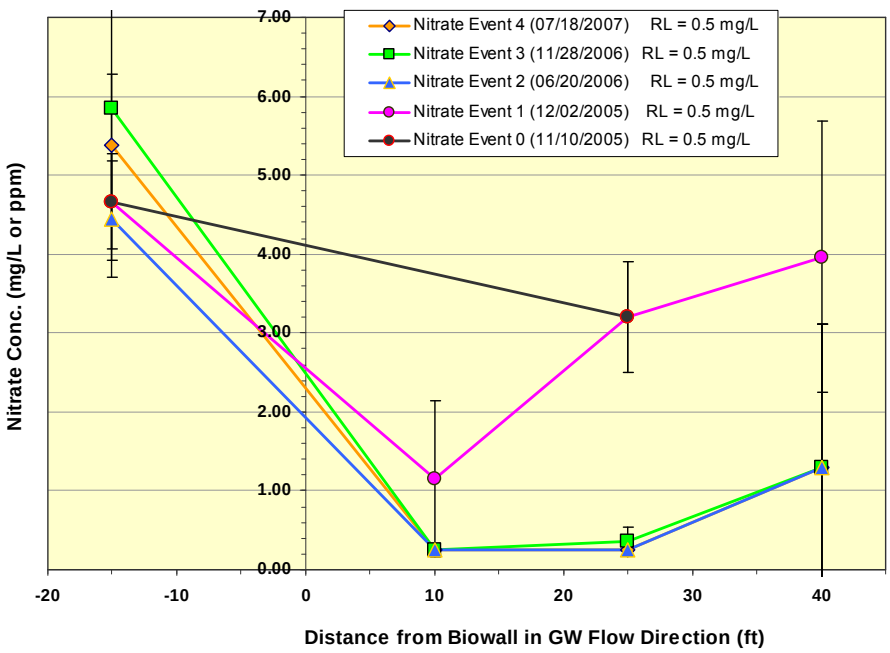


Figure 18. Row-averaged Nitrate Concentrations Over the Course of the Demonstration. Nitrate Reducing Conditions Were Established in All Downgradient Wells By the Second Post-PRB Monitoring Event in June 2006. Note That Nitrate is Preferentially Reduced Compared to RDX.

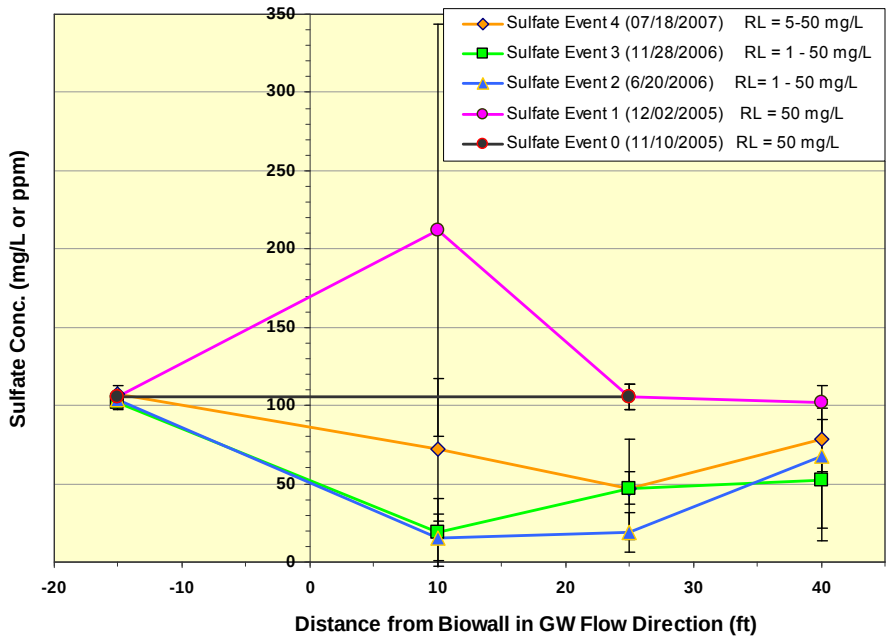


Figure 19. Row-averaged Sulfate Concentrations Over the Course of the Demonstration. Strong Sulfate Reducing Conditions Existed in Downgradient Row R2A and R3A Wells by June 2006.

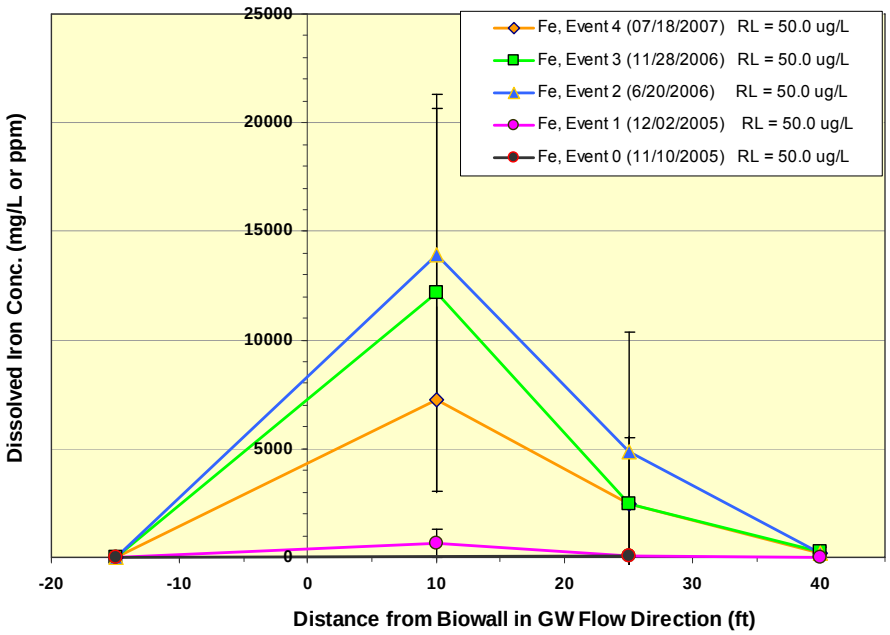


Figure 20. Row-averaged Dissolved Iron Concentrations Transects Over the Course of the Demonstration. Ferrous Iron was Mobilized From the Aquifer Matrix by the Reduction of Insoluble Ferric Iron.

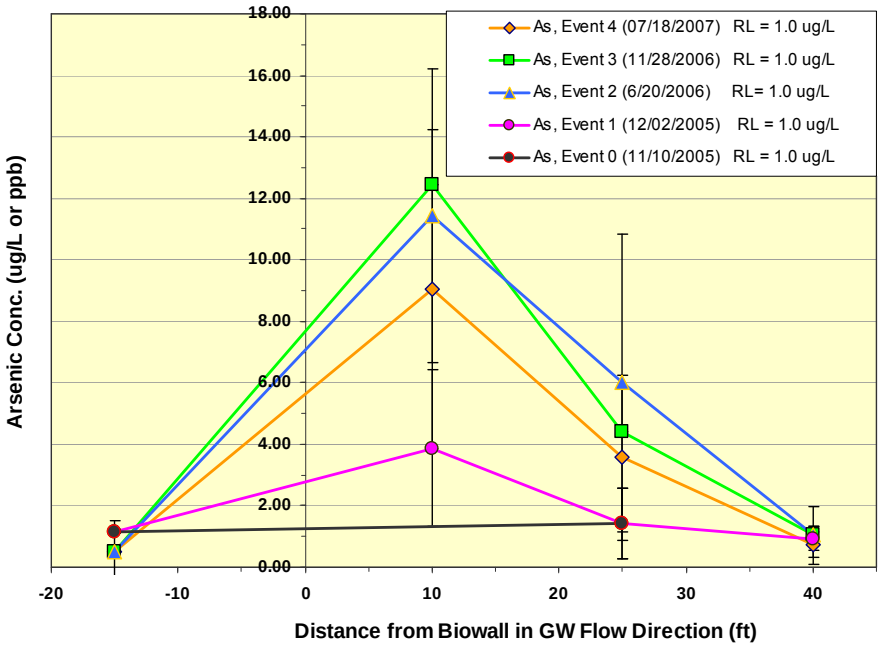


Figure 21. Row-averaged Total Arsenic Concentrations Over the Course of the Demonstration. Arsenic was Mobilized From by the Reduction of the Aquifer matrix. The Pattern was Similar to That Observed for Iron Concentration. Arsenic Concentrations Returned to Background Levels by Row R4A Wells.

4.3.3 Target Contaminant Removal & 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 22 and Table 8). 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 11). 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 (see Section 3.4.6 for further discussion).

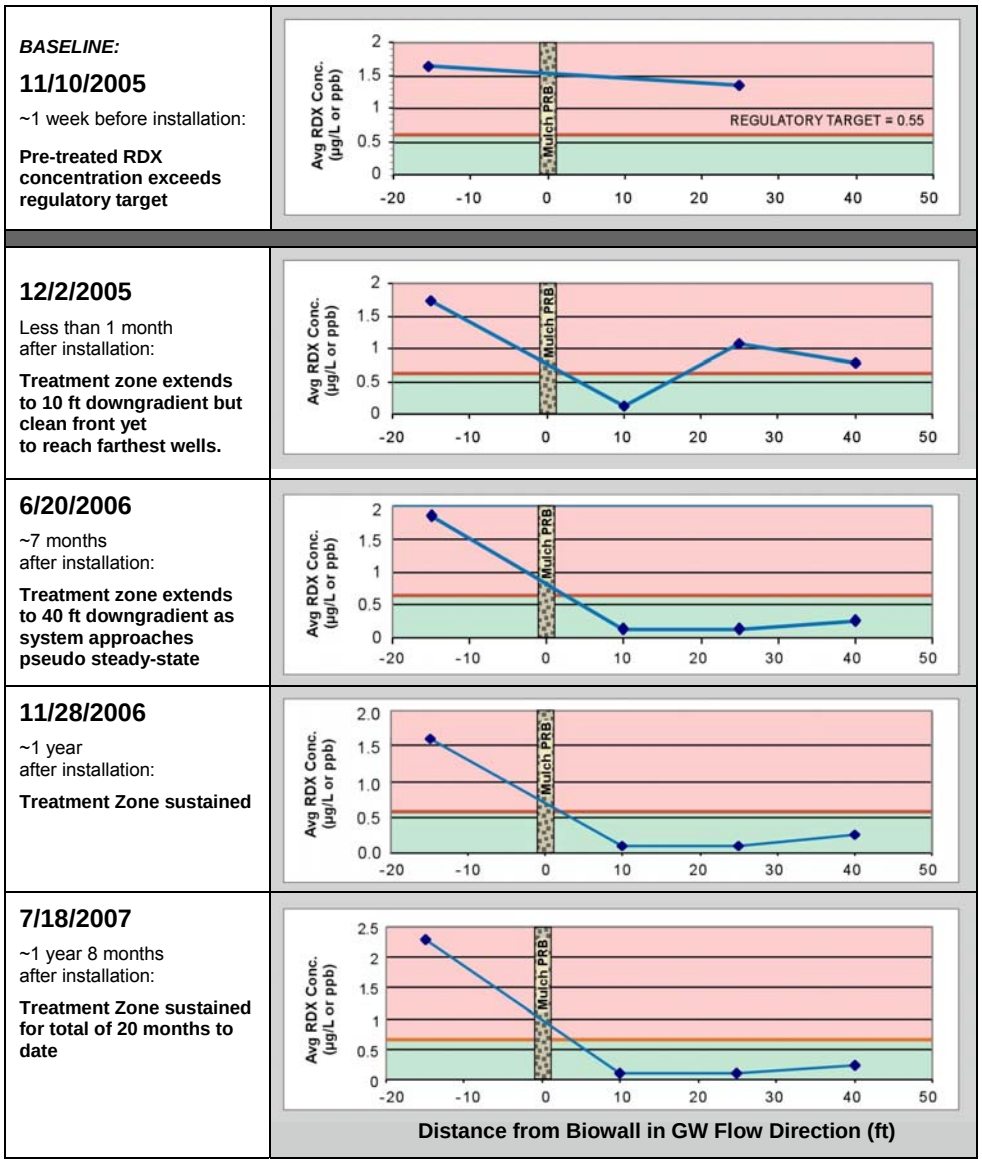


Figure 22. Row-averaged RDX Concentrations Over the Course of the Field Demonstration.

Table 11. Row-Specific Detection Frequencies and Regulatory Threshold Exceedances in Downgradient Wells.

Well Row ID	Distance from Biowall (ft)	Event 1 (12/02/2005)		Event 2 (06/20/2006)		Event 3 (11/28/2006)		Event 4 (07/18/2007)	
		No. of Detects	Detects > 0.55 ppb	No. of Detects	Detects > 0.55 ppb	No. of Detects	Detects > 0.55 ppb	No. of Detects	Detects > 0.55 ppb
R2A	10	0	0	0	0	0	0	0	0
R3A	25	2	2	0	0	0	0	0	0
R4A	40	2	2	1	0	1	1	1	0

Note: Blue-shaded cells indicate well-rows and monitoring events falling in the treatment zone.

RDX removal rates averaged over 93 percent across the mulch PRB and in the other treatment zone wells (Table 12 and Figure 23). Removals were calculated using half the reporting limit for non-detects.

Table 12. Row-Averaged RDX Removal as a Percentage of Upgradient (Row R1A) Well Concentrations.

Well Row ID	Distance from Biowall (ft)	Row-Averaged RDX Removal Percent (%)			
		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.

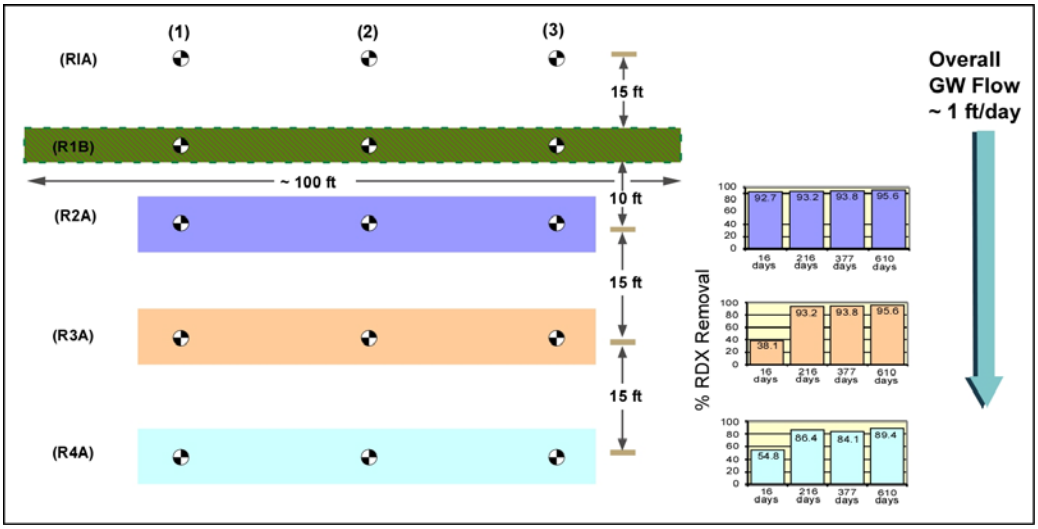


Figure 23. Row-averaged RDX Removal Over the Course of the Field Demonstration.

4.3.4 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.

4.3.5 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 9). This pattern has been reported in literature[3, 9, 26] 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, 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 13). These findings indicate that little to no fouling has occurred within the PRB.

Table 13. 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

4.3.6 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 liquid chromatography (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 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 (SW846 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. 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 14 below.

Table 14. Cost Tracking Parameters.

Cost Category	Sub Category	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. Also, 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 cubic yard) for hauling and off-site disposal of non-hazardous 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 (GW 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 4 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 sub-section.

5.2.1 Actual Demonstration Costs for ESTCP Project ER-0426

Actual capital and operating costs for the project are presented in Table 15 below.

Table 15. Actual Capital and Operating Costs for ER-0426.

Cost Category	Sub Category	Description	Actual Demo. 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	GW Flow Modeling and General Design	$38,384
		Analysis (Mulch, Geophysical)	$844
	Installation	Driller mobilization / demobilization & standby (Baseline Sampling)	$924
		Trencher mobilization / demobilization	$38,500
		Driller mobilization / demobilization & 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 Prep. 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 + Basline Sampling)	$27,043
		Other Expenses (Meals & Lodging, Travel, Consumables)	$12,836
		Monitoring equipment purchase	$778
2. OPERATING COSTS	*Dec 2005 Monitoring Event (GSI)*	Equipment rental	$1,000
		Labor	$13,129
		Other Expenses (Meals, Lodging, Travel, etc.)	$6,328
		Analytical, USACE/ERDC	$5,000
		Analytical, Other	$2,545
	Subcontract, GW Monitoring (3 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 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, & project mgmt 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 Pueblo Chemical Depot (PCD), a facility with a challenging hydrogeological flow regime. Hence, several precautionary steps were taken to ensure the project's success. Precautionary steps included 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/gallon. The volume treated was calculated using the parameters detailed in Section 3.5.3 for the 22-month period of field demonstration. Note that uncertainty in these costs is extremely low (i.e., <5%) because these are actual costs charged to the project.

Cost drivers for the 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 Pre-Tested Target Contaminant

Costs for installing a pilot-scale and a full-scale mulch PRB for a pre-tested target contaminant in a well-characterized flow regime are presented in Table 16. 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 estimated 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 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 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.

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: 1 engineer/geologist plus 1 technician; 2 mobilizations (1 sampling baseline wells, 1 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

Table 16. Pilot- and Full-Scale Costs for Treating a Pre-Tested Contaminant Using Mulch PRB.

Cost Category	Sub Category	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	GW Flow 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 & standby (Baseline Sampling)	*N/A*	*N/A*	
		Trencher mobilization / demobilization	$38,500	$38,500	Based on actual demo cost.
		Driller mobilization / demobilization & 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 Prep. 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	*N/A*	*N/A*	
		Labor (Supervision + Basline Sampling)	$13,522	$27,043	Estimated as approximately 2x actual demo cost.
		Other Expenses (Meals & Lodging, Travel, Consumables)	$6,418	$12,836	
		Monitoring equipment purchase	*N/A*	*N/A*	
2. OPERATING COSTS	*Dec 2005 Monitoring Event (GSI)*	Equipment rental	*N/A*	*N/A*	
		Labor	*N/A*	*N/A*	
		Other Expenses (Meals, Lodging, Travel, etc.)	*N/A*	*N/A*	
		Analytical, USACE/ERDC	*N/A*	*N/A*	
		Analytical, Other	*N/A*	*N/A*	
	Subcontract, GW Monitoring (3 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	**$186,451**	**$378,488**	
		QUANTITY TREATED* (VOLUME, ft^3)	**36,479.5**	**182,397.6**	
		UNIT COST ($/ ft^3)	**$5.11**	**$2.08**	

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

5.2.3 Life-Cycle Cost Comparison to an Alternative Technology

Costs were calculated for a full-scale mulch PRB and a full-scale zero-valent-iron PRB over a 10-yr technology lifecycle. For both cases, a pre-tested 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 2600 kg/m^3. Note that costs for handling and hauling the ZVI would also be significantly than those for the sand; however, these were assumed to be negligible. Costs for the two full-scale options are presented in Table 17. 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 lifecycle. 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 was 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 lifecycle 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 PRB would still be significantly lower than for ZVI PRB. Consequently, it is hard to imagine a scenario where discounted ZVI material costs would result in a lower lifecycle cost than for mulch PRB.

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 17, it was assumed that both the ZVI and the mulch PRB 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 testing 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 on-going SERDP and ESTCP projects have examined RDX transformation in ZVI PRB, 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 SEED project by the same Pis[24] 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 PRB, 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 PRB 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 PRB, 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 PRB 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 PRB, the cost associated with explosives analyses is 25% lower for the ZVI PRB in Table 17.

Table 17. Full-Scale Cost Comparison Between Mulch and ZVI PRB (10 yr lifecycle)**.**

Cost Category	Sub Category	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 (explosives)	*N/A*	*N/A*
		Analytical, Other	*N/A*	*N/A*
	Engineering Design Costs	GW Flow Modeling and General Design	$20,000	$20,000
		Analysis (Mulch, Geophysical)	*N/A*	*N/A*
	Installation	Driller mobilization / demobilization & standby (Baseline Sampling)	*N/A*	*N/A*
		Trencher mobilization / demobilization	$38,500	$38,500
		Driller mobilization / demobilization & 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 Prep. 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 + Basline Sampling)	$27,043	$27,043
		Other Expenses (Meals & Lodging, Travel, Consumables)	$12,836	$12,836
		Monitoring equipment purchase	*N/A*	*N/A*
2. OPERATING COSTS	*Dec 2005 Monitoring Event (GSI)*	Equipment rental	*N/A*	*N/A*
		Labor	*N/A*	*N/A*
		Other Expenses (Meals, Lodging, Travel, etc.)	*N/A*	*N/A*
		Analytical, USACE/ERDC	*N/A*	*N/A*
		Analytical, Other	*N/A*	*N/A*
	Subcontract, GW Monitoring (3 Events)	Subcontract (Lump Sum)	$168,121	$168,121
		Purge Water Disposal	$13,340	$13,340
		Analytical, USACE/ERDC (explosives)	$100,050	$100,050
		Analytical, Other	$6,531	$6,531
		GRAND TOTAL	**$617,794**	**$855,120**
		QUANTITY TREATED* (VOLUME, ft^3)	**994,892.7**	**994,892.7**
		UNIT COST ($/ ft^3)	**$0.62**	**$0.86**

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

6. 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 PRB/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 to ensure that the results that accurate and precise. Commercially-available analytical methods, especially SW846 Methods 8330 and 8095, cannot reliably achieve these requirements at trace level and must be amended to incorporate pre-concentration (or solid phase extraction) 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 PRB 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. Each of these problems, together with a potential plan of action that they should trigger, is summarized in Table 18 below.

Table 18. Contingency Matrix and Plan of Action (Reproduced from RRAD RAP, GSI).

CASE	*Problem 1:* Conc. > 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. *"Conc. > 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 HRC® and EOS® are available[25] can be utilized in the occurrence of mulch depletion.

7. REFERENCES

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POINTS OF CONTACT

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APPENDIX A: Analytical Methods Supporting Sampling Plan

1. Explosives: USACE SOP M-8330-ECBO-OA (Method SW-8330M)
2. Explosives: SW846 Method 3535a / 8095 (Method SW-8095M)
3. Inorganic Anions: STL SOP HE-ATM-WC003 (SW846 SW-9056)
4. Total Organic Carbon (TOC): STL SOP HE-ATM-WC007 (SW846 SW-9060)
5. Volatile Fatty Acids: Microseeps SOP-AM23G
6. Ferrous Iron in Water (Field Method): HACH Method 8146
7. Total Metals: STL SOP for SW-846 Method 6010

United States Army Corps of Engineers
Engineer Research and Development Center
Environmental Laboratory

Environmental Chemistry Branch

Omaha Facility

TITLE: **Explosives (SW-846 Method 8330M)**

SOP NUMBER: **M-8330-ECBO-OA**
VERSION: **2.4**

PREPARED BY: _____
Date

REVIEWED BY: _____
Technical Specialist Date

_____
QA Officer Date

_____
Branch Chief Date

SOP MANUAL CONTROL NUMBER

Official Document

Current SOP supercedes all previous versions.

Previous Versions of this SOP

SOP Number	Version	Date Issued
M-8330-CQAB-OA	1.0	September 16, 1996
M-8330-ECBO-OA	1.1	April 3, 2002
M-8330-ECBO-OA	2.1-draft	September 3, 2002
M-8330-ECBO-OA	2.2-draft	March 28, 2003
M-8330-ECBO-OA	2.3-draft	March 1, 2004

End of version history

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1. Scope and Application

1.1. The procedures in this Standard Operating Procedure (SOP) are used by the Environmental Chemistry Branch - Omaha (ECBO) for SW-846 Method 8330 for the extraction and trace analysis of explosive residues in water, soil/sediment, and plant matrices. Target analytes are determined by high performance liquid chromatography (HPLC) with a UV detector. The ECBO target analyte list for Method 8330 is given in Table 1. In the absence of project specific requirements, the analytes marked with a star,*, will be determined. The other analytes may be reported at the discretion of the analyst.

Table 1. SW-846 Method 8330M Target Compounds

Compound	Abbrev.	CAS No.
*Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
2,6-Diamino-4-nitrotoluene	2,6-DA-4-NT	59229-75-3
4,6-Diamino-2-nitrotoluene	4,6-DA-2-NT	6629-29-4
*Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
2-Amino-6-Nitrotoluene	2-A-6-NT	603-83-8
4-Amino-2-Nitrotoluene	4-A-2-NT	119-32-4
*1,3,5-Trinitrobenzene	TNB	99-35-4
2-Amino-4-Nitrotoluene	2-A-4-NT	99-55-8
*1,3-Dinitrobenzene	DNB	99-65-0
*Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
3,5-Dinitroaniline	DNAn	618-87-1
*Nitrobenzene	NB	98-95-3
*2,4,6-Trinitrotoluene	TNT	118-96-7
*4-Amino-2,6-dinitrotoluene	4-A-DNT	1946-51-0
*2-Amino-4,6-dinitrotoluene	2-A-DNT	355-72-78-2
*2,4-Dinitrotoluene	2,4-DNT	121-14-2
*2,6-Dinitrotoluene	2,6-DNT	606-20-2
*2-Nitrotoluene	2-NT	88-72-2
*3-Nitrotoluene	3-NT	99-08-1
*4-Nitrotoluene	4-NT	99-99-0

1.2. Method Detection Limits (MDL) and Laboratory Reporting Limits (LRL), or Quantitation Limits, are given in Appendix 1 for target analyte compounds in low- and high-level waters as well as soils. For plant tissue samples, MDL studies should be performed on comparable, non-contaminated material.

2. Method Summary

2.1. This SOP provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb (µg/L) levels of certain explosives residues in water and ppm (mg/kg) in soil, sediment, and plant tissue. Samples must be appropriately extracted prior to HPLC analysis.

2.2. There are three appropriate sample preparation techniques for aqueous samples.

2.2.1. Low-level Solid Phase Extraction (SPE) Method. Aqueous samples of low concentration are extracted by using solid phase extraction cartridges. Extracts are eluted from the cartridges with acetonitrile at a flow rate of approximately 10 mL/min with a vacuum manifold. The extract volume is adjusted to 20 mL with 1% acetic acid. An aliquot is separated on an ODS-20 reverse phase column, determined at 254 nm, and confirmed on a Phenyl-Hexyl column.

2.2.2. Low-level Salting-Out Method with No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure that uses acetonitrile and sodium chloride. The small volume of acetonitrile which remains undissolved above the salt water is drawn off and transferred to a small volumetric flask and back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed by using a Pasteur pipet. The concentrated extract is diluted 1:4 (v/v) with reagent grade water. An aliquot is separated on an ODS-20 reverse phase column, determined at 254 nm, and confirmed on a Phenyl-Hexyl column.

> **NOTE**: The SPE method is the default method for extraction of aqueous samples at the Environmental Chemistry Branch Omaha facility.

2.2.3. High-Level Direct Injection Method: Aqueous samples of high concentration can be diluted 3:1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a Phenyl-Hexyl column.. If HMX is an important target analyte, methanol is the preferred dilution solvent.

2.3. Soil, sediment, and tissue samples are extracted by using acetonitrile in an ultrasonic bath. The concentrated extract is diluted 1+3 (v/v) with 0.5% calcium chloride (aq), filtered, and analyzed as described above for water extracts.

3. Health and Safety

3.1. The Environmental Chemistry Branch – Omaha Chemical Hygiene Plan provides detailed information and guidance for performing laboratory work in a safe manner.

3.2. Soil samples with composition as high as 2% in 2,4,6-TNT have been safely ground. Samples containing higher concentrations must not be ground in the mortar and pestle.