ESTCP
Cost and Performance Report

(ER-200425)

In Situ Bioremediation of Energetic Compounds in Groundwater

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TABLE OF CONTENTS

Page

1.0 EXECUTIVE SUMMARY 1
- 1.1 OBJECTIVES OF THE DEMONSTRATION 1
- 1.2 TECHNOLOGY DESCRIPTION 1
- 1.3 DEMONSTRATON RESULTS 1
- 1.4 IMPLEMENTATION ISSUES 2

2.0 INTRODUCTION 3
- 2.1 BACKGROUND 3
- 2.2 OBJECTIVES OF THE DEMONSTRATION 5
- 2.3 REGULATORY DRIVERS 5

3.0 TECHNOLOGY 7
- 3.1 TECHNOLOGY DESCRIPTION 7
- 3.2 TECHNOLOGY DEVELOPMENT 10
- 3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY 11
  - 3.3.1 Advantages 11
  - 3.3.2 Limitations 11

4.0 PERFORMANCE OBJECTIVES 13

5.0 SITE DESCRIPTION 15
- 5.1 SITE LOCATION 15
- 5.2 SITE GEOLOGY/HYDROGEOLOGY 17
- 5.3 GROUNDWATER CONTAMINATION 18

6.0 TEST DESIGN 21
- 6.1 CONCEPTUAL EXPERIMENTAL DESIGN 21
- 6.2 LABORATORY TREATABILITY TESTING 22
- 6.3 BASELINE CHARACTERIZATION 23
- 6.4 FIELD TESTING 23
- 6.5 SAMPLING METHODS 24
- 6.6 SAMPLING RESULTS 25
  - 6.6.1 Total Organic Carbon 27
  - 6.6.2 TNT and Key TNT Degradation Products 27
  - 6.6.3 RDX and Degradation Intermediates 28
  - 6.6.4 HMX and Degradation Intermediates 30
  - 6.6.5 Other 8330 Nitroaromatics 30
  - 6.6.6 Other Analytes and Field Parameters 31
  - 6.6.7 Summary of Results 31

TABLE OF CONTENTS (continued)

Page

7.0 PERFORMANCE ASSESSMENT 33
7.1 PERFORMANCE CRITERIA 33
7.2 TREATMENT OF EXPLOSIVES IN GROUNDWATER 33
7.3 ACCUMULATION OF DEGRADATION INTERMEDIATES 33
7.4 ADEQUATE DISTRIBUTION OF COSUBSTRATE 34

8.0 COST ASSESSMENT 35
8.1 COST MODEL 35
8.1.1 Capital Costs 37
8.1.2 O&M Costs 37
8.1.3 Demonstration-Specific Costs 37
8.2 COST DRIVERS 38
8.2.1 General Considerations 38
8.2.2 Competing Treatment Technologies 39
8.3 COST ANALYSIS 41
8.3.1 Base Case Template 41
8.3.2 Semi-Passive Bioremediation of the Entire Plume 43
8.3.3 Semi-Passive Biobarrier 45
8.3.4 Passive Injection Biobarrier 47
8.3.5 Passive Trench Mulch Biowall 48
8.3.6 Passive Trench ZVI PRB 50
8.3.7 Pump and Treat 51

9.0 IMPLEMENTATION ISSUES 53
9.1 END-USER ISSUES 53
9.1.1 Technology Applicability and Performance under Local Site Conditions 53
9.1.2 Technology Scale-Up 55
9.1.3 Secondary Impacts to the Local Aquifer 55
9.1.4 Technology Cost Compared to Other Remedial Options 56

10.0 REFERENCES 57

APPENDIX A POINTS OF CONTACT A-1

LIST OF FIGURES

Page

Figure 1. Pathways of RDX biodegradation under anoxic conditions. 4
Figure 2. Schematic of ER design. 8
Figure 3. Photograph of the demonstration site. 8
Figure 4. Layout of the demonstration plot. 9
Figure 5. Location of Picatinny Arsenal and Group I sites. 15
Figure 6. Southeastern view of Building 823 in Area 157 and troughs used to carry washdown water located on the north side of Building 823 in Area 157. 17
Figure 7. Geology of Group I Sites: Area 157 and Area 40. 18
Figure 8. Overhead view and three cross sections of the RDX plume in Area 157. 19
Figure 9. Overhead view and three cross sections of the TNT plume in Area 157. 19
Figure 10. Layout of test plot wells. 26
Figure 11. TOC concentrations in treatment plot monitoring wells during the demonstration. 27
Figure 12. Concentrations of TNT in treatment zone monitoring wells and the control wells during the demonstration. 28
Figure 13. RDX concentrations in treatment zone monitoring wells and the control wells during the demonstration. 29
Figure 14. Concentrations of HMX in treatment zone monitoring wells and the control wells during the demonstration. 30
Figure 15. Base case plume characteristics 42
Figure 16. Semi-passive bioremediation alternative with cheese whey for whole plume treatment. 44
Figure 17. Semi-passive biobarrier alternative with cheese whey for plume cutoff. 46
Figure 18. Passive biobarrier alternative with EVO for plume cutoff. 47
Figure 19. Passive biobarrier alternative utilizing a mulch wall for plume cutoff. 49
Figure 20. Passive barrier alternative utilizing ZVI for plume cutoff. 50

LIST OF TABLES

Page

Table 1. Performance objectives. 13
Table 2. Sampling and operational schedule. 23
Table 3. Sampling parameters, preservatives, and analytical methods. 25
Table 4. Total samples collected during the project. 25
Table 5. Demonstration cost components. 35
Table 6. Summary of base case site characteristics and design parameters for treatment of explosives-impacted groundwater. 42
Table 7. Cost components for semi-passive bioremediation of an explosives-impacted groundwater plume. 45
Table 8. Cost components for semi-passive biobarrier treatment of explosives-impacted groundwater. 46
Table 9. Cost components for passive injection biobarrier treatment of explosives-impacted groundwater. 48
Table 10. Cost components for passive trench biowall treatment of explosives-impacted groundwater. 49
Table 11. Cost components for passive trench ZVI PRB treatment of explosives-impacted groundwater. 51
Table 12. Cost components for extraction and treatment of explosives-impacted groundwater. 52
Table 13. Summary of capital cost and NPV of costs for O&M and monitoring for treatment of explosives-impacted groundwater. 52

ACRONYMS AND ABBREVIATIONS

µg	microgram(s)
µg/L	micrograms per liter
1,3,5-TNB	1,3,5-trinitrobenzene
2-ADNT/4-ADNT	2-amino-4,6-dinitrotoluene and 4-amino-4,6-dinitrotoluene,
2,4-DNT/2,6-DNT	2,4- and 2,6-dinitrotoluene
2,6-DANT/2,4-DANT	2,6-diamino-4-nitrotoluene and 2,4-diamino-6-nitrotoluene
bgs	below ground surface
CZMW	control zone monitoring well
DNB	1,2-dinitrobenzene
DNT	dinitrotoluene
DNX	hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DO	dissolved oxygen
DoD	Department of Defense
DSERTS	Defense Site Environmental Restoration Tracking System
ER	extraction-reinjection
ESTCP	Environmental Security Technology Certification Program
ETD	Environmental Technology Division
EVO	emulsified vegetable oil
FBR	fluidized bed reactor
Fe	iron
FRTR	Federal Remediation Technologies Roundtable
FS	feasibility study
GAC	granulated activated carbon
HA	health advisory
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HRC	hydrogen release compound
IHDIV NSWC	Indian Head Division, Naval Surface Warfare Center
IPR	In-Progress Review
ISTW	in situ treatment well
K	hydraulic conductivity
kg	kilogram
L	liter
LHAAP	Longhorn Army Ammunition Plant
LOC	level of concern
LPM	liters per minute
MCGL	maximum contaminant goal level

MCL	maximum contaminant level
MEDINA	methylene dinitramine
mg	milligram
mL	milliliter
Mn	manganese
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MW	monitoring well
NDAB	4-nitro-2,4-diazabutanal
NJAC	New Jersey Administrative Code
NJDEP	New Jersey Department of Environmental Protection
NPV	net present value
NRC	National Research Council
O&M	operation and maintenance
OMB	Office of Management and Budget
ORP	oxidation-reduction potential
P&T	pump and treat
PETN	pentaerythritol tetranitrate
Picatinny	Picatinny Arsenal, Dover, NJ
PLC	programmable logic controller
PQL	practical quantitation limit
PRB	permeable reactive barrier
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RI	remedial investigation
RI/FS	remedial investigation/feasibility study
Shaw	Shaw Environmental, Inc.
Tetryl	2,4,6-trinitrophenylmethylnitramine
THPS	tetrakis (hydroxylmethyl) phosphonium sulfate
TNT	2,4,6-trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	total organic carbon
TZMW	treatment zone monitoring well
USACE	U.S. Army Corp of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
VOA	volatile organic analysis
WWTP	wastewater treatment plant
ZVI	zero-valent iron

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1.0 EXECUTIVE SUMMARY

1.1 OBJECTIVES OF THE DEMONSTRATION

This Environmental Security Technology Certification Program (ESTCP) demonstration was designed to evaluate the technical effectiveness of in situ bioremediation as a treatment technology for explosives in groundwater at the Picatinny Arsenal in Dover, NJ. A recirculation cell design with semi-passive operation was employed to distribute and mix cosubstrate with contaminated groundwater in order to promote the biodegradation of nitramine and nitroaromatic explosives by indigenous bacteria. Cheese whey was utilized as a cosubstrate during the project based on extensive treatability testing. The overall performance of this design for remediation was determined during the demonstration. The impacts of the technology on the geochemistry of treated groundwater also were evaluated. In addition to technical performance, the demonstration provided the capital and operation and maintenance (O&M) costs of this type of system at a scale that can then be extrapolated to different full-scale designs.

1.2 TECHNOLOGY DESCRIPTION

This project builds upon recent microbiological research suggesting that explosives-degrading bacteria are widespread but that they require one or more cosubstrates to completely degrade most nitramine and nitroaromatic explosives. During the demonstration, a groundwater extraction-reinjection (ER) system was installed to distribute and mix cheese whey as a cosubstrate with explosives-contaminated groundwater in the subsurface. The system, consisting of two extraction wells and a single injection well, was operated in a semi-passive mode, pumping for 3-5 days during injection of soluble cheese whey constituents ("active" phase), and then being shut down for 6-12 weeks ("passive" phase) once adequate mixing and distribution of the whey was achieved. The cheese whey was added in four active cycles during the initial 6 months of operation. A total of 830 kilograms (kg) of cheese whey was added during these cycles (dissolved constituents only), and the system was operated at ~38 liters per minute (LPM) flow. The final groundwater sampling event was conducted more than a year after the final active cycle. This approach facilitated modification of the aquifer geochemistry to enhance subsurface biodegradation of energetic compounds by indigenous bacteria while minimizing system O&M issues due to biofouling.

1.3 DEMONSTRATON RESULTS

The primary performance objective of this demonstration was to reduce explosives in groundwater at Picatinny to concentrations below regulatory concern. For 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the U.S. Environmental Protection Agency (USEPA) has issued Lifetime Health Advisory Limits (maximum contaminant goal level [MCGL] Values) of 2 micrograms per liter (µg/L), and the equivalent value for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is 400 µg/L. The New Jersey Department of Environmental Protection (NJDEP) also issued Interim Groundwater Quality Criteria for both RDX and TNT in 2008. The specific criteria are 0.3 µg/L and 1 µg/L for RDX and TNT, respectively. The key performance objective for this demonstration was achieved. Concentrations of TNT in the treatment zone monitoring wells (TZMW) declined rapidly after cheese whey injection. Initial concentrations ranged from 5 to 190 µg/L during the final baseline

sampling event. The concentration of TNT was below the analytical detection limit (practical quantitation limit [PQL] = 0.25 µg/L) in all of the TZMWs by Day 62 of the study and remained at or below this concentration in all TZMWs except one throughout the remainder of the 565-day demonstration. RDX concentrations in the TZMWs ranged from 5 µg/L to 170 µg/L during the final baseline sampling event, with a mean value of 66 µg/L. RDX loss occurred somewhat more slowly than for TNT, but 148 days after the initial injection of cheese whey, RDX concentrations were ≤5 µg/L in all 6 of the TZMWs, and concentrations in 5 of these wells were <1.5 µg/L. From Day 222 to Day 565, the concentration of RDX in all of the downgradient TZMWs was <1 µg/L, and all were <0.2 µg/L on Day 565. Thus, more than one year after the final injection of cheese whey on Day 181, RDX was <1 µg/L throughout the downgradient region of the treatment plot. A significant decline in HMX was also observed in all wells, and by Day 274, each of the four downgradient TZMWs had HMX concentrations <0.4 µg/L (from a starting mean concentration of 50 µg/L). A slight rebound was observed in one downgradient TZMW on Day 565, but HMX remained <1 µg/L in each of the other wells throughout the remainder of the study. Thus, as with RDX and TNT, the data from the downgradient TZMWs indicate that the addition of cheese whey to the Picatinny aquifer effectively promoted HMX biodegradation to sub µg/L concentrations.

1.4 IMPLEMENTATION ISSUES

Overall, this in situ bioremediation approach proved to be highly effective for the treatment of nitramine and nitroaromatic explosives in groundwater. The applicable regulatory guidance and/or action levels were achieved for RDX and TNT, there was no significant accumulation of degradation intermediates, and the active-passive treatment approach resulted in no significant O&M issues. Moreover, after only four active injection cycles, concentrations of total organic carbon (TOC) from the cheese whey remained high enough in downgradient monitoring wells to promote degradation of explosives and intermediates for more than a year after the final injection. The data showed that, as long as TOC concentrations greater than ~5 milligrams per liter (mg/L) were maintained, rebound of explosives was negligible. Thus, this project clearly shows that in situ bioremediation of explosives in groundwater using active-passive cosubstrate addition can be a viable long-term treatment approach. This technology is expected to be widely applicable at military installations across the United States.

2.0 INTRODUCTION

This ESTCP project was a collaborative effort among scientists at Shaw Environmental Inc., (Shaw) (Lawrenceville and Mt. Arlington, NJ, offices), the National Research Council (NRC) Biotechnology Research Institute (Montreal, Canada) and the Environmental Technology Division (ETD) at Picatinny Arsenal in Dover, NJ (Picatinny). The objective of this project was to demonstrate in situ bioremediation of energetic compounds in a contaminated aquifer using cosubstrate addition to stimulate indigenous bacteria capable of degrading these explosives. The demonstration project was performed at a former explosives packing facility (Area 157) at Picatinny. A groundwater recirculation system was installed to distribute and mix cheese whey as a cosubstrate with explosive-contaminated groundwater in the subsurface. The system was operated in a semi-passive mode, pumping for 3-5 days during injection of liquid cheese whey (active phase) and then being shut down for 6-12 weeks (passive phase) once adequate mixing and distribution of the whey was achieved. This approach facilitated modification of the aquifer geochemistry to enhance subsurface biodegradation of energetic compounds by indigenous bacteria while minimizing system O&M issues due to biofouling. The data suggest that bioremediation can be used effectively in groundwater to treat common energetic compounds, including TNT, RDX, and HMX. This approach is expected to be widely applicable for in situ remediation of these compounds at Department of Defense (DoD) sites.

2.1 BACKGROUND

The energetic compounds, TNT, RDX, HMX, and various breakdown products from these materials, such as 2,4- and 2,6-dinitrotoluene (DNT) are widespread soil contaminants at many current and former military facilities. Because these compounds can be transported through soils to the subsurface, they are now also impacting groundwater and drinking water at numerous locations across the country. According to a recent report from the U.S. Army Corps of Engineers (USACE), the U.S. Army has 583 sites at 82 installations that have explosives contamination in groundwater and 87 additional locations with suspected contamination (Wani et al., 2002). Picatinny has several sites in with explosives in soils and groundwater (Picatinny, 2001).

The biodegradation of nitramine and nitroaromatic explosives has been studied for more than two decades (e.g., McCormick et al., 1981; Walker and Kaplan, 1992; Preuss et al., 1993; Spain, 1995; Spain et al., 2000; Hawari et al., 2000a,b; Kitts et al., 1994). The biodegradation of RDX has been observed under both anoxic and aerobic conditions. Under anoxic conditions, RDX biodegradation proceeds by sequential reduction of the nitro groups to nitroso groups, resulting in the formation of hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) (Figure 1A). This compound is then reduced further to hydroxylamine derivatives, after which ring cleavage occurs, resulting in the formation of various products, including formaldehyde, nitrous oxide, methanol, and carbon dioxide (Fournier et al., 2002, 2004; Hawari et al., 2000a,b; 2002). A second anaerobic pathway has been identified that proceeds via initial denitration and direct ring cleavage of RDX to form methylene dinitramine (MEDINA) and bis(hydroxymethyl)nitramine; these compounds subsequently break down further to nitramine, formaldehyde, and nitrous oxide (Figure 1B). The anaerobic degradation of RDX generally requires an organic (or inorganic) cosubstrate to proceed. In some instances, RDX has been proposed to serve as an alternate electron acceptor for bacteria under anaerobic conditions (Beller, 2002), while in other cases, RDX appears to

serve as a microbial nitrogen source (Coleman et al., 1998). Within diverse microbial communities, RDX or its degradative intermediates may serve both purposes for some bacteria and may provide carbon and energy to some strains as well. During this demonstration, cosubstrate was added to an aquifer to promote the anaerobic degradation of RDX, HMX, TNT, and other explosives by native bacteria.

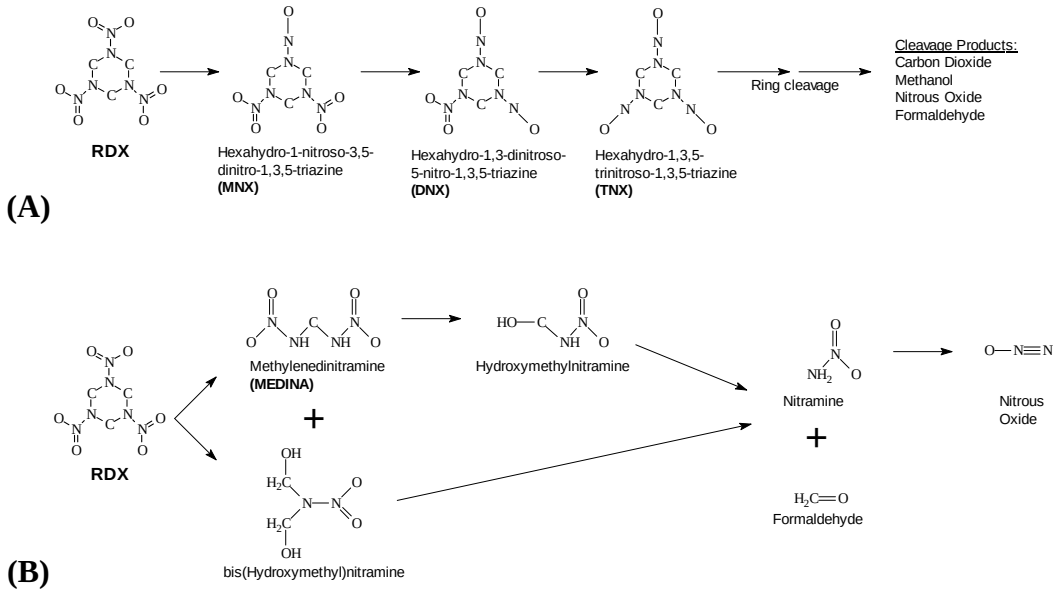

Figure 1. Pathways of RDX biodegradation under anoxic conditions.

A variety of different systems have been tested to promote in situ and ex situ bioremediation of explosives in soils (Pennington, et al., 1995; Boopathy and Manning, 1998; Widrig et al., 1997; Fuller et al., 2003). Unlike soils, however, efficient and cost-effective bioremediation technologies for groundwater containing explosives are very limited. The current methodologies for contaminated groundwater, which include granulated activated carbon (GAC) filtration (Bricka and Sharp, 1993) and ultraviolet (UV) oxidation (Bricka and Sharp, 1993) are either ineffective or very expensive for water treatment. In addition, the bioremediation technologies that are applicable for remediation of concentrated explosives (mg/kg to gram [g]/kg levels) in soils are not applicable for groundwater, where low contaminant concentrations (µg/L) are likely to be present in large plumes. Thus new treatment technologies, particularly in situ technologies, for groundwater contamination are necessary.

Various laboratory studies using columns and microcosms clearly show the potential for accelerating the degradation of explosive compounds in groundwater using various soluble cosubstrates, such as lactate, ethanol, acetate, and soluble starch (Envirogen, 2002; Wani and Davis, 2003; Davis et al., 2004). Schaefer et al., (2007) also recently reported the biodegradation of RDX and HMX in aquifer samples from a military site in Maryland, using an emulsified oil substrate to promote biological activity. Other reports have shown that both HMX and RDX can be mineralized to carbon dioxide under anoxic conditions in slurry reactors (Shen et al., 1998a,b, 2000; Young et al., 1997). In addition, a recent pilot study using contaminated groundwater from a military installation revealed that perchlorate, RDX, and HMX can be jointly biodegraded in acetate-fed fluidized bed reactors (FBRs) to effluent levels below regulatory requirements

(Fuller et al., 2007). These data, combined with data from other research projects on explosives degradation, support the development of an in situ biotreatment technology to remediate groundwater contaminated with energetic compounds. An in situ biological treatment regime offers the best possibility for efficient and cost effective remediation of explosive compounds-contaminated groundwater.

2.2 OBJECTIVES OF THE DEMONSTRATION

This project was designed to test and validate the following: (1) in situ anoxic bioremediation of energetics-contaminated groundwater through cosubstrate addition, and (2) the application of a semi-passive groundwater ER system to achieve mixing of the cosubstrate with the explosives-contaminated water and delivery of the mixture to indigenous explosives-degrading bacteria. One key was to demonstrate that cosubstrate addition can be used to efficiently and cost-effectively treat energetic compounds in subsurface groundwater to below levels of regulatory concern. One of the most critical issues in applying an organic cosubstrate or other amendment to the subsurface is how to facilitate mixing of that chemical with contaminated groundwater. If sufficient mixing is not achieved, areas of untreated water will pass through the treatment zone, and the technology will be ineffective as a long-term remedy. The creation of a recirculation cell within a subsurface aquifer using an engineered groundwater ER system helps to ensure proper mixing and delivery of cosubstrate at required concentrations. The semi-passive operation of this system is subsequently utilized to reduce O&M costs.

The semi-passive operation occurs as follows. During active treatment, the ER system removes contaminated groundwater from an aquifer via extraction wells. The extracted groundwater is then amended with the chosen cosubstrate and re-injected into one or more injection wells. The active phase generally occurs for a few days to a few weeks until the cosubstrate is adequately distributed in the aquifer. The ER system is subsequently shut down for weeks to months during the passive phase, during which time biodegradation occurs within the aquifer. The key advantage of a semi-passive approach compared to either a completely passive system (e.g., vegetable oil injection) or a completely active system, is the ability to effectively distribute cosubstrate while minimizing O&M issues (such as well biofouling) associated with continuous active pumping approaches. More information on active, passive, and semi-passive approaches is available in Stroo and Ward, 2009.

2.3 REGULATORY DRIVERS

There is currently no federal drinking water standard (maximum contaminant level [MCL]) for the nitroaromatic and nitramine explosives that are the object of this demonstration. However, the USEPA has listed RDX and 2,4- and 2,6-DNT – two breakdown products of TNT – on both the Draft Drinking Water Candidate Contaminant List and the Unregulated Contaminant Monitoring Regulation List (Federal Register, 1999). In addition, the USEPA has issued lifetime Health Advisory (HA) Limits (maximum contaminant goal level [MCGL]) of 2 µg/L for RDX and TNT and 400 µg/L for HMX (USEPA, 2004). The NJDEP has also issued Interim Groundwater Quality Criteria for both RDX (0.5 µg/L) and TNT (1 µg/L) in 2008 (New Jersey Administrative Code [NJAC], 2010).

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3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

This project builds upon recent microbiological research suggesting that explosives-degrading bacteria are widespread but that they require selected cosubstrates to completely degrade most nitramine and nitroaromatic explosives. The project also applies and tests an engineered groundwater recirculation design for cosubstrate mixing with energetic-containing water. This system was operated in a semi-passive mode to provide mixing of cosubstrate with groundwater while minimizing typical O&M issues associated with continuously active pumping approaches. Similar ER designs were shown to be highly effective for in situ treatment of perchlorate at Indian Head Division, Naval Surface Warfare Center (IHDIV NSWC) in Maryland (Hatzinger et al., 2006); at the Longhorn Army Ammunition Plant (LHAAP) in Karnack, TX (Krug and Cox, 2009); and at the former Whittaker-Bermite Site in Santa Clarita, CA (Hatzinger and Lippincott, 2009). To our knowledge, this project represents the first application of a semi-passive ER approach for nitramine and nitroaromatic explosives. This technology is anticipated to be widely applicable at DoD sites containing explosives or a mixture of explosives and propellants.

The demonstration project was performed at Picatinny. A site investigation at Picatinny revealed that several shallow monitoring wells near former explosives production areas contain energetic compounds, including HMX, RDX, and TNT. The energetics apparently migrated from the surface soils to the sandy, unconsolidated aquifer by leaching and infiltration, resulting in groundwater contamination. Two major plume areas of explosive compound migration have been identified (Group I Sites; Areas 40 and 157, respectively) (See Section 5.0). The Area 157 plume was selected for the demonstration based on contaminant concentrations and hydrogeological considerations.

A groundwater recirculation design was used to distribute and mix cosubstrate with explosives-contaminated groundwater and to deliver that substrate to indigenous bacteria (Figures 2 and 3). The recirculation design consisted of two groundwater extraction wells and one groundwater injection well installed in the aquifer cross-gradient to groundwater flow. A general schematic of the recirculation design is provided in Figure 2. The groundwater was removed from the aquifer through the two extraction wells, amended with a cheese whey additive as a cosubstrate at the surface, and then recharged into the formation through the single injection well. The injection well included a packer to allow injection of water under moderate pressure and a variable speed pump, which was used to mix the cosubstrate-amended groundwater within the well. This pump was also available to mix biofouling control agent with groundwater in the well although that process was not necessary based on well pressures. The operation of this system provided mixing of the cosubstrate with the explosives-contaminated groundwater and created a subsurface recirculation zone between the two extraction wells and the injection well. The operating conditions for the system, including pumping rates, pumping schedule (i.e., the system ran intermittently), and cosubstrate injection parameters, were readily controlled and easily modified. The initial system design and operational conditions for the demonstration were based on results from a site-specific reactive transport model developed for the project.

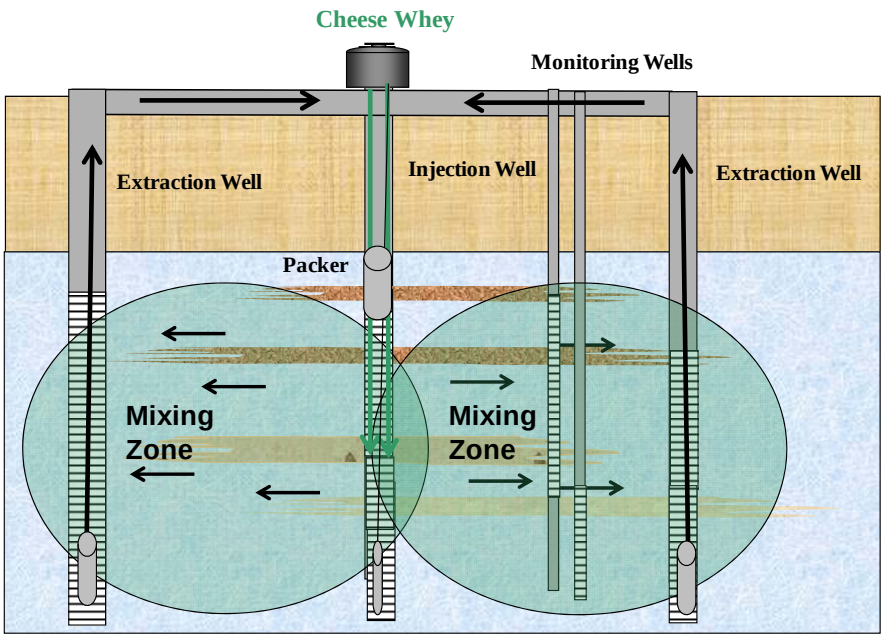

Figure 2. Schematic of ER design.

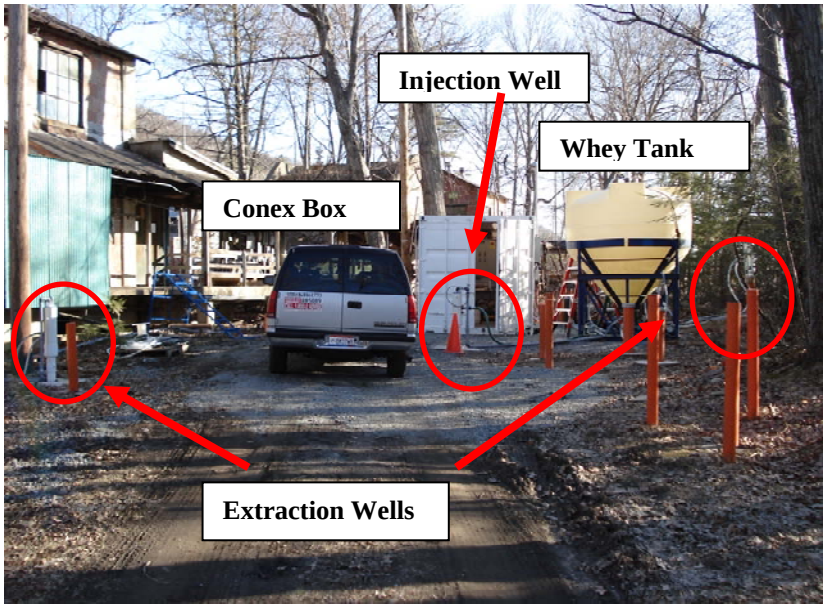

Figure 3. Photograph of the demonstration site.

A total of nine monitoring wells (MW) (including three nested wells) were used to evaluate the success of the demonstration (see Figures 4 and 10 for well layout). Four of these wells (157MW-1 to 157MW-4) were installed previously during investigative work in the Group 1 area. Well 157MW-5 was installed for this project as part of the initial site assessment work and to collect core samples for laboratory studies. The remaining nested wells (157MW-6S/6D, 157MW-7S/7D and 157MW-8S/8D) were installed in two phases. Nested wells 157MW-6S/6D were installed first and used for a pump testing. The remaining two pairs of nested wells were

installed later. Their location and screen intervals were based on the pump test and other site assessment results. The extraction (2) and injection wells (1) were installed at the same time as the final set of monitoring wells. One additional deep bedrock well (157MW-1D) was also sampled throughout the demonstration although it was anticipated to be screened well below the zone of influence of the treatment system, and contained only trace concentrations of explosives (i.e., <2 µg/L). A Conex box was designed to house the metering pumps, controls, and electrical equipment necessary to control the extraction and injection well pumps and to facilitate the amendment of groundwater with appropriate cosubstrate and biofouling control agents (see Figure 3).

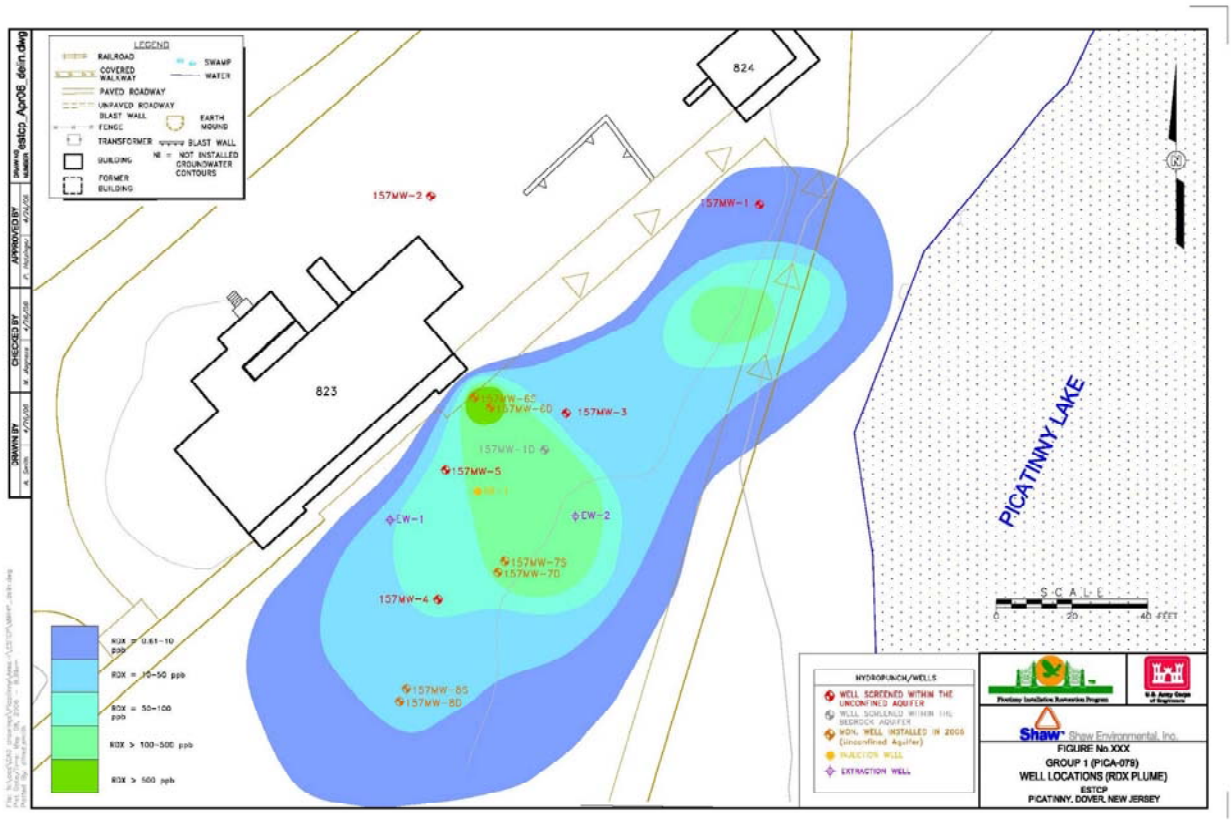

Figure 4. Layout of the demonstration plot.
The RDX plume map is shown with the well locations.
EW-1 and EW-2 are extraction wells. IW-1 is the injection well.
All other wells listed are monitoring wells.

The key design criteria for this type of system include the following: (1) the location, size, and screen intervals of extraction and injection wells; (2) the system pumping rates and pumping schedule (i.e., passive versus active phases), (3) the cosubstrate type, concentration, and dosing regimen; and (4) operational measures to minimize well biofouling. The location of the pumping wells and the pumping rate and schedule were determined using a site-specific reactive transport model. In turn, the parameters for this model were based on the measured hydrogeological conditions at the site, the concentration and extent of contamination requiring treatment, and the estimated rates of contaminant degradation derived from laboratory microcosms and column studies. A groundwater fate and transport model was developed for this site based on

hydrogeological data (geology, hydraulic gradient, hydraulic conductivity, etc.), contaminant concentrations, and estimated degradation rates from site-specific microcosm studies. This model was used to select locations for the injection well, extraction wells, and monitoring wells, and to evaluate different operating scenarios.

3.2 TECHNOLOGY DEVELOPMENT

At present, there is very little information in the literature on pilot or full-scale demonstrations of biostimulation for in situ explosives treatment in groundwater. Much of the in situ remedial work to date with these compounds has focused on approaches for contaminated soils. However, significant laboratory data support the potential for in situ treatment of explosives by indigenous organisms through addition of different cosubstrates. The development of a semi-passive approach for groundwater treatment has evolved in large part from operational issues associated with active pumping systems, and in particular, well biofouling issues. A discussion of O&M associated with active systems is provided in Hatzinger et al. (2009). An active system is perhaps the best way to effectively inject and mix substrates into groundwater as well as to provide hydraulic control at a site. However, technical and cost issues associated with biofouling of injection wells in active systems remain a significant detriment to the widespread application of this approach.

The semi-passive treatment approach potentially provides many of the benefits of active treatment, including effective distribution of a soluble carbon source, minimization of secondary impacts to groundwater quality associated with slow-release carbon sources (e.g., vegetable oil), and flexibility in design and operation, but has less overall potential for biofouling issues due to the limited time of operation of the extraction and reinjection wells. The development of a semi-passive pumping approach was initially proposed in the early 1990s as a potential mechanism to introduce required “nutrients” for enhancing pollutant bioremediation within a permeable barrier wall design while reducing O&M issues associated with constant pumping (Devlin and Barker, 1994). The approach was subsequently tested at the Canadian Forces Base site in Borden, Ontario, as a means to inject and distribute potassium acetate into groundwater via a “nutrient injection wall” (Devlin and Barker, 1999). The data from this study suggested that a pulsed injection could be used to introduce solutes uniformly within an aquifer (i.e., during the pumping phase) with only minimal impact to normal groundwater flow in the passive phase. This research group subsequently tested a semi-passive approach for in situ treatment of mixed chlorinated solvents using benzoate as an electron donor (Devlin et al. 2004) and then for nitrate in a drinking water aquifer near a municipal supply well (Gierczak et al., 2007). Both tests were successful, and pulsed addition of stoichiometric quantities of carbon source (acetate) in the second field test allowed reduction of nitrate to occur without significant production of nitrite or reduction of sulfate.

In addition to these projects, at least two perchlorate remediation demonstrations have been successfully completed using semi-passive designs. One study was completed at the at the former Whittaker-Bermite site in Santa Clarita, CA (Hatzinger and Lippincott, 2009) and a second in a perchlorate-contaminated aquifer at LHAAP in Karnack, TX (Krug and Cox, 2009). Additional details concerning these projects can be found in references provided. Although the number of field trials is limited, and implementation of a full-scale semi-passive system has yet to occur, the initial success of in situ semi-passive approaches for perchlorate treatment at the

Whittaker-Bermite Site and LHAAP provided optimism that this technology could be a viable alternative for explosives remediation in Area 157 at Picatinny.

3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

3.3.1 Advantages

The main advantages of utilizing an in situ approach for explosives treatment are as follows:

1. Appreciably reduced cost and infrastructure compared to traditional pump-and-treat approaches.
2. Complete destruction of explosives rather than transfer to a secondary medium, such as GAC.

In addition, the use of a semi-passive injection/extraction design to supply cosubstrate to the subsurface is advantageous in several ways:

1. Pumping wells increase the capture of contaminated groundwater and provide a wide treatment zone compared to completely passive donor systems.
2. The system provides active mixing of cosubstrate with explosives-contaminated groundwater, allowing general control of redox conditions and efficient distribution of amendments.
3. The design is dynamic and allows changes in operating parameters, including pumping rates, cosubstrate dosing regimen (i.e., pulsed versus continuous addition), and cosubstrate type.
4. The application of a semi-passive rather than a constant-pumping design can significantly reduce system O&M costs, including electrical and biofouling control costs.

3.3.2 Limitations

One potential limitation with this and any in situ technology in which organic substrate is added to an aquifer is that the addition results in zones of groundwater with low oxidation-reduction potential (ORP). This reduction in ORP is necessary to create conditions conducive to treatment of many contaminants, including explosives. However, there are secondary geochemical impacts as well. A reduction in ORP results in mobilization of metals (e.g., dissolved iron [Fe] [II] and manganese [Mn] [III] from dissolution of Fe and Mn oxides), sulfide production, and other changes in groundwater geochemistry that impact local groundwater quality. These issues generally occur with the addition of high quantities of slow release substrates, such as vegetable oil, molasses, or polylactate ester (e.g., hydrogen release compound [HRC]). In this demonstration, a cheese whey feed additive was metered and thoroughly mixed with the contaminated groundwater. Mobilization of Fe and Mn, sulfate reduction, and methanogenesis were evident in the monitoring wells near the system's injection well.

A second potential concern with this technology is that microbial fouling may have a significant impact on performance and long-term operational cost. Biofouling is one of the most significant operational issues affecting many in situ bioremediation applications. In order to mitigate any potential fouling, we (1) designed the demonstration with intermittent rather than continuous groundwater pumping and cosubstrate injection; (2) injected groundwater through a packer to promote movement of water into the formation; and (3) purchased tetrakis (hydroxymethyl) phosphonium sulfate (THPS) (a readily biodegradable anti-fouling agent) for application in the injection well if pressure increases were observed during active cosubstrate addition. Due to the semi-passive operation, well fouling was not an issue during this demonstration. Injection well pressures during cheese whey addition did not increase to a point where intervention was necessary.

4.0 PERFORMANCE OBJECTIVES

Performance objectives were established for this demonstration to provide a basis for evaluation the performance and costs of in situ bioremediation of energetic compounds in groundwater. The primary performance objectives for this demonstration are summarized in Table 1.

Table 1. Performance objectives.

Number	Type	Primary Performance Criteria	Success Criteria	Results: Criteria Met?
1	Quantitative	Reduction of TNT, RDX, and HMX in groundwater	TNT and RDX in groundwater to ≤2 µg/L (USEPA drinking water lifetime HA values[1]). HMX in groundwater to ≤400 µg/L (USEPA drinking water lifetime HA values).	Yes: All wells in treatment area impacted by cheese whey reached <2 µg/L for TNT and RDX. HMX was reduced to ≤1 µg/L in 5/6 treatment wells impacted by cheese whey.
2	Quantitative	No significant long-term accumulation of common explosives degradation products	2,4-DNT and 2,6-DNT to <5 µg/L (USEPA 10^{-4} cancer risk[1]). MNX, TNX, DNX, 2-ADNT, 4-ADNT, 2,6-DANT, 2,4-DANT to <2 µg/L (no USEPA values available[2])	Yes: 2,4-DNT and 2,6-DNT to <5 µg/L throughout demonstration in treatment wells. Other intermediates generally <2 µg/L in all treatment wells.
3	Quantitative	Adequate distribution of cosubstrate within plot	TOC levels >10 mg/L in local monitoring wells	Yes: TOC levels >10 mg/L in local monitoring wells receiving cheese whey
4	Qualitative	Biofouling control in injection well	Operation for at least 6 months without well redevelopment.	Yes: No biofouling control necessary. No well redevelopment necessary.

[1] From USUSEPA (2004). The lowest USEPA health advisory values were chosen for each compound.
[2] No USEPA health advisory values are available for these compounds.

MNX = hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
DNX = hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
2-ADNT = 2-amino-4,6-dinitrotoluene
4-ADNT = 4-amino-4,6-dinitrotoluene
2,6-DANT = 2,6-diamino-4-nitrotoluene
2,4-DANT = 2,4-diamino-6-nitrotoluene
2,4-DNT = 2,4-dinitrotoluene
2,6-DNT = 2,6-dinitrotoluene

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5.0 SITE DESCRIPTION

The semi-passive recirculation cell design used for this ESTCP project is expected to be widely applicable at DoD sites for mixing cosubstrate and other amendments in explosives-contaminated groundwater. Picatinny was chosen for the demonstration.

5.1 SITE LOCATION

Picatinny is located approximately 4 miles north of the City of Dover in Rockaway Township, Morris County, NJ. State Route 15 skirts the southern end of Picatinny, and Interstate 80 is about one mile southeast of the main entrance (Figure 5). The land area consists of 6491 acres situated in an elongated classic U-shaped glacial valley that trends northeast-southwest between Green Pond Mountain and Copperas Mountain on the northwest and an unnamed hill on the southeast (Sims, 1958). Most of the buildings and other facilities at Picatinny are located on the narrow valley floor or on the slopes along the southeast side. Several firing and testing ranges are located on Green Pond Mountain.

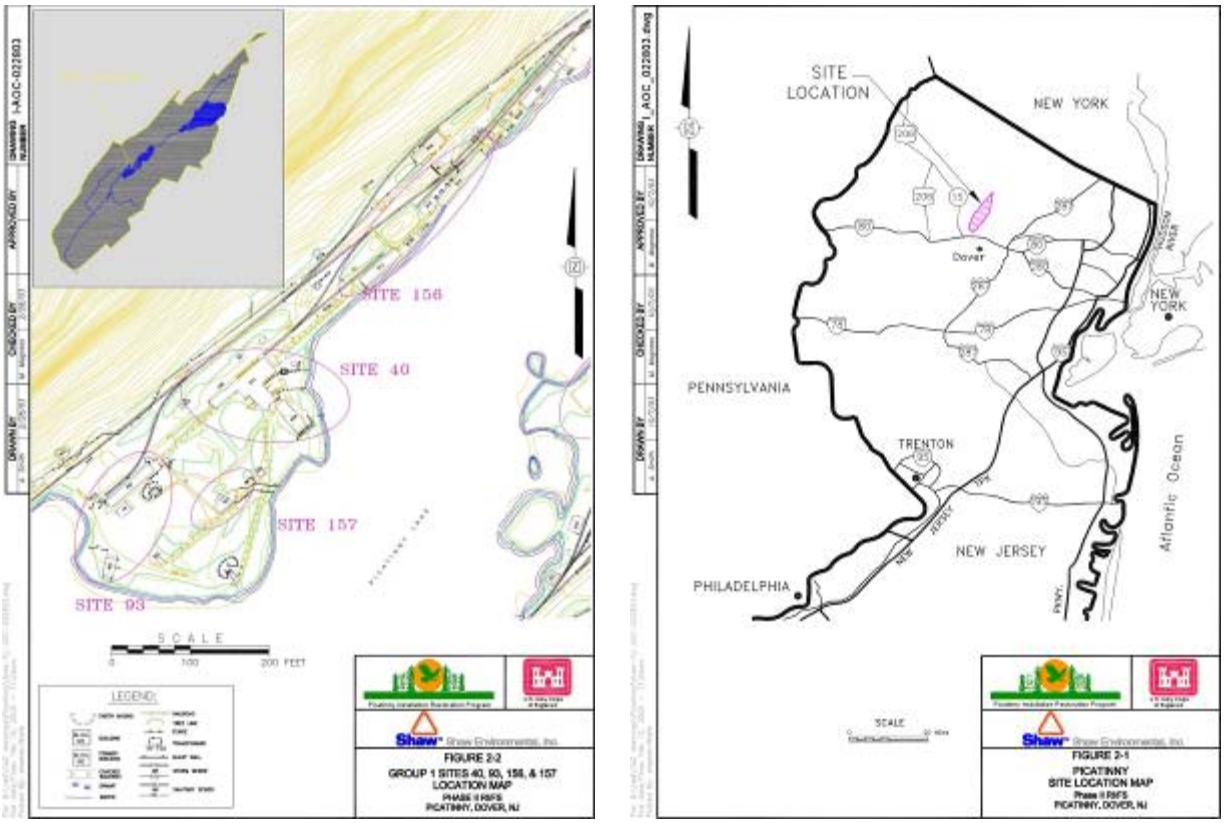

Figure 5. Location of Picatinny Arsenal (left) and Group I sites (right).
The demonstration was conducted at Site 157 (from Gerdes et al., 2004).

The demonstration was performed at Site 157. This site is defined as one of four locations within the Group 1 Area west of Picatinny Lake in the central portion of the Arsenal (Figure 5). The Group 1 study sites, which were defined in a 2004 Remedial Investigation (RI)/Feasibility Study (FS) document prepared for this area (Gerdes et al., 2004) consist of the following:

Site 40: Buildings 809 and 810, Explosives Manufacturing Wastewater Treatment Plant (WWTP) (Defense Site Environmental Restoration Tracking System [DSERTS] #079)

Site 93: Buildings 800 and 807, Ordnance Facilities (DSERTS #139)

Site 156: Buildings 813, 816, and 816-B, Ordnance Facilities (DSERTS #151)

Site 157: Buildings 820, 823, and 824 Ordnance Facilities (DSERTS #152).

The buildings listed above comprise the majority of the 800 Building area. This 2400 ft line of buildings, known as the melt load line or completed rounds division, was established to load, assemble, and pack for shipment various calibers of loaded shells and bombs. The buildings are interconnected by conveyors and walkways to permit the smooth flow of materials in the production process. Site 157 was selected as the Demonstration Site for this ESTCP project based on contaminant concentrations, the existence of five monitoring wells, availability of site characterization data, and nonrestricted site access. Site 157 consists of buildings 820 and 823. Both buildings were used as large caliber projectile loading plants.

Building 820 was constructed in 1930 as a packing and shipping facility for the completed rounds loading production line. Operations included packaging, palletizing, strapping, and stenciling of ammunition items. Building 820 has currently been reactivated as an ammunition repack and surveillance facility. According to interviews with personnel, no energetic wastes are presently stored, disposed of, or generated at Building 820. Repackaging and surveillance operations are generally dry; therefore, no washdown water is produced.

Building 823 is thought to be the primary source for contamination in Area 157. A photo of this building is provided as Figure 6. The building was constructed in 1930 as a melt-load facility responsible for the loading of melted TNT and RDX explosives into shells positioned on a conveyor. Overpour from the operation was collected in a catch trough below the conveyor. Washdown water produced during decontamination activities at Building 823 was collected by troughs, which ran along the building (Figure 6). A settling and filtering system was used to treat operation wastewaters and washdown waters. The wastewater and washdown water were discharged to collection boxes located northeast of Building 823. The collection boxes ultimately discharged to Picatinny Lake. Building 823 also had a rotoclone, which was used to filter airborne energetic particles. There is historical evidence of uncontrolled discharge of explosives-contaminated water in and around Building 823. Investigations conducted in 1974 found excessive condensation of explosives from the melt kettles collecting on the building ceiling. In another report later that year, cracks in the floor were found to contain energetic materials. Since the wastewater filtering system at Building 823 was a 1950s process modification, it is likely that previous wastewater was discharged untreated to Picatinny Lake (Gerdes et al., 2004).

Figure 6. Southeastern view of Building 823 in Area 157 (left) and troughs used to carry washdown water located on the north side of Building 823 in Area 157 (right).

5.2 SITE GEOLOGY/HYDROGEOLOGY

A geologic cross section of Group 1 sites is presented in Figure 7. Deltaic and sublacustrine sand with varying percentages of silt, clay, and gravels was encountered within the unconsolidated unit at Group 1. This unit is discontinuous across the valley; however, it was logged in boreholes advanced along the delta extending into Picatinny Lake where the Group 1 sites are located. This unit extended from the ground surface to 107 ft below ground surface (bgs) in boreholes advanced during the field investigation and was logged as primarily fine to coarse, subrounded to rounded sand, which was generally loose and well graded. The secondary component varied across the study area and with depth. At Site 157, the secondary component of silt and clay decreased with depth to little or no fine material. The base of this unit is characterized by 20 to 25 ft of gravel, cobbles, and boulders to the top of bedrock. The Hardyston Quartzite was identified at Site 40 and Site 157 during installation of the bedrock monitoring wells. The formation was described from cuttings as a medium- to fine-grain, green orthoquartzitic sand. The formation unconformably overlies the Precambrian basement rock. The depth to bedrock from ground surface ranges between 86 ft at 40MW-2D to 107 ft at 40MW-1D.

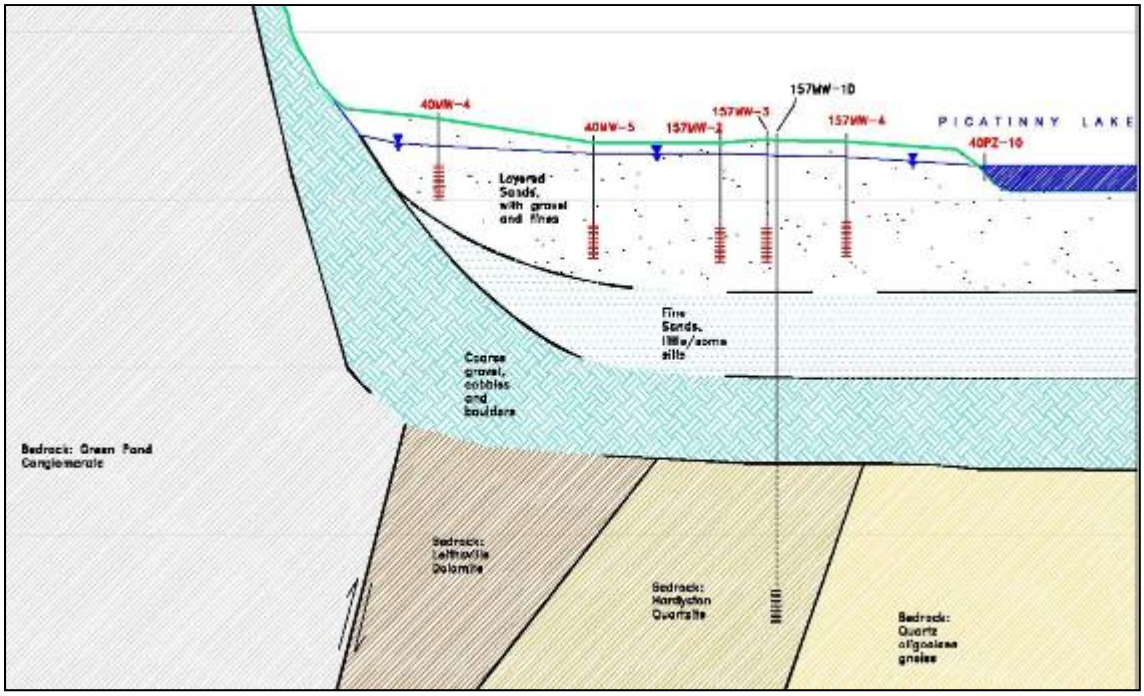

Figure 7. Geology of Group I Sites: Area 157 and Area 40.
(Modified from Gerdes et al., 2004)

Two distinct aquifers, the unconsolidated and bedrock, were characterized during the previous field investigations. The unconsolidated aquifer was encountered along the entire western shore of Picatinny Lake and in the small deltas, which extend into the lake, with the exception of Site 156, where competent bedrock was encountered at less than 10 ft bgs. This aquifer is thickest along the shores of the lake adjacent to the delta and pinches out where bedrock is close to the ground surface. The total thickness of this aquifer on the delta ranges between 86 ft at 40MW-2D to 107 ft at 40MW-1D.

5.3 GROUNDWATER CONTAMINATION

Eighty-one groundwater samples were collected from the Group 1 Sites prior to the beginning of this ESTCP demonstration project, including four rounds of monitoring well sampling, discrete interval sampling during deep monitoring well installation, Hydropunch sampling, and piezometer sampling. In general, the RDX groundwater contamination is more widespread than the TNT groundwater contamination. TNT was detected above its level of concern (LOC) of 2 µg/L in 18 groundwater samples, collected from seven monitoring wells. RDX was detected above its LOC of 0.61 µg/L in 46 groundwater samples, collected from monitoring wells, Hydropunch points, and discrete interval samples collected during deep monitoring well installation. Concentrations of RDX, above the LOC, ranged from 0.70 µg/L to 490 µg/L. Based on the analytical results from groundwater samples collected in August 2002, preliminary plume maps of the RDX and TNT contamination were developed. These plume maps were augmented with the results from the site investigation work in 2004 and 2005 for this ESTCP project, which included Hydropunch data and groundwater monitoring data from newly installed wells. Maps of RDX and TNT plumes in Area 157 are provided in Figures 8 and 9, respectively. These maps were based on all available data at the time that the system was installed.

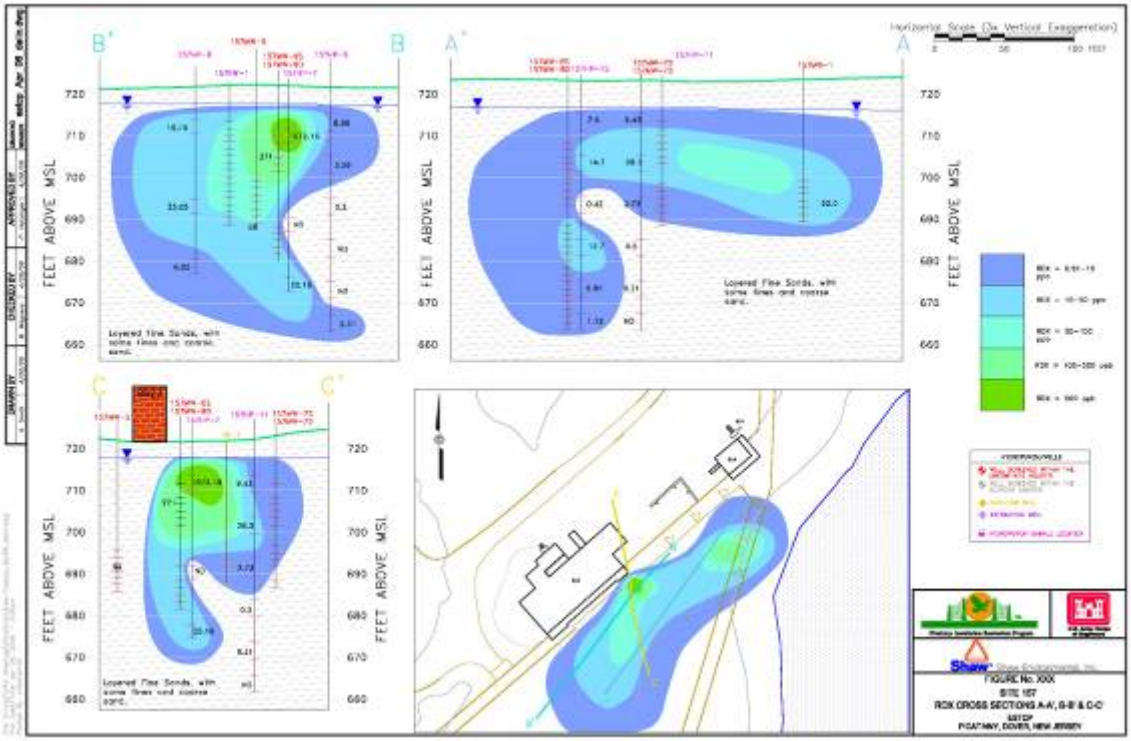

Figure 8. Overhead view and three cross sections of the RDX plume in Area 157.

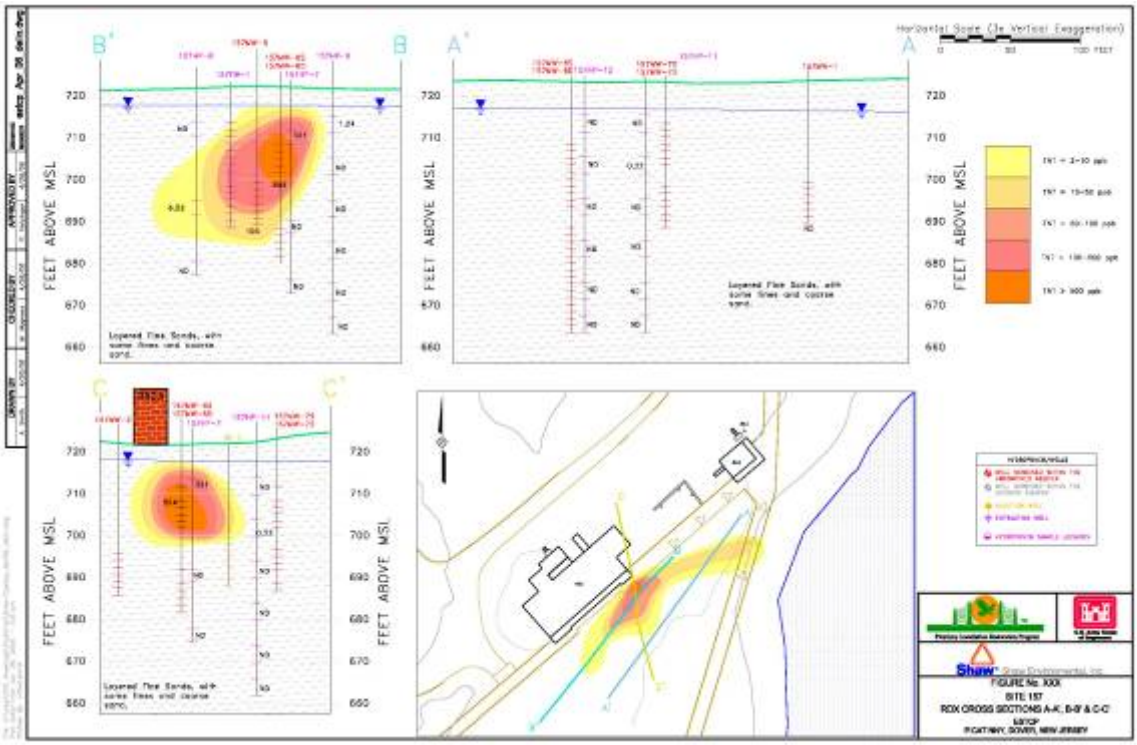

Figure 9. Overhead view and three cross sections of the TNT plume in Area 157.

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6.0 TEST DESIGN

Design of the in situ mixing and amendment injection system required detailed site-specific knowledge of the contaminant distribution, hydrogeology, and microbiology. Specific system parameters directly influenced by the hydrogeology and microbiology include cosubstrate selection, spacing of the injection/extraction and monitoring wells, pumping rates and schedules, well screen intervals and depths, and cosubstrate injection rates. All available site characterization data was reviewed prior to selecting the location of the demonstration. However, additional local characterization of Area 157 was required to facilitate system design. Specific activities included laboratory microcosms and column experiments to evaluate biodegradation kinetics, monitoring well installation, groundwater sampling to determine contaminant distribution and hydraulic gradients, supplemental soil and groundwater investigation to identify potential contaminant sources and delineate the dissolved contaminant plume, and slug and pump testing to determine aquifer hydrogeologic parameters. Details of these activities are provide in the project final report (Hatzinger and Lippincott, 2012).

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The results from the treatability studies and site characterization work were used to design the test system and to determine the most effective means to operate this system. As detailed previously, a groundwater recirculation design was used to distribute and mix cosubstrate with explosives-contaminated groundwater and to deliver that substrate to indigenous bacteria (Figures 2 and 3). The recirculation system consisted of two groundwater extraction wells and one groundwater injection well installed in the aquifer cross-gradient to groundwater flow. The groundwater was removed from the aquifer through the two extraction wells, amended with cheese whey as a cosubstrate at the surface, and then recharged into the formation through the single injection well. A semi-passive (also called active-passive) mode of operation was utilized to mix cosubstrate with groundwater (active phase) and then to allow degradation to occur under static conditions (passive). This type of operation, as previously detailed, is optimal to promote contaminant degradation while limiting injection well biofouling and other O&M issues. Baseline sampling, treatment phase sampling during four additions of cheese whey, and rebound sampling were conducted at TZMWs that were impacted by cheese whey and at control zone monitoring wells (CZMWs), which were upgradient and downgradient of the treatment plot. The demonstration was conducted over a period of 696 days, including baseline sampling events.

The system conceptual design was based on results of the laboratory microcosm study, the hydraulic investigations described previously, and a groundwater hydrogeologic fate and transport model. Various conceptual system designs were evaluated using the MODLFOW/SEAM3D fate and transport model (U.S. Geological Survey [USGS], 1996; Waddill and Widdowson, 1998). Specifically, the model was used to ensure that the biotreatment system would accomplish the following:

- *Completely intercept the contaminant plume in the targeted demonstration zone*. Hydraulic capture of the contaminant plume was evaluated by evaluating the radius of influence of the simulated extraction wells in MODFLOW and by evaluating particle capture.

- *Provide sufficient mixing of injected amendments with groundwater*. Simulated amendment concentrations in the treatment zone were evaluated as a function of depth and distance from the injection well to determine the well flow rates, spacing, and screen interval needed to ensure proper mixing.

- *Biologically degrade TNT and RDX within the treatment zone, thereby preventing downgradient contaminant migration*. Simulated contaminant biodegradation rate constants were based on the results of the laboratory microcosm study. These rate constants were used within the model to verify that the conceptual system design provided sufficient residence time such that TNT and RDX concentrations decreased to target levels within the effective influence of the bio-treatment system. The biodegradation of HMX was also evaluated in the model.

- *Provide a monitoring well network to sufficiently evaluate system performance*. The model was used to determine locations and screen intervals for monitoring wells so that system performance could be assessed. Specifically, wells were placed in locations so that simulated extraction well capture (i.e., drawdown), amendment delivery, and contaminant concentrations could be observed.

6.2 LABORATORY TREATABILITY TESTING

Laboratory microcosm and column tests were performed to evaluate the most effective cosubstrates for promoting the biodegradation of explosive compounds in batch experimental systems prepared from soil collected from 157MW-5 (during installation of this monitoring well in December 2004) and groundwater collected from 157MW-4. The cosubstrates evaluated in microcosms were as follows: (1) lactate, (2) citrate, (3) benzoic acid, (4) yeast extract, (5) cheese whey feed additive, (6) hydrogen, (7) glucose, (8) acetate, and (9) ethanol. These cosubstrates were selected based on a literature review and previous laboratory or field studies to evaluate the degradation of explosives. Initial microcosm studies revealed that only cheese whey and yeast extract were effective for promoting the biodegradation of TNT and RDX by indigenous bacteria. These cosubstrates were then utilized in column studies to better simulate aquifer conditions. During the ~100-day column study, the most significant and consistent biodegradation of TNT, RDX, and HMX occurred in the columns receiving cheese whey. RDX levels declined from ~50 µg/L to <1 µg/L within 20 days of introducing the cosubstrate at 1000 µg/L. Although the lag period was a little longer, HMX levels also declined from ~65 µg/L to <1 µg/L in the effluent of this column. Yeast extract was much less effective, so cheese whey was chosen as the cosubstrate for the field demonstration. For additional information on the treatability studies and the composition of the cheese whey, please see the project final report.

6.3 BASELINE CHARACTERIZATION

After reviewing all previous soil, groundwater, and hydrogeological data from Area 157 (see Section 5), additional characterization work was conducted prior to completing the final design of the demonstration system, including monitoring well installation, soil and groundwater sampling, water elevation measurements, and slug and pump testing. The hydrogeological testing showed that the horizontal hydraulic gradient in area is relatively flat (approximately 1×10^{-4} ft/ft) with a flow direction that varies but generally trends between southeast and southwest. Subsequent pump testing was used to determine aquifer hydraulic conductivity, transmissivity, and storativity values of 19.9 ft/day, 1434 ft^2/day, and 0.066 (dimensionless) respectively. These data were consistent with slug test results and with expectations for a sandy, unconfined aquifer. These parameters were used to refine the site groundwater model and verify the final treatment system conceptual design. Additional groundwater sampling, Hydropunch sampling, and soil sampling were also conducted in Area 157 to better define the vertical and horizontal extent of groundwater contamination and to better define potential source areas. The detailed results from the contaminant characterization studies as well as the hydrogeological testing are provided in the project final report. The final plume maps are provided in Figures 8 and 9.

6.4 FIELD TESTING

The basic field testing plan is summarized in Table 2. Field testing consisted of 5 phases: (1) baseline monitoring before initiation of groundwater flow (two events); (2) bromide tracer testing and baseline monitoring after system start-up but prior to cheese whey addition (four events for bromide, two events for baseline); (3) system operation and performance monitoring (seven events); and (four) rebound evaluation (three events). Groundwater sampling was conducted using dedicated bladder pumps installed in each of the site's 12 monitoring wells (157MW-1, 157MW-1D, 157MW-2, 157MW-3, 157MW-4, 157MW-5, 157MW-6S, 157MW-6D, 157MW-7S, 157MW-7D, 157MW-8S, and 157MW-8D). See Figure 10 for the well layout and for the purpose of each well (i.e., treatment zone versus control zone monitoring). The total duration of sampling form the first baseline event to the final rebound event was 696 days.

Table 2. Sampling and operational schedule.

Starting Date	Activity	Day of Operation
Baseline Monitoring (before recirculation)		
1/17/2007	Baseline Sampling Event #1	Day 131
3/15/2007	Baseline Sampling Event #2	Day 76
System Start-up		
3/27/2007	Systems Testing & Start-up	Day 66
Bromide Tracer Testing & Baseline Monitoring (after recirculation)		
3/27/2007	Bromide tracer injection and recirculation	Day 66
4/3/2007	Bromide sampling event #1	Day 61
4/10/2007	Bromide sampling event #2	Day 57
4/18/2007	Bromide sampling event #3 & baseline sampling event #3	Day 42
5/3/2007	Bromide sampling event #4 & baseline sampling event #4	Day 27

Table 2. Sampling and operational schedule (continued).

Starting Date	Activity	Day of Operation
Operation & Performance Monitoring		
5/30/2007	First Cosubstrate Injection (3 days recirculation)	Day 0
6/14/2007	Performance Sampling Event #1 (TOC and anions only)	Day 14
7/2/2007	Performance Sampling Event #2	Day 33
7/10/2007	Second Cosubstrate Injection (4 days recirculation)	Day 41
7/31/2007	Performance Sampling Event #3	Day 62
9/5/2007	Performance Sampling Event #4	Day 98
9/10/2007	Third Cosubstrate Injection (4 days recirculation)	Day 103
10/25/2007	Performance Sampling Event #5	Day 148
11/27/2007	Fourth Cosubstrate Injection (4 days recirculation)	Day 181
12/3/2007	Additional recirculation without injection (4 days)	Day 188
1/7/2008	Performance Sampling Event #6	Day 222
2/28/2008	Performance Sampling Event #7	Day 274
Rebound Evaluation		
5/7/2008	Rebound Sampling Event #1	Day 343
7/23/2008	Rebound Sampling Event #2	Day 420
12/15/2008	Rebound Sampling Event #3 (subset of wells)	Day 565
Decommissioning		

6.5 SAMPLING METHODS

Groundwater samples were collected during the demonstration based on USEPA Region 9's Standard Operating Procedure for Low Stress (Low Flow)/Minimal Draw-down Ground-Water Sample Collection (http://www.epa.gov/region9/qa/pdfs/finalsopls1217.pdf). Samples were obtained from each well using dedicated submersible bladder pumps with Teflon bladders and tubing. A flow-through cell connected to a YSI 600XL field meter (YSI, Inc., Yellow Springs, OH) or equivalent was utilized to measure field geochemical parameters (pH, ORP, temperature, specific conductivity, and dissolved oxygen [DO]). Sampling was conducted only after field parameters were stable based on low-flow sampling guidelines, and exceptions were noted on field sheets when they occurred. Groundwater elevation measurements were collected using an electronic water level indicator prior to collecting groundwater samples and every 5 minutes during low-flow sampling. Table 3 lists the sampling parameters, preservatives, and analytical methods employed during the demonstration and the total samples collected are provided in Table 4. Additional details on sampling and analytical procedures are provided in the project final report.

Table 3. Sampling parameters, preservatives, and analytical methods.

Parameter	Method/Procedure	Preservative	Bottle Size
Nitrate	USEPA 300.0	4°C	100 mL[1]
Sulfate	USEPA 300.0	4°C	100 mL[1]
Nitrite	USEPA 300.0	4°C	100 mL[1]
Chloride	USEPA 300.0	4°C	100 mL[1]
Bromide	USEPA 300.0	4°C	100 mL[1]
TOC	USEPA 415.1	Phosphoric acid	40 mL VOA
Total manganese	USEPA 200.7	Nitric acid	500 mL[2,4]
Total iron	USEPA 200.7	Nitric acid	500 mL[2,4]
Explosives (TNT, HMX, RDX) and degradation products (MNX, DNX, TNX, 2-ADNT, 4-ADNT, 2,4-DNT, 2,6-DNT, 2,4-DANT, 2,6-DANT)	USEPA 8330	4°C	1000 mL[3]
Methane, ethane, ethene, propane	USEPA 3810, RSK-175	Hydrochloric acid	40 mL VOA
Redox potential	Field meter	--	--
DO	Field meter	--	--
pH	Field meter	--	--
Conductivity	Field meter	--	--

[1] The same sample bottle will be used for the analyses noted.
[2] The same sample bottle will be used for all analyses noted.
[3] The same sample bottle will be used for all analyses noted.
[4] Performed for only selected wells and sampling events.

VOA = volatile organic analysis
mL = milliliter

Table 4. Total samples collected during the project.

Parameter	Baseline	Operational	Rebound	Total
USEPA 300.0 anions	80	89	36	205
TOC	27	86	14	127
Total iron and manganese	12	28	28	68
Explosives	52	84	36	172
Methane, ethane, ethene	0	23	21	44
Field parameters	78	84	36	198
Total	249	394	171	814

6.6 SAMPLING RESULTS

The complete sampling results for the project are provided in the project final report. As shown in Figure 10, monitoring wells 157MW-4, 157MW-5, 157MW-6S, 157MW-6D, 157MW-7S, and 157MW-7D are TZMWs because each was anticipated to be impacted by the recirculation system based on modeling results and to receive significant cheese whey during the period of system operation. The remaining 6 wells are upgradient (157MW-1, 157MW-2 and 157MW-3), below (bedrock well 157MW-1D), or downgradient (157MW-8S and 157MW-8D) of the treatment area, presuming a slight southwesterly flow of groundwater as was indicated during various groundwater elevation mapping events. These wells serve as control wells to assess changes in contaminant concentrations outside the treatment area.

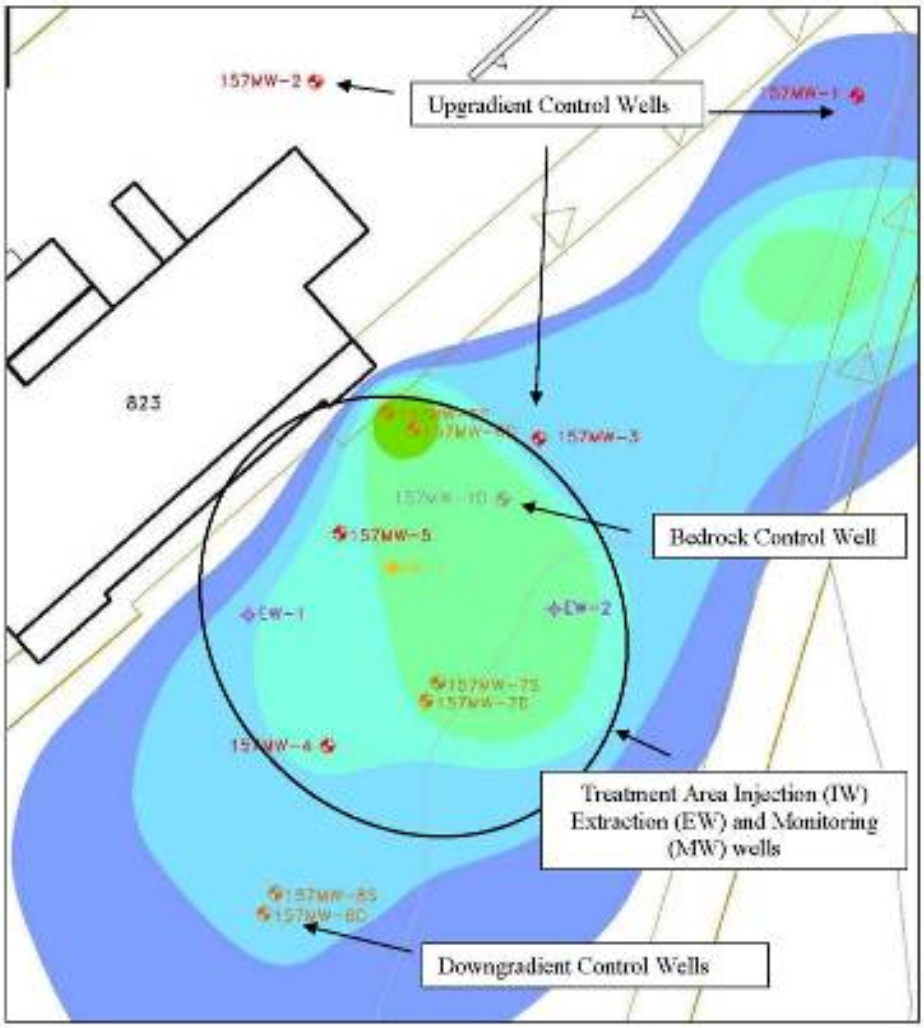

Figure 10. Layout of test plot wells.
Shaded areas represent estimated RDX concentrations at the beginning of the demonstration.

6.6.1 Total Organic Carbon

TOC analysis was utilized as a measure of cheese whey distribution in the aquifer. A significant increase in TOC concentration within the treatment zone was observed following the initial system operation and injection of cheese whey (corresponding to Day 0) (Figure 11). TOC in all wells in the treatment zone quickly reached concentrations exceeding 90 mg/L after the initial injection, with some wells exceeding 200 mg/L. TOC in monitoring wells outside the treatment zone did not increase above the background concentration of ~2 mg/L The initial rate of TOC decline after the first injection varied from ~2.2 to 4.5 mg/day (Day 15-Day 33). Significant increases in TOC were again observed after the third and fourth injection events in all wells except 157MW-6S and 157MW-6D. These wells were upgradient of the injection well, and it is presumed that they were not impacted by the later whey additions due to an increased rate of groundwater flow in the area after significant rainfall.

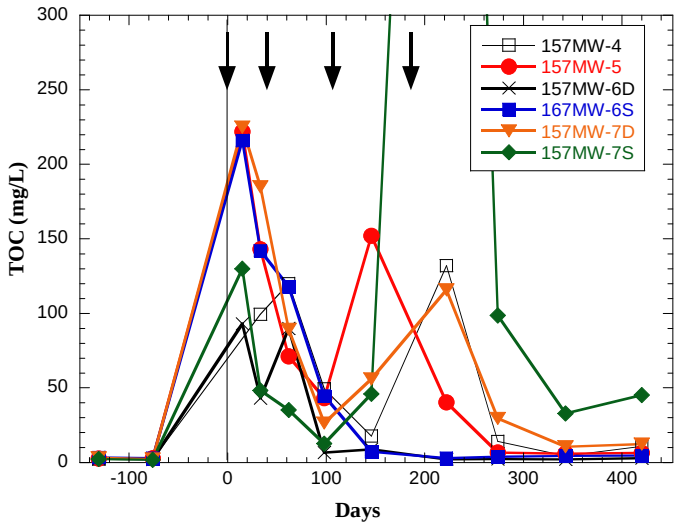

Figure 11. TOC concentrations in treatment plot monitoring wells during the demonstration.
Whey was injected as indicated by the arrows.
Values for control wells are not provided.

6.6.2 TNT and Key TNT Degradation Products

TNT concentrations in the treatment zone monitoring wells declined rapidly after the initial cheese whey addition (Figure 12). TNT concentrations were below analytical detection limits (PQL = 0.25 µg/L) in all of the TMZWs by Day 62 of the study, and remained at or below this concentration in all TZMWs except 157MW-6S throughout the remainder of the demonstration. In Well 157MW-6S, which was not impacted significantly by cheese whey additions after the first event and second events and reached background TOC levels by Day 222, TNT was detected at 6.3 µg/L on Day 222, from a starting concentration of 310 µg/L. The TNT in this well had declined back to 0.39 µg/L by the end of rebound sampling on Day 420. TNT concentrations in upgradient and downgradient monitoring wells, as well as the deep bedrock well 157MW-1D, were largely unaffected by system operation.

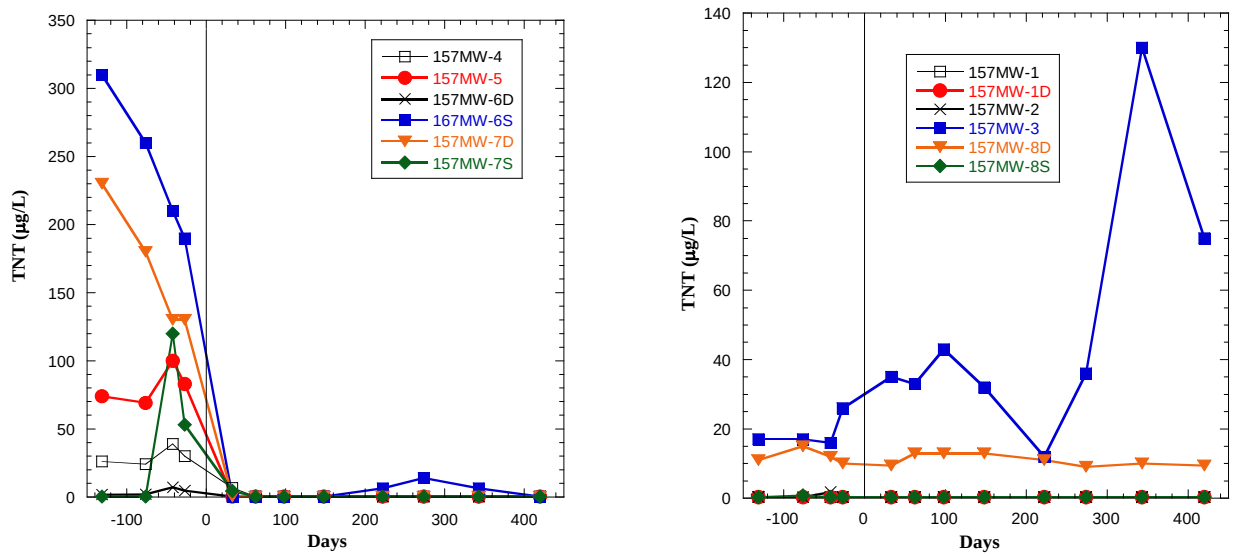

Figure 12. Concentrations of TNT in treatment zone monitoring wells (left) and the control wells (right) during the demonstration.
The initial cheese whey injection occurred at Day 0.

Two common TNT daughter products, 4-ADNT and 2-ADNT were present from ~ 1 to 120 µg/L in groundwater monitoring wells at the demonstration site. A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. In fact, neither TNT daughter product was present above the analytical PQL of 0.25 µg/L in the TZMWs by Day 148. There was a slight rebound of these compounds in upgradient wells 157MW-6S and 157MW-6D after this time, but neither of these wells was impacted by cheese whey after the initial two injections in Day 0 and Day 41, as evidenced by the low TOC in each by Day 222. For each of the other TZMWs, levels of these compounds remained below detection (<0.25 µg/L) from Day 148 to Day 420. There was no appreciable increase or decrease in the concentration of these compounds in the wells outside the treatment zone. With the exception of one detection in well 157MW-5, 2,4-DANT and 2,6-DANT were not present in Picatinny groundwater prior to whey injection. These compounds, each of which is an expected degradation intermediate of TNT, increased in the TZMWs as TNT biodegraded and then declined in concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in TZMWs 157MW-4, 157MW-5, 157MW-7S, and 157MW-7D. The compounds declined and then rebounded in Well 167MW-6S once all the TOC from cheese whey was depleted. Data tables and graphs for these compounds are provided in the project final report.

6.6.3 RDX and Degradation Intermediates

RDX biodegradation occurred somewhat more slowly than for TNT as expected based on previous laboratory studies. However, 148 days after the initial injection of cheese whey, RDX concentrations were <5 µg/L in all six of the TZMWs, and concentrations in five of these wells were <1.5 µg/L (Figure 13). The TZMWs had RDX concentrations ranging from 5 µg/L to 170 µg/L during the final baseline sampling event (Day 27), with a median value of 66 µg/L. From Day 222 to Day 565, the concentration of RDX in all the downgradient TZMWs (157MW-4,

157MW-5, 157MW-7S, 157MW-7D) remained <1 µg/L. Thus, more than one year after the final injection of cheese whey (Day 181), RDX was <1 µg/L throughout the downgradient region of the treatment plot. Upgradient TZMWs 157MW-6S and 157MW-6D also reached <1 µg/L on Day 148. However, as previously noted, this well pair was not impacted by cheese whey after the initial two injections on Days 0 and Day 41, presumably due to an increased rate of groundwater flow in the plot area. As the TOC from cheese whey declined during the course of the study, the RDX rebounded somewhat in both wells as expected. In those wells where TOC from cheese whey remained above ~5 mg/L, rebound was not observed. The data clearly show that cheese whey effectively promoted RDX biodegradation throughout the treatment zone, and that as long as a minimal concentration of TOC was maintained, rebound did not occur. The RDX concentrations in the upgradient and downgradient CZMWs remained reasonably constant throughout the demonstration period.

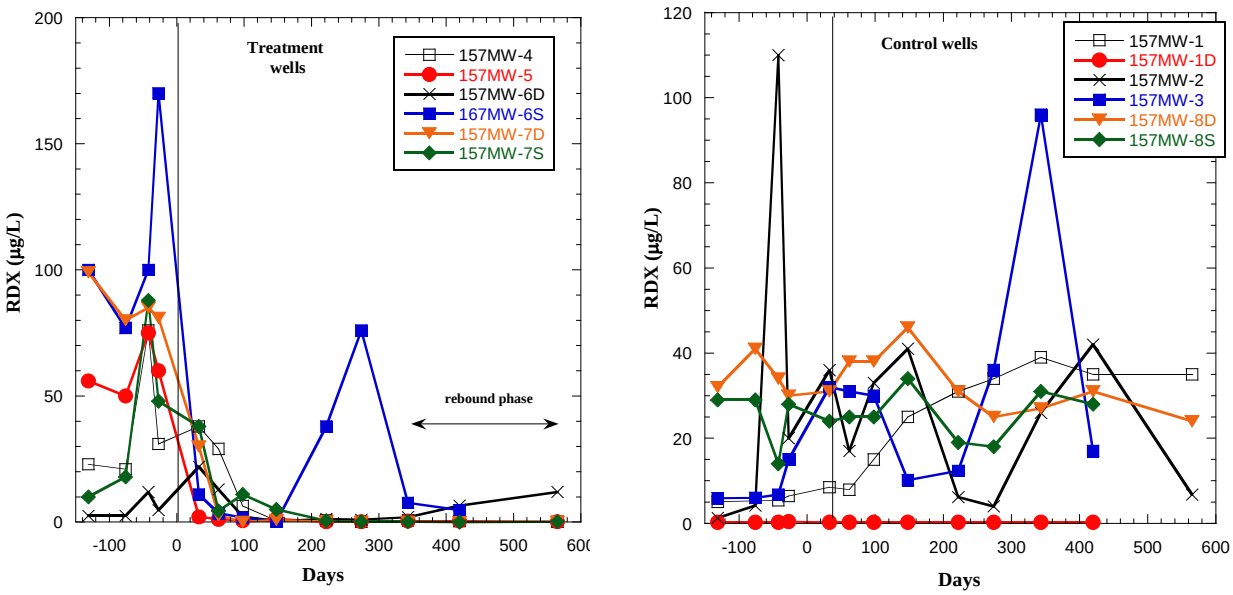

Figure 13. RDX concentrations in treatment zone monitoring wells (left) and the control wells (right) during the demonstration.
The initial cheese whey injection occurred at Day 0.

The concentrations of the RDX daughter products MNX, DNX, and TNX increased in one or more of the TZMWs but not in the CZMWs. However, the total concentrations were <20 µg/L in all cases and generally much lower, and all three nitroso-derivatives were transient. The production of these intermediates is expected during reductive biodegradation of the nitramine, and clearly indicates that the explosive is being biologically reduced in the treatment area wells. Neither MEDINA nor 4-nitro-2,4-diazabutanal (NDAB) were detected in any of the system wells during select sampling events even though significant RDX biodegradation was indicated in all of the TZMWs. Thus, the data suggest that significant accumulation of ring cleavage products from RDX, including NDAB and MEDINA, during in situ RDX biodegradation via cheese whey addition is unlikely.

6.6.4 HMX and Degradation Intermediates

Degradation of HMX was not observed in any of the treatment wells during the initial two months of operation. However, an initial decline in this nitramine was noted in all of the TMZWs between Day 62 and Day 148 (Figure 14). HMX concentrations continued to decline thereafter in all of the downgradient TZMWs, and by Day 274, the HMX concentration in each of these wells was <0.4 µg/L. A slight rebound was observed in Well 157MW-5 at Day 565 (384 days after the last injection) to 6.2 µg/L, but HMX was <1 µg/L each of the other wells throughout the remainder of the study. HMX also declined initially in upgradient TZMW 157MW-6S, but rebounded quickly as the TOC concentration in this well declined to <5 mg/L on Day 222. The HMX concentration in upgradient TZMW 157MW-6D reached 0.52 µg/L on Day 148 and then increased somewhat. However, HMX was <3 µg/L from Day 222 to Day 343 and <2 µg/L during the final sampling events at Day 420 and Day 565. Thus, as with RDX, the data from the downgradient TZMWs suggest that the addition of cheese whey to the Picatinny aquifer effectively promoted HMX biodegradation to sub µg/L concentrations. When TOC concentrations were maintained >5 mg/L, rebound of HMX was not observed.

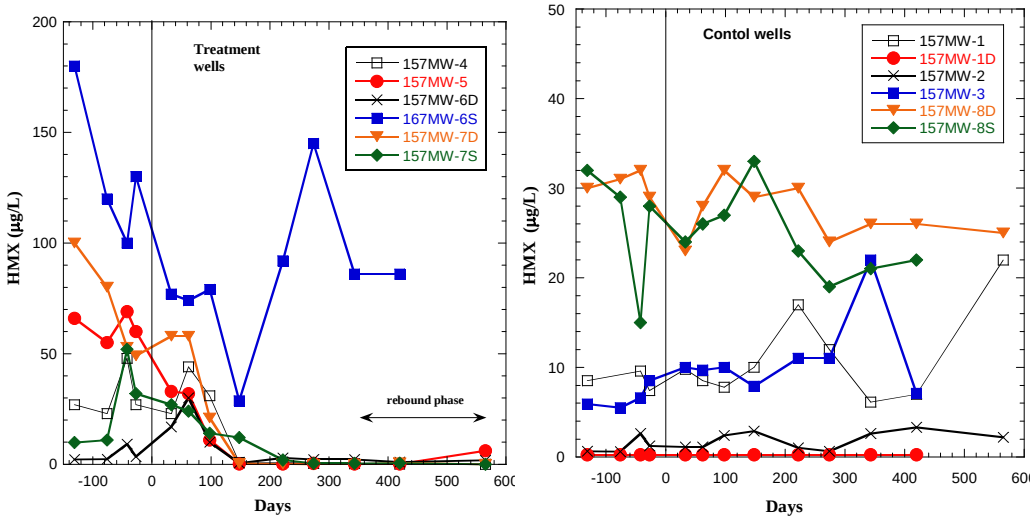

Figure 14. Concentrations of HMX in treatment zone monitoring wells (left) and the control wells (right) during the demonstration.

6.6.5 Other 8330 Nitroaromatics

A number of other nitroaromatic compounds were quantified via USEPA 8330 analysis throughout the demonstration, including several nitrobenzenes and nitrotoluenes, 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and pentaerythritol tetranitrate (PETN). Among these compounds, 1,3,5-trinitrobenzene (1,3,5-TNB) was present throughout the demonstration plot at ~10 to 70 µg/L prior to cheese whey injection. A rapid decline in the concentrations of this compound was observed in all TZMWs. In fact, 1,3,5-TNB in all the TZMWs was <0.25 µg/L by Day 62, while the upgradient and downgradient CZMWs remained near baseline levels. The concentration of 1,3,5-trinitrobenzene was <0.6 µg/L in all TZMWs from Day 62 until the final samples for this compound were collected on Day 420.

Among the other compounds detected in the treatment plot, 2,4-DNT and 2,6-DNT also were biologically degraded in the treatment zone wells. 2,4-DNT was detected consistently in wells 157MW-3, 157MW-5, 157MW-6D, 157MW-6S, 157MW-7D, and 157MW-8D during baseline sampling at concentrations ranging from ~0.5 to 1.7 µg/ L (0.25 µg/L PQL). The compound was not detected in any of the other wells except the extraction wells during system operation. After cheese whey addition, 2,4-DNT declined to <0.25 µg/L in the TZMWs by Day 33, and with a few exceptions, remained below this concentration throughout the demonstration. There was no apparent decline in 2,4-DNT in CZMWs 157MW-3 or 157MW-8D during the study. Similar results were observed for 2,6-DNT in the same wells. The other compounds that were measured during each sampling event by USEPA 8330 included 1,2-dinitrobenzene (DNB), 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, PETN, picric acid, and Tetryl. Overall, the occurrence of these compounds during baseline sampling and throughout the demonstration was too sporadic to determine the effectiveness of the cheese whey injection for treatment of each. The data for all 8330 explosives measured are provided in the project final report.

6.6.6 Other Analytes and Field Parameters

Data for field parameters, including pH, ORP, DO, and temperature as well as common anions, dissolved metals (Fe and Mn), and methane are provided in the project final report.

6.6.7 Summary of Results

The key findings of this ESTCP demonstration with respect to explosives biodegradation are as follows: (1) anaerobic biodegradation of the key explosives impacting the Area 157 was stimulated by the injection and distribution of cheese whey in groundwater; (2) biodegradation of key explosives and intermediates including TNT, RDX, HMX, 2-DNT, 2,6-DNT, and 1,3,5-TNB to sub µg/L concentrations occurred; (3) degradation intermediates of TNT and RDX were detected, but these compounds were transient in cheese whey impacted wells; (4) rebound of explosives occurred in wells once TOC from cheese whey reached low concentrations (i.e., <5 mg/L) but not in wells in which cheese whey TOC remained elevated; and (5) TOC from cheese whey persisted for more than a year at concentrations sufficient to prevent rebound of explosives in the downgradient region of the demonstration plot. All critical performance objectives of this demonstration were met.

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7.0 PERFORMANCE ASSESSMENT

7.1 PERFORMANCE CRITERIA

Performance objectives were established for this demonstration to provide a basis for evaluating the results of the in situ remediation approach for explosives in groundwater. Performance criteria were selected based on factors that would likely be considered when bringing the proposed technology to full-scale application. The performance objectives are provided in Table 1. The critical performance objectives for this demonstration were achieved. The following subsections summarize the data collected and provide an assessment of the performance objectives, including the extent to which the criteria were achieved.

7.2 TREATMENT OF EXPLOSIVES IN GROUNDWATER

The key performance objective of this demonstration was to reduce the explosives RDX, HMX, and TNT in groundwater at Picatinny to concentrations that are below levels of regulatory concern. As previously noted, those values are 2 µg/L for TNT and RDX and 400 µg/L for HMX (MCGL values) (USEPA, 2004). In addition, New Jersey has established Interim Ground Water Quality Criteria for both TNT (1 µg/L) and RDX (0.3 µg/L) that are somewhat lower than the federal MCGL. The key performance objective for this demonstration was achieved. Concentrations of TNT in the TZMWs declined rapidly after the initial cheese whey addition. TNT concentrations were below analytical detection limits (PQL = 0.25 µg/L) in all of the TZMWs by Day 62 of the study and remained at or below this concentration in all TZMWs except 157MW-6S throughout the remainder of the demonstration. RDX biodegradation occurred somewhat more slowly than for TNT, but RDX concentrations declined from a plot average of 66 µg/L just prior to cheese whey addition to <1.5 µg/L in 5/6 TZMWs after 148 days of treatment. Moreover, on Day 565, more than 1 year after the final cheese whey injection, the concentration of RDX in all of the downgradient TZMWs was <0.2 µg/L. A significant decline in HMX also was observed in all wells, and by Day 274 each of the 4 downgradient TZMWs had HMX concentrations <0.4 µg/L. A slight rebound was observed in Well 157MW-5 at Day 565 (384 days after the last cheese whey injection) but HMX remained <1 µg/L in each of the other wells throughout the remainder of the study. Several other nitroaromatics, including 1,3,5-TNB, 2,4-DNT, and 2,6-DNT, were also effectively treated by the cheese whey injection. The data from the downgradient TZMWs clearly showed that the addition of cheese whey to the Picatinny aquifer effectively promoted biodegradation of TNT, RDX, and HMX to sub µg/L concentrations. Moreover, as long as TOC concentrations were maintained >5 mg/L, rebound of these explosives was not observed. Thus, the potential for long-term effectiveness of this semi-passive groundwater ER approach appears to be very good.

7.3 ACCUMULATION OF DEGRADATION INTERMEDIATES

Another critical performance objective for this demonstration was to show that there was no long-term accumulation of common daughter products of TNT and RDX biodegradation, including MNX, DNT and TNX (for RDX) and 2-ADNT, 4-ADNT, 2,4-DANT, or 2,6-DANT (for TNT). This performance objective was met during the study. Two of the most common TNT daughter products, 4-ADNT and 2-ADNT, were present from ~1 to 120 µg/L in groundwater monitoring wells at the demonstration site during baseline sampling, either because they were

released from the facility during processing or because they formed after disposal to land surface via natural biological reactions. A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. Neither was detected above 0.25 µg/L in the TZMWs by Day 148. For each of the downgradient TZMWs, concentrations of these compounds remained below 0.25 µg/L through Day 420 (the final day of sampling for these intermediates). 2,4-DANT and 2,6-DANT, each of which is an expected degradation intermediate of TNT during anaerobic treatment, increased in the TZMWs as TNT degraded and then declined in concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in all downgradient TZMWs. Thus, no accumulation of typical TNT degradation intermediates was indicated.

The concentrations of the common RDX daughter products MNX, DNX, and TNX increased in the TZMWs during the demonstration. However, the total concentrations were <20 µg/L in all cases, and generally much lower, and all three nitroso-derivatives were transient. A significant decrease in the concentrations of each of these daughter products was observed during the demonstration, and all were near or below detection by Day 420 of groundwater monitoring. All three products remained below detection in TZMWs sampled on Day 565. In addition, on Day 199, each of the TZMWs except 157MW-6S was analyzed for NDAB and MEDINA. Three of the CZMWs were also analyzed for comparison. Neither of these intermediates (which form after ring cleavage of RDX) were detected in the test or control wells at concentrations exceeding the MDL of 10 µg/L. Overall, the data indicate that known intermediates of RDX degradation by anaerobic processes, including the three nitroso-derivatives, MEDINA and NDAB are unlikely to accumulate during in situ anaerobic bioremediation explosives using cheese whey as a cosubstrate.

7.4 ADEQUATE DISTRIBUTION OF COSUBSTRATE

A significant increase in TOC concentration within the treatment zone was observed following the initial system operation and injection of cheese whey. TOC in all wells in all TZMWs quickly reached concentrations exceeding 90 mg/L after the initial injection, with some wells exceeding 200 mg/L. The initial goal was to achieve at least 10 mg/L TOC in each well. TOC in monitoring wells outside of the treatment zone did not increase above the background concentration. Significant increases in TOC were again observed after the third and fourth injection events in all wells except 157MW-6S and 157MW-6D. These wells were upgradient of the injection well, and it is presumed that they were not impacted by the later whey additions due to an increased rate (or slight shift in direction) of groundwater flow in the area. The gradient in the treatment area was relatively flat and prone to alterations with the water table.

Overall, the intermittent pumping design was extremely effective at distributing cosubstrate within the core treatment zone as indicated by TOC concentrations in downgradient wells. It is anticipated that a wider zone of influence could have been achieved with more frequent pumping cycles. However, the trade-off for increased operation is an increased likelihood of injection well fouling (which did not occur during this demonstration) as well as increased O&M costs, as daily visits to the system (and multiple filter changes) were required during the active treatment phases. For full-scale operation, lower O&M costs for in situ system are always desirable.

8.0 COST ASSESSMENT

8.1 COST MODEL

In order to evaluate the cost of a potential full-scale bioremediation program and compare it against other remedial approaches, costs associated with various aspects of the demonstration were tracked throughout the course of the project. Table 5 summarizes the various cost elements and total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable (FRTR) Guide to Documenting Cost and Performance for Remediation Projects (FRTR, 1998). Many of the costs shown on this table are a product of the innovative and technology validation aspects of this project and would not be applicable to a typical site application. Therefore, a separate "discounted costs" column that excludes or appropriately discounts these costs has been included in Table 5 to provide a cost estimate for implementing this technology at the same scale as the demonstration (i.e., pilot scale).

Table 5. Demonstration cost components.

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs[1]
Capital Costs			
Groundwater modeling	Labor	$3600	$3600
System design	Labor	$37,000	$30,000
Well installation, development, & surveying[2]	Labor	$37,200	$24,000
	Materials	$6100	$4000
	Subcontracts (driller/surveyor)	$39,700	$25,000
System installation (electrical service, Conex box and programmable logic controller (PLC), monitoring equipment, cheese whey mixing and injection system, groundwater recirculation system)[3]	Labor	$66,700	$50,000
	Equipment & materials	$66,000	$48,000
	Subcontracts (electrical, Conex box/PLC)	$41,900	$34,000
Travel		$6000	$5000
	Subtotal	**$304,200**	**$223,600**
Operation and Maintenance Costs			
Groundwater sampling[3]	Labor	$36,300	$12,000
	Materials	$7900	$2500
Analytical	In-house labor	$12,700	$3800
	Outside labs (metals & explosives)[2]	$54,100	$12,500
System O&M (including testing & start-up)	Labor	$13,200	$13,200
	Materials (cheese whey, consumables)	$2700	$2700
Utilities	Electric	$1600	$1600
Reporting & data management	Labor	$25,300	$24,000
Travel		$300	$200
	Subtotal	**$154,100**	**$72,500**

Table 5. Demonstration cost components (continued).

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs[1]
Other Technology Specific Costs			
Site selection	Labor & travel	$5300	$0
Site characterization (surface soil investigation, 2 direct-push investigations, installation of 2 monitoring wells, slug tests, pump tests)	Labor (including in-house analytical)	$68,600	$0
	Materials	$12,200	$0
	Subcontractor (driller)	$12,000	$0
Laboratory microcosm and column testing	Labor (including in-house analytical)	$59,500	$20,000
Tracer testing	Labor (including in-house analytical)	$5600	$0
	Materials	$300	$0
In-progress review (IPR) meeting and reporting	Labor & travel	$27,700	$0
Technology transfer (presentations, papers)	Labor & travel	$10,800	$0
Demonstration plan/work plan	Labor	$33,100	$25,000
Final report	Labor	$24,200	$16,000
Cost and performance report	Labor	$19,400	$0
	Subtotal	**$278,700**	**$61,000**
	TOTAL COSTS	**$737,000**	**$357,100**
	ESTIMATED TREATMENT VOLUME (cubic yards)	**5500**	**5500**
	ESTIMATED TREATMENT VOLUME (gallons)	**277,700**	**277,700**
	APPROXIMATE TREATMENT COST (per cubic yard)	**$134.00**	**$65.00**
	APPROXIMATE TREATMENT COST (per gallon)	**$2.65**	**$1.29**

[1] Discounted costs are defined as estimated costs to implement this technology at the same scale as the demonstration. These costs do not include the technology validation aspect of this ESTCP demonstration, such as site selection, some laboratory testing, tracer testing, extensive groundwater sampling, ESTCP demonstration reporting and meeting requirements, and preparation of technical and cost and performance reports.
[2] Includes two extraction wells and one injection well. Seven additional monitoring wells were installed for demonstration. Three additional monitoring wells assumed for discounted costing.
[3] Baseline and 10 performance monitoring events were performed during demonstration. A total of five sampling events assumed for discounted costing.

Costs associated with the in situ bioremediation of energetic compounds demonstration at Picatinny were tracked from September 2004 until April 2010. The total cost of the demonstration was $737,000, which included $304,200 in capital costs, $154,100 in O&M costs, and $278,700 in demonstration-specific costs (cost related to ESTCP requirements or site selection and characterization). A total of approximately 5500 cubic yards, or 277,700 gallons (assuming a 25% soil porosity) of contaminated aquifer were treated during the demonstration. This corresponds to a unit cost of approximately $134.00 per cubic yard or $2.65 per gallon of contaminated aquifer (Table 5). By excluding an estimated $379,900 of research-oriented costs (primarily the costs associated with the installation and sampling of extra monitoring wells, system monitoring equipment used for technology validation, and ESTCP reporting requirements), unit costs are estimated at approximately $65.00 per cubic yard, or $1.29 per gallon of contaminated aquifer for a project of this scale (Table 5).

For this site, the ability to use a cosubstrate that was readily available in soluble form (such as lactate, citrate, or emulsified oil) would have further reduced the cost of remediation by

approximately $30,000 to $35,000. This is the estimated cost savings associated with the design, procurement and construction of the system used to mix and inject the cheese whey cosubstrate, as well as the labor required to perform mixing and injection operations. Further, it should be noted that costs associated with an approach that did not involve groundwater recirculation (i.e. direct-push injection or multiple well injections) could be considerably lower, depending on site conditions. However, the success of such treatment approaches would depend extensively on hydrogeologic characteristics and contaminant distribution at the individual site.

8.1.1 Capital Costs

Capital costs (primarily system design and installation) accounted for $304,200 (or 41%) of the total demonstration costs. As indicated in Table 5, these costs far exceed what would be expected during a typical remediation project due partially to the following unique cost elements:

- The large number of performance monitoring wells (nine) installed within the relatively small (60 ft x 80 ft) demonstration area.
- The installation of extensive data collection and recording equipment (such as injection and extraction well pressure transducers and related data recording equipment) built into the groundwater recirculation and amendment delivery systems.
- A specially designed mixing tank and pumping system to thoroughly mix the powdered cheese whey feed additive into solution. Given that cheese whey addition was required far less frequently than initially expected, a more cost effective approach could be developed, including application of liquid whey.

8.1.2 O&M Costs

O&M costs accounted for $154,100 (or 21%) of the total demonstration cost. These costs consisted primarily of groundwater monitoring (including analytical), systems O&M, and reporting costs. System O&M costs (which includes cheese whey material, mixing, and injections) were $15,900, or 2% of total demonstration costs. The cost of the 830 kg of cheese whey added during the demonstration was less than $1500 (including freight charges), or 0.2% of total demonstration costs. Treatment dosage during the demonstration is estimated at approximately 0.36 pounds of cheese whey per cubic yard of treated aquifer. Extensive monitoring activities were conducted to effectively validate this technology, including 14 groundwater sampling events and over 750 samples being collected and analyzed over a 23-month period, not including tracer testing.

8.1.3 Demonstration-Specific Costs

Other demonstration-specific costs (those costs not expected to be incurred during non research-oriented remediation projects) accounted for $278,700 (or 38%) of the total demonstration cost. These costs included site selection, laboratory and tracer testing, ESTCP demonstration reporting and meeting requirements, and preparation of extensive technical and cost and performance reports.

8.2 COST DRIVERS

8.2.1 General Considerations

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

- Depth of the plume bgs
- Width, length, and thickness of the plume
- Aquifer lithology and hydrogeology
- Regulatory/acceptance of groundwater extraction and re-injection
- Regulatory considerations concerning secondary groundwater impacts (i.e., metals mobilization, sulfate reduction, etc.)
- Length of time for cleanup (e.g., necessity for accelerated cleanup)
- The presence of indigenous bacteria capable of degrading explosive compounds
- Concentrations of contaminants and alternate electron acceptors (e.g., NO_3^-, SO_4^{2-}, and O_2)
- Presence of cocontaminants, such as chloroform, chlorinated ethenes, or chlorinated ethanes
- The types of cosubstrates determined to be effective at promoting the biodegradation of explosive compounds at a given site (i.e., those that are packaged in soluble form versus those that need to be mixed into solution prior to injection)
- O&M costs and related issues (particularly injection well fouling).

Another major factor that could potentially lead to significant long-term O&M cost during active in situ bioremediation pumping system is well fouling control. During this active treatment project, as well as others that we have recently completed (e.g., Hatzinger and Lippincott, 2009; Hatzinger et al., 2009), control of injection well fouling was a key component of system design and operation. Fouling of wells and other system components during this project was prevented through proper well design, filtration of recirculated groundwater, and design of the substrate injection program (i.e., high concentrations at low frequency via semi-passive addition). The use of an anti-biofouling agent, such as THPS, on a regular basis also can help to minimize well fouling, although such treatment was not required during this demonstration due to the semi-passive approach employed. This issue remains a critical technical and economic constraint to full-time active pumping designs for in situ groundwater treatment using bioremediation (e.g., Hatzinger et al., 2009).

As discussed in detail in Section 6.1, microcosm screening and column treatability testing showed that cheese whey was the most effective cosubstrate (out of the nine tested) for

promoting biological reduction of RDX and suggested that this cosubstrate would be effective in the field for HMX as well. Based on the laboratory studies, cheese whey was chosen as the cosubstrate for field injection. Because the cheese whey product used in laboratory tests (feed additive) (see project final report for full details) was packaged in powdered form, dissolution of this cosubstrate in site groundwater in the field was required. Laboratory solubility testing with the cheese whey suggested that a robust mixing system would be required to effectively mix large quantities of the powder into solution. As discussed in Section 8.1, costs associated with the design, procurement and construction of the system used to mix and inject the cheese whey cosubstrate, as well as the labor required to perform mixing and injection operations accounted for a significant portion of the project expenditures. The ability to use a cosubstrate that was readily available in soluble form (such as lactate, acetate, or emulsified vegetable oil [EVO]) would have reduced the cost of remediation significantly. It should be noted that soluble cosubstrates (such as acetate and EVO) have been shown to be effective at treating explosives aquifer materials collected from other sites (e.g., Davis et al., 2004; Schaefer et al., 2007; Kwon et al., 2011), although they were not effective at this location (See Section 6.2).

8.2.2 Competing Treatment Technologies

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

- Pump and treat (P&T) with carbon treatment
- Zero-valent iron (ZVI) permeable reactive barriers (PRBs)
- Mulch biowalls.

Additional technologies, including in situ chemical oxidation using permanganate (Albano et al., 2010), an electrolytic barrier (ESTCP Project ER-200519; SERDP-ESTCP.org) and in situ treatment wells (ISTW) with granular iron placed outside the well screens (ESTCP Project ER-200223; SERDP-ESTCP.org), have been tested at the field scale but have failed to consistently reduce concentrations to below regulatory LOCs.

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

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

As previously discussed, bioremediation approaches can be either active, where distribution of amendments is achieved using groundwater recirculation, or passive, where distribution is

accomplished during initial injection or via ambient groundwater flow (Stroo and Ward, 2009). Active groundwater treatment approaches often involve pairs or groups of injection and extraction wells to recirculate groundwater and effectively distribute injected amendments within the subsurface. Passive treatment approaches generally involve injection of amendments via closely-spaced injection wells or direct-push technology. A hybrid approach (and the one used during this demonstration) is the semi-passive approach, where groundwater is recirculated for a short period to distribute amendments followed by a longer period of no groundwater recirculation. In each of the above three approaches, a carbon source is typically added in order to promote and maintain the reducing, anoxic conditions and supply carbon needed for in situ growth of bacteria capable of degrading target contaminants. A slow-release carbon source, such as EVO is often utilized with passive treatment approaches to reduce injection frequency.

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

The plume characteristics and those of the local aquifer will play an important role in the cost and applicability of the above technologies for remediation of explosives-contaminated groundwater. For shallow groundwater plumes (<50 ft bgs), passive in situ options, such as installation of a PRB consisting of either injection well or direct-push applied slow-release substrates (like EVO), are likely to be cost effective options, providing the selected substrates have been shown to stimulate indigenous microorganisms capable of degrading target contaminants at the treatment site. Trench installation of mulch biowalls or ZVI PRBs may also provide cost effective options for passively treating contaminants at the downgradient edge of groundwater plumes. These passive systems require little O&M after installation and have the ability to prevent plumes from spreading or leaving a site. However, they may be less suitable at sites where concerns about secondary groundwater contaminants (e.g., reduction and mobilization of Fe, Mn and As, sulfide from sulfate reduction, etc.) exist. Additionally, trench installed barrier technologies may require replacement (ZVI PRBs) or regular rejuvenation with EVO injections (mulch PRBs) to remain effective.

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

contaminated water (e.g., extracted groundwater with amendments) is either prohibited due to water usage and rights concerns or subject to regulatory injection permits.

8.3 COST ANALYSIS

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

- Semi-passive bioremediation of the entire plume using cheese whey
- Semi-passive biobarrier using cheese whey
- Passive injection biobarrier with EVO
- Passive trench mulch biowall
- Passive trench ZVI PRB
- P&T.

Because of the limited applicability of these other treatment technologies (i.e., limited to barrier applications or limited depths), semi-passive bioremediation of the entire plume cannot be directly compared to the other technologies. Therefore, cost analyses comparing the above approaches are presented based on a 30-year operating scenario.

8.3.1 Base Case Template

As discussed above, the base case presented in Krug et al., (2009) is used as a template for the cost analysis of the above technologies and approaches. In the current scenario, however, TNT and RDX are substituted for perchlorate as the contaminants of concern. The base case presents a situation where a shallow aquifer, consisting of homogeneous silty sands, is contaminated with TNT and RDX. The explosives-impacted groundwater extends from 10 to 40 ft bgs, along the direction of groundwater flow for 800 ft, and is 400 ft in width (Figure 15). The specific base case site characteristics, including aquifer characteristics and design parameters for each of the remedial approaches analyzed are summarized in Table 6. The costing for the template site assumes that the source zone has been treated and that there is no continuing source of groundwater contamination.

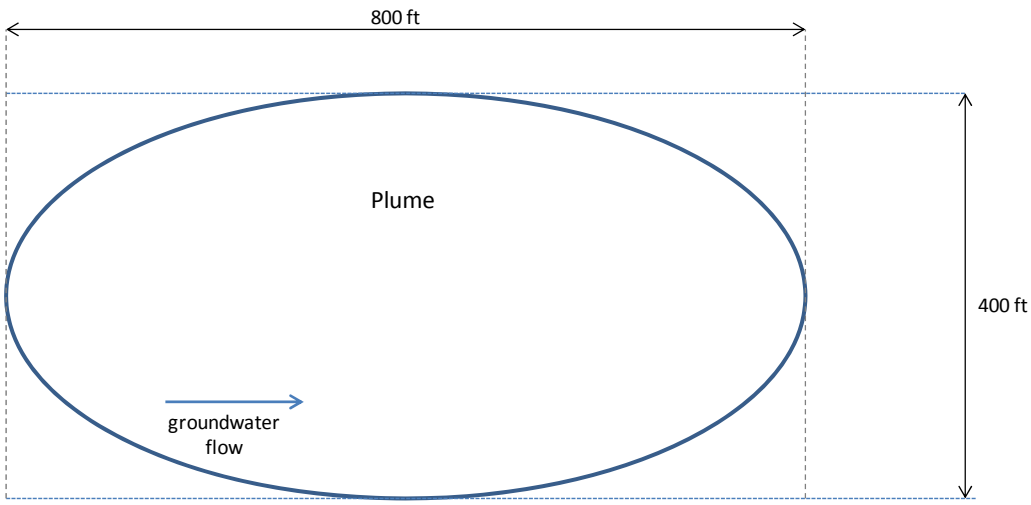

Figure 15. Base case plume characteristics.
(modified from Krug et al., 2009)

Table 6. Summary of base case site characteristics and design parameters for treatment of explosives-impacted groundwater.

Design Parameter	Units	Alternative					
		Active Plume Treatment (Whey)	Semi-Passive Biobarrier (Whey)	Passive Injection Biobarrier (EVO)	Passive Trench Mulch Biowall	Passive Trench ZVI PRB	P&T
Width of plume	ft	400	400	400	400	400	400
Length of plume	ft	800	800	800	800	800	800
Depth to water	ft	10	10	10	10	10	10
Vertical saturated thickness	ft	40	40	40	40	40	40
Porosity	dimensionless	0.25	0.25	0.25	0.25	0.25	0.25
Gradient	dimensionless	0.008	0.008	0.008	0.008	0.008	0.008
Hydraulic conductivity	ft/day	2.8	2.8	2.8	2.8	2.8	2.8
Groundwater seepage velocity	ft/year	33	33	33	33	33	33
Upgradient combined TNT & RDX concentration	µg/L	2000	2000	2000	2000	2000	2000
Downgradient combined TNT & RDX concentration	µg/L	10	10	10	10	10	10
Nitrate concentration	mg/L	15	15	15	15	15	15
DO concentration	mg/L	5	5	5	5	5	5
TNT treatment objective	µg/L	2	2	2	2	2	2
RDX treatment objective	µg/L	2	2	2	2	2	2
Assumed number of pore volumes to flush plume	each	2	2	2	2	2	2

Table 6. Summary of base case site characteristics and design parameters for treatment of explosives-impacted groundwater (continued).

Design Parameter	Units	Alternative					
		Active Plume Treatment (Whey)	Semi-Passive Biobarrier (Whey)	Passive Injection Biobarrier (EVO)	Passive Trench Mulch Biowall	Passive Trench ZVI PRB	P&T
Number of barriers	each	NA	1	1	1	1	NA
Number of monitoring wells	each	10	10	10	10	10	10
Number of amendment injection wells	each	0	0	30	20	0	0
Number of groundwater extraction wells	each	64	4	0	0	0	4
Number of groundwater re-injection wells	each	72	5	0	0	0	0
Groundwater travel time to barrier	years	NA	24	24	24	24	NA
Years to clean up groundwater	years	3	48	48	48	48	NA

NA – Not applicable

Table 6 indicates that the base case assumes a groundwater seepage velocity of approximately 33 ft/year and that two pore volumes of clean water will need to flush through the impacted area to achieve the cleanup objectives. However, as stated in Krug et al., (2009), there are a number of factors, such as the degree of heterogeneity of the geological media, that will determine the actual number of pore volumes of clean water required to flush through the subsurface to achieve target treatment objectives. Variations in the hydraulic conductivity (K) of the aquifer materials can allow a significant fraction of the total mass of contaminants to diffuse into low K layers, and then act as an ongoing source to the higher K zones. In most geological settings, it is likely that more than two pore volumes would be required to achieve treatment objectives, thus leading to longer treatment times (and costs) for passive and P&T approaches.

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

8.3.2 Semi-Passive Bioremediation of the Entire Plume

The semi-passive bioremediation alternative assumes that a series of alternating rows of injection and extraction wells are installed throughout the entire 320,000 sq ft plume to recirculate groundwater and distribute cheese whey as a cosubstrate for explosives bioremediation. As

shown in Figure 16, well and row spacing is 50 ft, with 8 rows of 9 injection wells, and 8 rows of 8 extraction wells, for a total of 136 wells. Groundwater will be recirculated between the rows of wells, and cheese whey added for approximately 3 weeks, after which the system will be shut down for a period of 9 months. Treatment will occur at one-quarter of the wells at a time (rows 1 through 4, followed by rows 5 through 8, etc.) to minimize the size of the groundwater recirculation, the cheese whey mixing systems, the number of submersible groundwater extraction pumps, and associated equipment required. Treatment will be performed three times over the first 3 years of the project, providing greater than 2½ years of continued treatment of the contaminated aquifer (almost twice as long as the treatment period that was shown to be successful during the demonstration). This alternative also assumes no O&M costs after year 3, and no long-term monitoring costs after year 20.

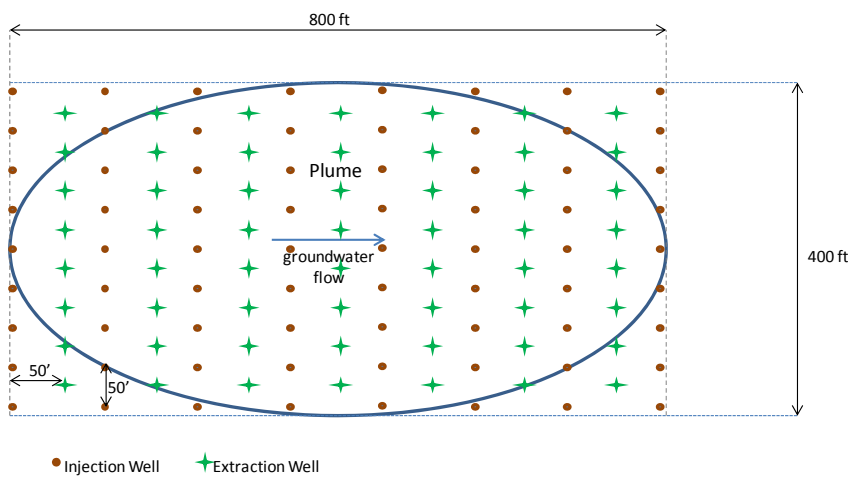

Figure 16. Semi-passive bioremediation alternative with cheese whey for whole plume treatment.

As summarized in Table 7, the estimated total costs for this alternative over 20 years are $1,950,000 with a total NPV of lifetime costs of $1,890,000. The capital cost including design, work plan, installation of recirculation and monitoring wells, construction of the groundwater recirculation and cheese whey mixing systems, and system start-up and testing is approximately $1,140,000. Approximately two-thirds of these costs (approximately $710,000) are associated with installation of the groundwater recirculation and monitoring wells. The NPV of the O&M is estimated at approximately $430,000 for the first 3 years of treatment. The O&M costs include the labor costs associated with three rounds (12 weeks each) of cheese whey mixing and injection, labor for system O&M, costs for equipment repair and replacement, and cost for the cheese whey. The NPV of the 20 years of monitoring and reporting costs is estimated to be $320,000.

Table 7. Cost components for semi-passive bioremediation of an explosives-impacted groundwater plume.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 20		
Capital Costs									
System design	95,142	—	—	—	—	—		95,142	95,142
Well installation	709,662	—	—	—	—	—		709,662	709,662
System installation	331,417	—	—	—	—	—		331,417	331,417
Start-up and testing	5040	—	—	—	—	—		5040	5040
Subcost ($)	**1,141,261**	**—**	**—**	**—**	**—**	**—**		**1,141,261**	**1,141,261**
O&M Costs									
System O&M	144,888	144,888	144,888	—	—	—		426,198	434,664
Subcost ($)	**144,888**	**144,888**	**144,888**	**—**	**—**	**—**		**426,198**	**434,664**
Long-Term Monitoring Costs									
Sampling/analysis/reporting (quarterly through 5 yrs, then annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	324,725	370,545
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**173,166**	**324,725**	**370,545**
Total Cost ($)	**1,323,151**	**181,890**	**181,890**	**37,002**	**37,002**	**12,369**	**173,166**	**1,892,184**	**1,946,470**

*NPV calculated based on a 2% discount rate

While this alternative has the lowest estimated total remedy cost of the six alternatives analyzed, the NPV of lifetime costs ranks third at $1,890,000 (see Table 13). This is primarily due to the high capital costs incurred during the first year of implementing this technology. As discussed below, while the other alternatives may have higher O&M and monitoring costs, these costs are spread out over 30 years, and the 2% discount rate used in the NPV estimates decreases the effect of longer term costs on the NPV of lifetime costs. However, it should be noted that should the passive treatment technologies require more than 30 years of implementation to achieve site objectives (which is likely), then additional O&M and long-term monitoring costs for these alternatives could easily make the NPV of lifetime costs higher than this alternative. Additionally, it is also likely that long-term monitoring costs (currently 20 years) could be reduced for this alternative, if successful remediation leads to reduced monitoring frequency and duration. In many cases, the accelerated cleanup (3 years versus 30+ years) and reduction in long-term liability will be worth slightly higher lifetime costs.

8.3.3 Semi-Passive Biobarrier

The semi-passive biobarrier alternative assumes that a series of four extraction and five injection wells will be installed at the downgradient edge and perpendicular to the axis of the plume (Figure 17). Groundwater will be recirculated between the rows of wells, and cheese whey added for approximately 3 weeks, after which time the system will be shut down for a period of 9 months. The biobarrier will be operated in this semi-passive mode for a period of 30 years. This alternative also assumes 30 years of associated O&M and long-term monitoring costs.

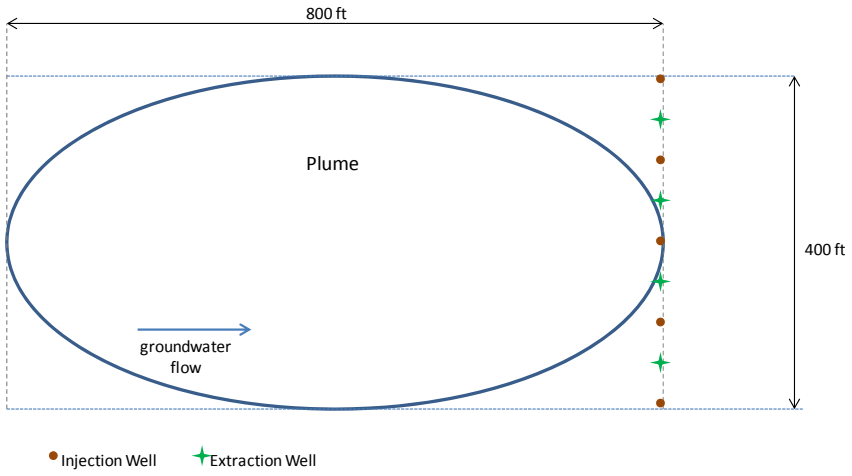

Figure 17. Semi-passive biobarrier alternative with cheese whey for plume cutoff.

As summarized in Table 8, the estimated total costs for this alternative over 30 years are $2,240,000 with a total NPV of lifetime costs of $1,840,000. The capital cost including design, work plan, installation of recirculation and monitoring wells, construction of the groundwater recirculation and cheese whey mixing systems, and system start-up and testing are approximately $460,000. The NPV of the O&M is estimated at approximately $980,000 for the 30 years of treatment. The O&M costs include the labor costs associated with regular rounds (every 9-10 months) of cheese whey mixing and injection, labor for system O&M, costs for equipment repair and replacement, and cost for the cheese whey. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

Table 8. Cost components for semi-passive biobarrier treatment of explosives-impacted groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
Capital Costs									
System design	95,142	—	—	—	—	—		95,142	95,142
Well installation	80,738	—	—	—	—	—		80,738	80,738
System installation	265,980	—	—	—	—	—		265,980	265,980
Start-up and testing	17,978	—	—	—	—	—		17,978	17,978
Subcost ($)	**459,838**	**—**	**—**	**—**	**—**	**—**		**459,838**	**459,838**
O&M Costs									
System O&M	27,732	43,482	43,482	43,482	43,482	43,482	43,482 every year	977,580	1,288,710
Subcost ($)	**27,732**	**43,482**	**43,482**	**43,482**	**43,482**	**43,482**	**1,043,568**	**977,580**	**1,288,710**
Long-Term Monitoring Costs									
Sampling/analysis/reporting (quarterly through 5 yrs, then annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**296,856**	**400,991**	**494,235**
Total Cost ($)	**524,572**	**80,484**	**80,484**	**80,484**	**80,484**	**55,851**	**1,340,424**	**1,838,409**	**2,242,783**

*NPV calculated based on a 2% discount rate

This alternative ranks third in estimated total remedy cost and second in NPV of lifetime costs (see Table 13). While this technology has relatively modest estimated capital costs, the long term O&M costs make it less attractive, especially if the system needs to operate beyond 30 years.

8.3.4 Passive Injection Biobarrier

The passive injection biobarrier alternative assumes that a series of 30 injection wells will be installed at the downgradient edge and perpendicular to the axis of the plume (Figure 18). An initial injection during year 1, and reinjection of EVO every 3 years after, will be performed to create a passive biobarrier. The biobarrier will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long-term monitoring costs.

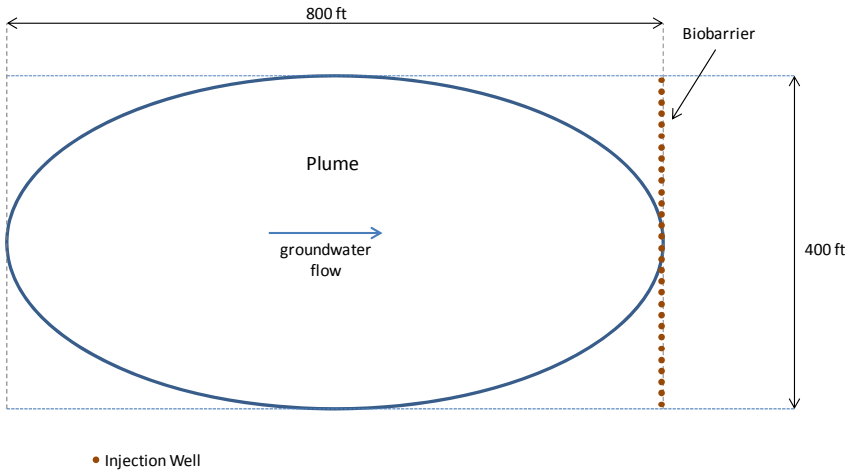

Figure 18. Passive biobarrier alternative with EVO for plume cutoff.

As summarized in Table 9, the estimated total costs for this alternative over 30 years are $2,390,000 with a total NPV of lifetime costs of $1,910,000. The capital cost including design, work plan, installation of injection and monitoring wells, and the initial EVO injection is approximately $320,000. The NPV of the O&M is estimated at approximately $1,180,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with regular injections (every 3 years) of EVO. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

Table 9. Cost components for passive injection biobarrier treatment of explosives-impacted groundwater.

	Year Cost is Incurred								NPV of Costs*	Total Costs
	1	2	3	4	5	6	7	8 to 30		
Capital Costs										
System design	71,505	—	—	—	—	—	—	—	71,505	71,505
Well installation (30 1" PVC wells)	67,393	—	—	—	—	—	—	—	67,393	67,393
Substrate injection	184,573	—	—	—	—	—	—	—	184,573	184,573
Start-up and testing	—	—	—	—	—	—	—	—	0	0
Subcost ($)	**323,471**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**323,471**	**323,471**
O&M Costs										
Substrate injection	—	—	—	174,598	—	—	174,598	174,598 every 3 years	1,181,345	1,571,382
Subcost ($)	**—**	**—**	**—**	**174,598**	**—**	**—**	**174,598**	**1,222,186**	**1,181,345**	**1,571,382**
Long-Term Monitoring Costs										
Sampling/analysis/reporting (quarterly through 5 yrs, then annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369	12,369 every year	400,991	494,235
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**12,369**	**284,487**	**400,991**	**494,235**
Total Cost ($)	**360,473**	**37,002**	**37,002**	**211,600**	**37,002**	**12,369**	**186,967**	**1,506,673**	**1,905,807**	**2,389,088**

* NPV calculated based on a 2% discount rate
**No "Start-up and testing" costs are included because no operating equipment is left behind following substrate injection.

This alternative ranks fifth in estimated total remedy cost and fourth in NPV of lifetime costs (see Table 13). The estimated capital costs for this approach are the lowest of the six alternatives because of the limited infrastructure required. However, the long-term O&M costs associated with regular injections of EVO make this one of the more expensive alternatives, with total remedy costs second only to the P&T alternative. As with the other barrier approaches (including P&T), total remedy costs will increase if the treatment needs to extend beyond 30 years.

8.3.5 Passive Trench Mulch Biowall

The passive trench mulch biowall alternative assumes an initial installation of a mulch biowall in a trench at the downgradient edge and perpendicular to the axis of the plume (Figure 19). The mulch biowall will be installed using the one-pass trenching/installation method, and will be 400 ft long, 2 ft thick, and extend down to 40 ft bgs. The biowall will be rejuvenated 4 and 8 years after installation, then every 3 years thereafter by injecting EVO into 20 injection wells installed within the mulch biowall. The EVO injections are required because the organics in the mulch will eventually be depleted. The biowall will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long-term monitoring costs.

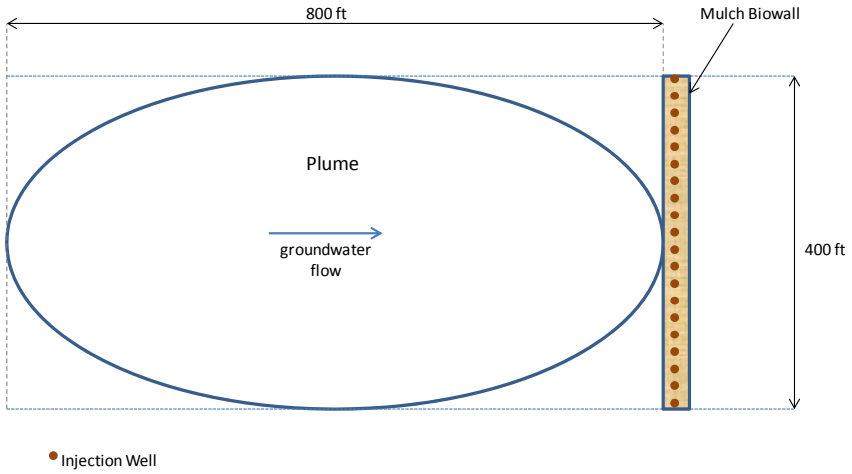

Figure 19. Passive biobarrier alternative utilizing a mulch wall for plume cutoff.

As summarized in Table 10, the estimated total costs for this alternative over 30 years are $2,170,000 with a total NPV of lifetime costs of $1,710,000. The capital cost including design, work plan, mulch biowall installation, and installation of injection and monitoring wells is approximately $360,000. The NPV of the O&M is estimated at approximately $950,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with injections of EVO to maintain the biowall. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

Table 10. Cost components for passive trench biowall treatment of explosives-impacted groundwater.

	Year Cost is Incurred									NPV of	Total
	1	2	3	4	5	6	7	8	9 to 30	Costs*	Costs
Capital Costs											
System design	62,205	—	—	—	—	—	—	—	—	65,205	65,205
Well installation	53,064	—	—	—	—	—	—	—	—	53,064	53,064
Trench installation	191,013	—	—	—	—	—	—	—	—	191,013	191,013
Substrate injection	52,500	—	—	—	—	—	—	—	—	52,500	52,500
Start-up and testing	—	—	—	—	—	—	—	—	—	0	0
Subcost ($)	**361,782**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**361,782**	**361,782**
O&M Costs											
	—	—	—	145,968	—	—	—	145,968	145,968 every 3 years	957,111	1,313,712
Subcost ($)	**—**	**—**	**—**	**145,968**	**—**	**—**	**—**	**145,968**	**1,021,776**	**957,111**	**1,313,712**
Long Term Monitoring Costs											
Sampling/analysis/ reporting (quarterly through 5 yrs then annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369	12,369	12,369 every year	400,991	494,235
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**12,369**	**12,369**	**272,118**	**400,991**	**494,235**
Total Cost ($)	**398,784**	**37,002**	**37,002**	**182,970**	**37,002**	**12,369**	**12,369**	**158,337**	**1,293,894**	**1,719,884**	**2,169,729**

* NPV calculated based on a 2% discount rate

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

This alternative ranks second in estimated total remedy cost and lowest in NPV of lifetime costs (see Table 13). The estimated capital costs for this approach are higher than those of the passive injection biobarrier because of the higher costs associated with the construction of the trench biowall relative to the costs for the initial injection of EVO. However, the long-term O&M costs associated with maintaining the mulch biowall are less than those of the passive injection biobarrier because less frequent injections (and less quantity) of EVO will be required to maintain the mulch biowall relative to the passive injection biobarrier. As with the other barrier approaches (including P&T), total remedy costs will increase if the treatment extends beyond 30 years.

8.3.6 Passive Trench ZVI PRB

The passive trench ZVI PRB alternative assumes an initial installation of a ZVI PRB in a trench at the downgradient edge and perpendicular to the axis of the plume (Figure 20). The PRB will consist of 25% ZVI filings and 75% coarse sand fill mixture (v/v). Like the passive mulch biowall, the PRB will be installed using the one-pass trenching/installation method, and will be 400 ft long, 2 ft thick, and extend down to 40 ft bgs. Pricing for this alternative assumes the PRB will need to be replaced after 15 years due to decline in ZVI reactivity or plugging. The PRB will be maintained for a period of 30 years. This alternative also assumes 30 years of associate O&M and long-term monitoring costs.

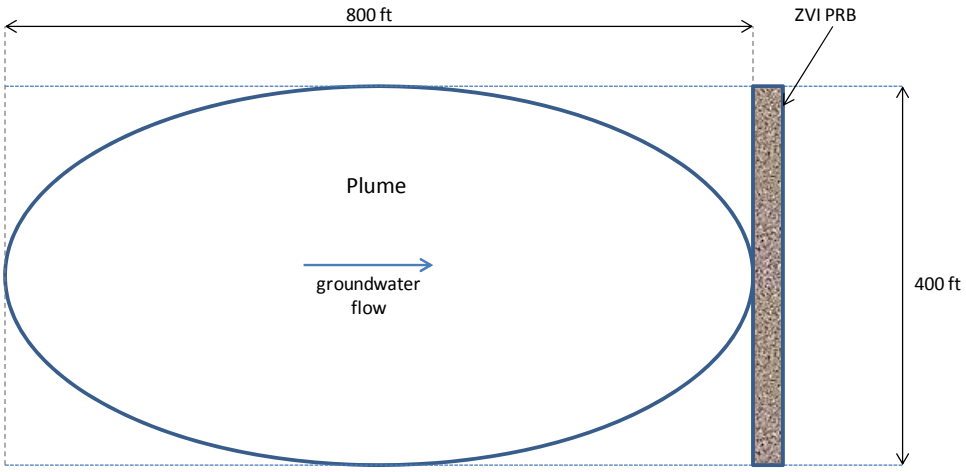

Figure 20. Passive barrier alternative utilizing ZVI for plume cutoff.

As summarized in Table 11, the estimated total costs for this alternative over 30 years are $2,270,000 with a total NPV of lifetime costs of $1,970,000. The capital cost including design, work plan, ZVI PRB installation, and installation of monitoring wells is approximately $940,000. The NPV of the O&M is estimated at approximately $640,000, which is the NPV associated with the replacement of the PRB after 15 years. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

Table 11. Cost components for passive trench ZVI PRB treatment of explosives-impacted groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5 to 14	15	16 to 30		
Capital Costs									
System design	62,205	—	—	—		—		65,205	65,205
Well installation	29,084	—	—	—		—		29,084	29,084
Trench installation	191,013	—	—	—		—		191,013	191,013
PRB material	650,000	—	—	—		—		650,000	650,000
Start-up and testing	—	—	—	—		—		0	0
Subcost ($)	**935,302**	**—**	**—**	**—**		**—**		**935,302**	**935,302**
O&M Costs									
PRB replacement cost	—	—	—	—		841,013		637,383	841,013
Subcost ($)	**—**	**—**	**—**	**—**		**841,013**		**637,383**	**841,013**
Long-Term Monitoring Costs									
Sampling/analysis/reporting (quarterly through 5 yrs, then annually)	37,002	37,002	37,002	37,002	12,369 every year	12,369	12,369 every year	400,991	469,602
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**123,690**	**12,369**	**185,535**	**400,991**	**469,602**
Total Cost ($)	**972,304**	**37,002**	**37,002**	**37,002**	**123,690**	**853,382**	**185,535**	**1,973,675**	**2,245,917**

* NPV calculated based on a 2% discount rate

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

This alternative ranks fourth in estimated total remedy cost and fifth in NPV of lifetime costs (Table 13). The estimated capital costs for this approach are higher than those of the passive trench mulch biowall because of the much higher costs associated with ZVI PRB material relative to the costs for the mulch biowall material. However, the long term O&M costs associated with maintaining the ZVI PRB are less than those of the mulch biowall because no injections are required to maintain the mulch biowall. The total remedy costs for this alternative would increase significantly if the PRB lifespan was less than 15 years, or if treatment extended beyond 30 years.

8.3.7 Pump and Treat

The groundwater extraction and treatment (P&T) system alternative would be similar to the semi-passive biobarrier system, in that a row of four extraction and five injection wells would be used to recirculate groundwater at the downgradient edge and perpendicular to the axis of the plume (Figure 17). However, in this case, the extracted groundwater would be treated above ground by passing it through GAC and the treated groundwater re-injected (providing hydraulic control and mass removal at the downgradient edge of the plume). The P&T system will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long-term monitoring costs.

As summarized in Table 12, the estimated total costs for this alternative over 30 years are $3,340,000 with a total NPV of lifetime costs of $2,690,000. The capital cost including design, work plan, installation of extraction/injection and monitoring wells, construction of the groundwater treatment system, and system start-up and testing is approximately $510,000. The NPV of the O&M is estimated at approximately $1,780,000. The O&M costs include the labor costs associated with system O&M, costs for equipment repair and replacement, electrical costs,

and cost for the replacement and disposal of the GAC. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

Table 12. Cost components for extraction and treatment of explosives-impacted groundwater.

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
Capital Costs									
System design	95,142	—	—	—	—	—		95,142	95,142
Well installation	80,738	—	—	—	—	—		80,738	80,738
System installation	306,980	—	—	—	—	—		306,980	306,980
Start-up and testing	26,250	—	—	—	—	—		26,250	26,250
Subcost ($)	**509,110**	**—**	**—**	**—**	**—**	**—**		**509,110**	**509,110**
O&M Costs									
System O&M	55,809	82,059	82,059	82,059	82,059	82,059	82,059 every year	1,781,478	2,435,520
Subcost ($)	**55,809**	**82,059**	**82,059**	**82,059**	**82,059**	**82,059**	**1,969,416**	**1,781,478**	**2,435,520**
Long-Term Monitoring Costs									
Sampling/analysis/reporting (quarterly through 5 yrs, then annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
Subcost ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**296,856**	**400,991**	**494,235**
Total Cost ($)	**601,921**	**119,061**	**119,061**	**119,061**	**119,061**	**94,428**	**2,266,272**	**2,691,578**	**3,438,865**

*NPV calculated based on a 2% discount rate

This alternative ranks last in both estimated total remedy cost and NPV of lifetime costs (Table 13). The estimated capital costs for this alternative are higher than those of the semi-passive alternative because of the higher costs associated with constructing a groundwater treatment system compared to constructing a whey mixing system. The high O&M costs associated with operating the pump and treat system are what makes this alternative the least attractive of the six alternatives. As with the other barrier approaches, total remedy costs will increase if the treatment needs to extend beyond 30 years.

Table 13. Summary of capital cost and NPV of costs for O&M and monitoring for treatment of explosives-impacted groundwater.

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30-Year Remedy Costs
Active plume treatment (whey)	$1140	$430	$320	$1890	$1950
Semi-passive biobarrier (whey)	$460	$980	$400	$1840	$2240
Passive injection biobarrier (EVO)	$320	$1180	$400	$1910	$2390
Passive trench biowall	$360	$960	$400	$1720	$2170
Passive trench ZVI PRB	$940	$640	$400	$1970	$2270
P&T	$510	$1780	$400	$2690	$3340

All costs are in thousands of dollars.
NPV – Net present value; current value of future costs based on a 2% annual discount rate.

9.0 IMPLEMENTATION ISSUES

9.1 END-USER ISSUES

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

9.1.1 Technology Applicability and Performance under Local Site Conditions

The technology utilized during this demonstration was the injection of a cosubstrate through semi-passive pumping. This approach is both highly flexible and widely applicable under differing aquifer conditions. The development of a semi-passive approach for groundwater treatment has evolved in large part from operational issues associated with full-time active pumping systems for in situ treatment, and in particular, well biofouling issues. A full-time active pumping system is perhaps the best way to effectively inject and mix substrates into groundwater, in addition to providing hydraulic control at a site. However, technical and cost issues associated with biofouling of injection wells in active systems remain a significant detriment to the widespread application of this approach. The semi-passive treatment approach provides many of the benefits of full-time active treatment, including effective distribution of a soluble carbon source and flexibility in design and operation, but has less overall potential for biofouling due to the limited time of operation of the extraction and reinjection wells. A number of different pilot and full-scale systems have successfully employed a semi-passive remedial design for substrate addition as described previously in Section 3.2 (see also Devlin and Barker, 1994; Devlin and Barker, 1999; Devlin et al. 2004; Gierczak et al., 2007; Hatzinger and Lippincott, 2009; Krug and Cox, 2009; Hyndman et al., 2000). This approach can also be used cost-effectively in deep as well as shallow aquifers and to aerially wide plumes. Aquifer depth is one of the limiting factors for fully passive designs, which become increasingly expensive due to close spacing of injection points or technically impractical (e.g., for passive trench barriers) as the depth to the water table increases (Stroo and Ward, 2009). A semi-passive pumping design has fewer limitations with depth. Similarly, wide plumes are more readily treated with active or semi-passive approaches than with fully passive designs as a few wells (and high flow rates) can often be used to distribute cosubstrate over a large area rather than closely spaced wells or injection points. See Stroo and Ward (2009) for further comparisons of different amendment designs.

The primary issues with applying semi-passive cosubstrate addition as a remedial approach are (1) designing the system based on the local hydrogeology and plume characteristics to optimize substrate distribution; (2) operating the system to minimize O&M; and (3) choosing the most effective cosubstrate to promote contaminant biodegradation. As with any in situ system, it is critical to have a good understanding of the plume characteristics and hydrogeology of the region requiring treatment. The semi-passive design is flexible with respect to extraction and injection well numbers, well placement, and flow rates, and various designs have been utilized including several alternating extraction and injection wells as a cutoff barrier (e.g., Krug and Cox, 2009),

or only two extraction wells and a single injection well, as was employed in this demonstration for source area treatment and at the former Whittaker-Bermite site for perchlorate (Hatzinger and Lippincott, 2009).

Extensive site assessment work was conducted during this demonstration as well as the others cited above in order to determine the extent of contamination in groundwater (Hydropunch, well installation, and baseline sampling over time) and the groundwater hydrology, including aquifer storativity, hydraulic conductivity, and the groundwater flow rate and direction (slug tests, pump tests, groundwater elevation measurements on multiple occasions). In addition, treatability studies were conducted to evaluate the most effective cosubstrates to promote explosives biodegradation in the local aquifer, as the literature has shown that many different soluble carbon sources may be applicable at specific sites. Degradation rates for key explosives were then determined for the various cosubstrates and a choice was made based on effectiveness and cost. All site data was subsequently incorporated into a model and simulations were conducted to determine the zone of influence and to evaluate the influence of modifying flow rates and pumping cycles. This basic site assessment and treatability study approach employed during this demonstration is routinely used to determine the most effective technologies for site cleanup and is recommended for implementing a semi-passive treatment approach for explosives at small or large scale. Groundwater modeling is a critical component of this approach (and nearly any other in situ system) because it allows educated decisions on system design (well placement and screening, flow rates) and provides a basis for evaluating operational data and making operational changes.

The cosubstrate utilized during this demonstration (a powdered cheese whey feed additive) was dictated by treatability study results. Among nine different cosubstrates tested (acetate, lactate, benzoate, hydrogen gas, citrate, ethanol, glucose, yeast extract, and cheese whey), only the cheese whey and yeast extract effectively promoted biodegradation of RDX, HMX, and TNT. Between these two cosubstrates, biodegradation rates were appreciably higher for both RDX and HMX using the powdered whey compared to yeast extract. The reason for the high substrate selectivity at Picatinny Area 157 is unclear and may reflect either the groundwater geochemistry or the explosives degrading microbial community. Although effective, the powdered whey product was difficult to apply to the aquifer at large scale because it is not completely soluble in water, and solids remain after thorough mixing. This issue was overcome by constructing a conical bottom tank with a bottom port to allow solids removal and an engineered system with a jet pump to thoroughly mix the whey with injection water. However, when possible based on treatability studies, it is desirable to utilize a completely soluble single chemical (e.g., acetate) as a cosubstrate rather than a complex mixture, such as cheese whey. The use of a single soluble substrate (1) simplifies the injection process, as the material can be metered into the groundwater from a drum or small tank; (2) allows both understanding and prediction of the routes of cosubstrate metabolism and the likely degradation intermediates; and (3) provides for better potential control of cosubstrate amount and groundwater ORP, as the stoichiometry of cosubstrate oxidation can easily be determined. In the case of the cheese whey product used, it was not possible to determine molar concentrations of the complex mixture (rather, TOC was used), and it is likely that some (or much) of the mixture was utilized by organisms other than those involved in explosives biodegradation, via fermentation or reduction of alternate electron acceptors such as Mn, sulfate, and Fe. Thus, while the powdered cheese whey additive was

extremely effective in promoting explosives biodegradation in this study, the application of a single, soluble substrate is desirable when possible based on the reasons stated above.

9.1.2 Technology Scale-Up

Some reasonably large applications of this semi-passive approach have already been applied for contaminants other than nitroaromatic and nitramine explosives. For example, Krug and Cox, (2009) designed a system as a cut-off barrier for a 250 ft wide perchlorate plume emanating from a landfill at the Longhorn Army Ammunition Plant, that included a total of 13 extraction and injection wells. This system was operated with periodic manual injection of cosubstrate during pumping phases (3 weeks "on" and 8 months "off"), which dramatically reduced costs. The system described herein at Picatinny Arsenal also was designed and built with all of the components required for application over a much larger plume area. The only changes required to utilize this system for a larger plume (as a cutoff barrier or source area treatment) would be the installation of additional extraction and/or injection wells, and the modification of piping runs to accommodate those extra wells. In this case, the system could be operated in an active mode at specific well loops (each consisting of two extraction wells and one injection well) at different times so that the only changes required during active operation at different well loops would be piping connections to the Conex box and cheese whey tank. Conversely, if long-term operation is anticipated, additional piping runs from the injection and extraction wells could be permanently added within the Conex box and programmed for simultaneous extraction and injection during active cycles. Thus, all the required components for a large-scale system are described in the final report for this project.

9.1.3 Secondary Impacts to the Local Aquifer

One of the typical benefits of active or semi-passive in situ treatment is a reduction in secondary groundwater impacts that are typical of passive approaches (e.g., vegetable oil injection), such as mobilization of dissolved iron and manganese, production and accumulation of methane gas, and generation of hydrogen sulfide. The injection and mixing of moderate amounts of cosubstrate into an aquifer, rather than quantities that are expected to persist for several years, minimizes the microbial reductive processes that cause the production of many of these secondary contaminants. In a typical application, Fe and Mn will be mobilized within the treatment zone to mg/L concentrations, but these metals will be back to background levels within a several meters downgradient of the injection wells (Krug and Cox, 2009; Hatzinger and Lippincott, 2009). Similar results are expected for methane and hydrogen sulfide, each of which are quickly oxidized in an aerobic aquifer. It should also be noted, however, that the longer the interval between active cosubstrate addition phases, the higher the expected concentrations of secondary contaminants, such as dissolved Fe and Mn, within the aquifer. If shorter cycles are used, less cosubstrate can be injected at each cycle, and less excess will be available to promote biological reduction of sulfate, Fe, Mn, etc.

During this demonstration, reasonably high concentrations of Fe, Mn, and methane were observed in some of the monitoring wells. For example, both Fe and Mn were detected at >40 mg/L in 157MW-4 and 157MW-5, and methane exceeded 10 mg/L in 157MW-7S and 157MW-7D. Because this was largely a source zone treatment application and groundwater transport was slow, it was not possible during the time frame of the study to assess whether these

compounds were still present in downgradient monitoring wells (i.e., the treated water did not reach downgradient wells 157MW-8S or 157MW-8D during the course of the study). However, one of the reasons for the relatively high concentration of these compounds during this study was the application of cheese whey rather than a single carbon substrate. In addition, relatively high concentrations of whey were added at each injection cycle so that the number of cycles could be minimized. This approach proved to be highly effective for remediation of explosives and degradation intermediates over the 565 day study, and no significant operational issues were experienced, such as well fouling. However, a trade-off for this approach was the production and mobilization of some secondary groundwater contaminants, such as Fe, Mn, and methane. Because there were no drinking wells in the local area and no close downgradient receptors, these contaminants were not deemed to be an important issue. However, mobilization of such contaminants should be considered in cases where downgradient receptors are present, and system operation and carbon sources should be chosen or adjusted accordingly.

9.1.4 Technology Cost Compared to Other Remedial Options

The expected cost drivers for the installation and operation of a semi-passive in situ bioremediation system for explosives and comparisons to other remedial approaches are provided in Section 8.

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APPENDIX A

POINTS OF CONTACT

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