FINAL REPORT

Field Demonstration/Validation of Electrolytic Barriers for Energetic Compounds at Pueblo Chemical Depot

ESTCP Project ER-0519

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EXECUTIVE SUMMARY

This report documents the results from the third field demonstration of a novel electrolytic reactive barrier technology (referred to as e^{-}barriers) that treats contaminants in groundwater. Field efforts have been complemented by numerous laboratory-scale studies. Collectively, these efforts have led to advances in the e^{-}barrier technology, with this field demonstration reflecting the highest evolution of the technology. Funding for e^{-}barrier development has come from industry and government. This project was wholly funded by government through ESTCP.

The technology is founded upon the concept of a permeable reactive barrier (PRB). Contaminants are carried through the reactive barrier via the natural flow of groundwater. Within the barrier, contaminants are degraded as they pass through titanium screen electrodes charged with low voltage DC current. Contaminants are sequentially exposed to electrolytic oxidation ➔ reduction ➔ oxidation ➔ reduction. The primary appeal of e^{-}barriers has been the low power cost (cents/day/m^2) and the potential to address contaminants that might otherwise be difficult to treat with existing technologies.

This demonstration was conducted at Pueblo Chemical Depot (PCD), located 15 miles east of Pueblo, Colorado. Built during World War II, PCD served as an ammunition and material storage and shipping center. Activity at PCD included demilitarization of expired munitions via washout operations conducted at Solid Waste Management Unit 17 (SWMU-17). Former washout ponds associated with SWMU-17 created groundwater plumes more than a mile in length containing elevated concentrations of RDX and other energetic compounds. In 1998, sediments associated with the former washout ponds were removed by excavation. Despite source excavation, the remaining soils are sustaining concentrations of RDX, HMX, 2,4-DNT, 2,4,6-TNT, and 1,3,5-TNB in groundwater.

The e^{-}barrier was located between two former washout ponds. Between 12 and 15 feet of sandy alluvium was encountered above the regionally extensive Pierre Shale formation. Groundwater was encountered in the lower five to seven feet of the alluvium. The average groundwater Darcy velocity was 250 ft/yr. Concentrations of RDX in groundwater have dropped from historic highs of ~400 μg/L to current levels of <10 μg/L. Similarly, concentrations of other energetic compounds have declined from past levels. The most recent data indicates concentrations of: <1 μg/L HMX; 10-400 μg/L 2,4,6-TNT; 10-40 μg/L 2,4-DNT; and 300-3,000 μg/L 1,3,5-TNB.

The overarching objective of the demonstration was to define the viability of e^{-}barriers as an option for managing energetic compounds (and other persistent contaminants) in groundwater at U.S. Department of Defense (DoD) facilities. This included the goal of employing promising design improvements that were advanced from the 2002-2005

ESTCP e^-barrier demonstration conducted at F.E. Warren Air Force Base, Wyoming (ER-0112). These included:

- Using a sequence of four active electrodes (all previous studies employed only two active electrodes)
- Mounting electrodes on vinyl sheet pile sections with sealable interlocks
- Emplacing a cement-bentonite seal at the base of the barrier to prevent underflow
- Using cement/bentonite wing walls at each barrier to focus flow through the barrier
- Using a solar power supply to energize the electrodes

The e^-barrier was installed at PCD in January 2006. The total width was 35 feet, and at peak water table elevations the barrier intercepted a 240 ft^2 section of the plume. The e^-barrier was energized in March 2006 and was operated for 770 days. A three-week interruption in operations occurred in late 2007 due to failure of a DC-DC voltage controller. During operations, the imposed electrical potential was increased in 6 steps from 1.4 to 6.3 volts. Performance was measured as a function of imposed electrical potential.

The primary performance metric was depletion of energetic compounds in groundwater. Maximum depletion of target compounds, based on comparison of upgradient and downgradient water quality, were: RDX 40%, 2,4,6-TNT 60%, HMX 82%, 2,4-DNT 67%, and TNB 65%. These values are low as compared to bench-scale laboratory studies, which indicated up 99% RDX depletion, and the field-scale e^-barrier at F.E. Warren AFB, which achieved up to 95% removal of trichloroethene. Possible explanations for the limited success of the PCD field application include:

- At higher voltages, concentrations of RDX and HMX upgradient and downgradient of the e^-barrier dropped to levels near detection limits. It is possible that the e^-barrier was affecting concentrations of these contaminants on both sides of the barrier (supported by Eh data). If this is the case, the comparison of upgradient water quality to downgradient water quality may be creating a false negative result.

- Based on high resolution analysis of soil cores, a large fraction of the contaminant mass is stored as a sorbed phase on soils. In particular, the Pierre Shale has a 2% fraction of organic carbon and correspondingly high sorbed concentrations of energetic compounds. The observed limited performance of the e^-barrier may reflect the challenge of achieving large improvements in water quality when a large fraction of the total contaminant mass is present as a sorbed phase.

No major problems were encountered during installation and operation of the e^-barrier. Our estimate is that primary systems could be operated for a decade without replacements. Technologies that may compete with e^-barriers include permeable bark mulch walls (ER-0426) and iron walls (ER-0223). Results from parallel ESTCP demonstrations suggest that these are likely to be even simpler to install and operate.

Regarding cost, e^{-}barriers are more expensive than bark mulch walls and iron walls by a factor of three. Alternative assumptions could be employed to create a more favorable economic analysis. Unfortunately, it seems unlikely that this would lead to a scenario in which e^{-}barriers could compete on a cost basis with bark mulch or iron walls. Combining implementation and cost results, it appears that the e^{-}barrier's niche is at sites where the limitations of bark mulch or iron wall would preclude their use. Considering this narrow niche and the limited number of RDX sites (approximately 20) identified through this project, at best there may be a handful of sites where e^{-}barriers could be a viable technology for treating energetic compounds in groundwater.

As a footnote, technology developed through advancement of the e^{-}barrier is currently being adapted to other novel treatment technologies. These include:

- Above ground systems for "point of use" groundwater treatment - The vision is that point of use treatment of groundwater is an emerging solution for large and dilute plumes and that the electrolytic process can be a critical component of practical above ground treatment systems.

- *In situ* systems for oxygen delivery - Components of e^{-}barrier technology are currently being considered for delivery of oxygen to soils and groundwater at sites impacted by petroleum hydrocarbons.

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**Dedicated to the technical lead for this project,
our now absent friend and colleague**

**Dave Gilbert
(1962-2008)**

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List of Acronyms and Abbreviations

AFB	Air Force Base
BRAC	Base Realignment and Closure
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
CFB	Canadian Forces Base
CSU	Colorado State University
DoD	United States Department of Defense
DoE	United States Department of Energy
2,4-DNT	2,4-dinitrotoluene
e^-barrier	Electrically Induced Redox Barrier
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FUDS	Formerly Used Defense Site
GC	Gas Chromatography
HDPE	High density polyethylene
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (His Majesty’s eXplosive)
ID	Inner Diameter
LC/MS	Liquid Chromatography-Mass Spectroscopy
MCL	Maximum Contaminant Level
MSDS	Material Safety Data Sheet
NRC	National Research Council
OSHA	Occupational Safety and Health Administration
OVA	Organic Vapor Analyzer
OVM	organic vapor monitor
PFLA	phospholipid fatty acid
PQL	potential quantification limit
PCD	Pueblo Chemical Depot
PID	photoionization detector
PI	Principal Investigator
PRB	permeable reactive barrier
PVC	Polyvinyl chloride
QAPP	Quality Assurance Project Plan
RAB	Remedial Action Board
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition eXplosive)
SERDP	Strategic Environmental Research and Development Program
SHE	Standard Hydrogen Electrode
SOP	Standard Operating Procedure

SWMU	Solid Waste Management Unit
TDS	Total dissolved solids
Ti-mmo	Titanium-mixed metal oxide
1,3,5-TNB	1,3,5-trinitrobenzene
2,4,6-TNT	2,4,6-trinitrotoluene
USEPA	U.S. Environmental Protection Agency
UXO	Unexploded Ordnance

1.0 INTRODUCTION

In 2005, ESTCP funded a three-year field demonstration of an Electrically Induced Redox Barrier for treatment of energetic compounds in groundwater. The demonstration was conducted at the Pueblo Chemical Depot (PCD) near Pueblo, Colorado. Contaminants of concern include 2,4,6-TNT, 2,4-DNT, RDX, HMX, and 1,3,5-TNB. An electrolytic reactive barrier (e^-barrier) is a permeable reactive barrier (PRB) driven by low voltage direct current. This project builds on previous e^-barrier field demonstrations at F.E. Warren Air Force Base, Wyoming (ER-0112) and Canadian Forces Base Borden, Ontario. Furthermore, it builds on numerous laboratory studies including CU-1234 - Sequential Electrolytic Degradation of Energetic Compounds in Groundwater. The overarching vision of this project is to complete a definitive field demonstration of a new technology for treating persistent contaminants in groundwater.

1.1 BACKGROUND

This report has been prepared by Colorado State University (CSU) as final documentation for ESTCP project ER0519, titled Electrolytic Reactive Barrier for Treatment of Energetics in Groundwater. The scope of the project includes laboratory studies and a field demonstration at the Pueblo Chemical Depot. In 2007, the project was extended to include complementary field and laboratory activities based on the data collected during 2005 and 2006. This report presents documentation of all tasks conducted as part of ESTCP project ER0519.

1.2 OBJECTIVES OF THE DEMONSTRATION

The primary objective of the project is to define the viability of e^-barriers as an option for managing energetic compounds (and other persistent contaminants) in groundwater at U.S. Department of Defense (DoD) facilities. Previous e^-barrier demonstrations have shown promise in terms of cost and efficacy. Furthermore, they provided insight regarding promising design improvements. Employing these improvements, this demonstration provides a rigorous basis for predicting performance, estimating full-scale cost, and implementing full-scale projects.

1.3 REGULATORY DRIVERS

Regulations under CERCLA and RCRA, and their equivalents at the state level, require cleanup of groundwater to strict numerical concentrations (NRC 1994). However, current remedial technologies are often ineffective in eliminating *in situ* sources of contamination. Consequently, long-term containment is often required for plumes emanating from source zones (USEPA 1992). The primary challenge of long-term containment is that it can be labor- and cost-intensive. The focus of this effort is to develop a new containment technology that is effective in reducing groundwater concentrations and has low operation and maintenance costs. PCD is currently required (by the Colorado Department of Public Health and Environment) to clean up RDX concentrations in groundwater to less than 0.55 µg/L. Groundwater goals for other energetic compounds include: 0.0885 µg/L for 2,4-DNT; 2.01 µg/L for 2,4,6-TNT; 361µg/L for 1,3,5-TNB; and 602 µg/L for HMX.

1.4 TECHNOLOGY DESCRIPTION

The e^-barrier consists of a panel of closely spaced permeable electrodes, which is installed beneath the ground's surface, intercepting a plume of contaminated groundwater. Applying electrical potential to the electrodes imposes oxidizing conditions at the positive electrodes and reducing conditions at the negative electrodes. By imposing sequential oxidizing and reducing conditions, thermodynamic conditions are shifted to drive the transformation of target compounds to non-toxic products. A field-scale conceptualization of an e^-barrier is illustrated in Figure 1.

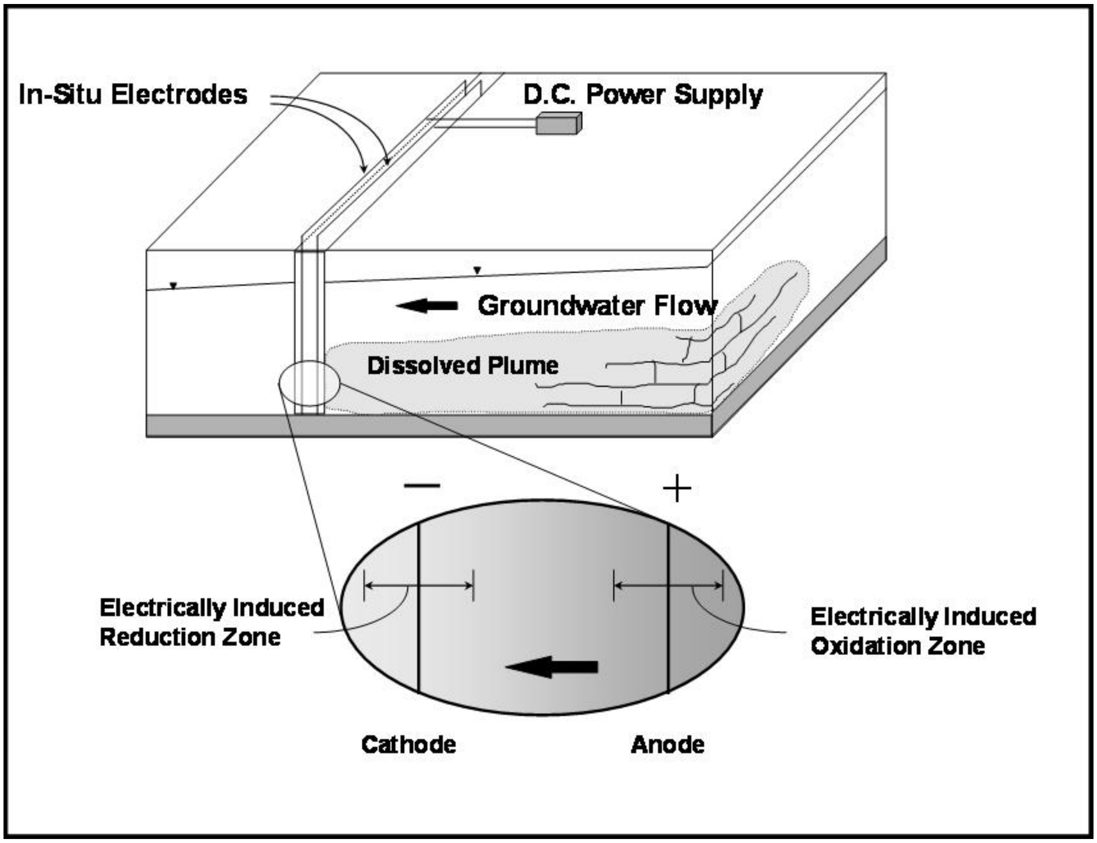


Figure 1 - Conceptualization of a field-scale e^-barrier.

1.5 TECHNOLOGY DEVELOPMENT

Research into e^-barriers has been ongoing at Colorado State University since September 1998. A summary of projects and results is provided in Table 1. In chronological order, related publication include:

- Petersen M, (2003), Sequential Electrolytic Processes for the Treatment of Trichloroethene in Ground Water, Masters Thesis Colorado State University, Fort Collins, Colorado.

- Gilbert D, Sale T. (2005). Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. Environ Sci Technol 39:9270-9277.

- Sale, TC,, Petersen MA, Gilbert DM, (2005), Final Report Electrically Induced Redox Barriers for Treatment of Groundwater, Project Report for ESTCP project CU-0112.

- Petersen M, (2007), Characterizing Reaction and Transport Processes in an Electrolytic Reactor for In Situ Groundwater Treatment, Ph.D. Dissertation Colorado State University, Fort Collins, Colorado.

- Petersen, M, Sale T, Reardon K ,(2007), Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes, Chemosphere Volume 67, Issue 8, April 2007, Pages 1573-1581.

- Gilbert D, Sale T, Petersen M. 2008. Addendum to Final Report: Electrically Induced Redox Barriers for Treatment of Groundwater. Addendum to Environmental Security Technology Certification Program (ESTCP) Project CU-0112 Final Report. ESTCP, Arlington, VA, USA.

- Gilbert, D. Sale, T., and M. Petersen (2009), Electrolytic Reactive Barriers for Chlorinated Solvents Remediation, Chapter 17 of the ESTCP Monograph on Plumes, In final publication

Table 1 – Summary of e$^-$barrier research

SPONSOR	PERIOD	ACTIVITIES	RESULTS TO DATE
Solvents in Groundwater Research Consortium	1998-Present	Laboratory column and tank proof of concept experiments for chlorinated solvents, testing of panel materials, design and installation of a small prototype (CFB Borden), prototype operations and monitoring (1/25/02-6/15/04).	Laboratory studies indicate efficacy for 1,1,1-TCA, PCE, TCE; titanium electrodes and HDPE spacers shown to be stable (>16 months); techniques for scale management demonstrated; successful installation of prototype; field results indicate potential to achieve flux reduction. Removal of e$^-$barrier materials following 18 months of field testing indicates stability of construction materials.
United Technologies Corporation	2000-2002	Column proof of concept experiments for arsenic.	Removal of arsenic via *in situ* precipitation, MCLs sustained in active column effluent after 14 months of operation. Titanium-mmo electrodes stable after 14 months of operation.
National Science Foundation	2000-2002	Enhanced biological attenuation of contaminants via electrolytic manipulation of redox conditions.	Laboratory methods developed to test electrolytic enhanced biodegradation. Results were inconclusive due to difficulties in sustaining anaerobes in column studies.
ESTCP (ER-0112)	2001-2004	17 m^2 field demonstration and validation of an electrolytic reactive barrier	Field data indicates TCE flux reduction of 95%. Costs are similar to the high end of other

		for treatment of TCE.	reactive barrier technologies.
SERDP (CU-1234)	2002 - 2004	Electrolytic batch reactor experiments for RDX, HMX, 2,4,6-TNT and 2,4-DNT. Flow-through reactor experiments for 2,4,6-TNT and RDX.	High fractional transformation of energetic compounds observed in laboratory column experiments. Minimal formation of detrimental intermediates observed. Preliminary work on reaction pathways.
U.S. Army Corps of Engineers	2003-2005	The influence of pH on electrolytic transformation of dissolved energetic compounds.	Results indicate that alkaline conditions developed at the cathode surface are not a necessary mechanism for electrolytic transformation of dissolved 2,4,6-TNT or RDX.
ESTCP ER-0519	2005-present	Demonstration/validation of Electrolytic Reactive Barriers for treatment of energetic compounds at the Pueblo Chemical Depot	This project

1.6 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Advantages motivating our interest in the e^-barrier approach include:

- The method is environmentally benign, requiring no chemical introduction,
- No *in situ* mixing of reagents or nutrients is required,
- Electrical power costs associated with driving transformations are low (i.e., \$0.05-0.01/day/m^2),
- With additional optimization, the cost of construction materials may be less than that for comparable niche technologies,
- Rates of chemical transformation can be modified remotely by adjusting applied voltage,
- The potential at electrodes can be periodically reversed or adjusted to remove inorganic precipitates (e.g., $CaCO_3$), a common constraint of other technologies,
- Electrode materials appear to be resilient under standard treatment conditions; it is expected that subsurface components of the system can remain effective for ten or more years (Addendum to ER-0112). This compares favorably against other PRB technologies (e.g., zero valent iron), in which PRB materials are consumed.
- The process of sequential oxidation and reduction has the potential to degrade a wide range of contaminants, including mixtures that are difficult to address with current technologies.

Limitations that we are presently aware of include:

- Deep installations of a barrier will be challenging. In general, from a construction perspective, shallow applications will be most feasible.

- In waters containing high alkalinity, scale formation at the negative electrode may inhibit degradation of contaminants. Success in high carbonate environments will require effective measures to minimize and/or periodically remove scale from the negative electrode. To date, measures identified through previous field efforts and in the laboratory appear effective in managing scale formation.

- Downgradient benefits may be limited due to desorption and/or back-diffusion of contaminant out of low-permeability zones. However, this limitation applies to other PRB-type remediation technologies as well.

2.0 PERFORMANCE OBJECTIVES

The primary focus of the demonstration is to resolve whether e^-barriers are a viable option for treatment of groundwater impacted with energetic compounds (and, potentially, other contaminants) at DoD sites. Through the activities in this demonstration, the appropriate application niches for e^-barriers will be resolved. Performance objectives, data requirements, success criteria and our final results are presented in Table 2.

Table 2 - Field demonstration performance objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Contaminant removal	Concentrations of energetic compounds in groundwater immediately downgradient of the e^- barrier.	Concentrations less than site cleanup goals.	Unfortunately, results from the demonstration failed to show large improvement in water quality downgradient of the e^-barrier. In general, site cleanup goals were not achieved. Declining upgradient contaminant concentrations during operations complicates analysis of the results.
Long term viability	Sustained contaminant removal as above, with no measurable increases in head loss through the impacted interval, loss in electrical properties of the e^-barrier, or degradation of physical properties of the barrier components.	Low concentrations maintained throughout study; steady electrical demand.	The solar power supply and electrodes were reliable. Problems were encountered with voltage regulators and data logging systems. Similar problems can likely be avoided in future systems. Desired shifts in redox potential through the e^-barrier were sustained for 120 out of 123 weeks. The three-week down period was associated with failure of a voltage regulator.
Cost	Documentation of construction, operation, maintenance and monitoring costs in the final reports.	Installation and operational costs are comparable or lower than those for similar technologies.	Costs for e^-barriers are a factor of three greater than zero valent iron and bark mulch barriers
Qualitative Performance Objectives			
Implement-ability	Documentation of construction and operation experience in the final reports. This will include insight regarding the optimal niche for e^-barriers.	Installation of a functional system.	No major issues arose regarding installation. Like other PRB technologies, operations and maintenance costs were minimal.

2.1 CONTAMINANT REMOVAL

A primary quantitative performance objective was removal of energetic compounds in groundwater. Site cleanup goals are presented by EarthTech (2007). These include: 0.550 µg/L of RDX; 0.0885 µg/L of 2,4-DNT; 2.01 µg/L of 2,4,6-TNT; and 602 µg/L of HMX in groundwater. To be effective at the PCD site, the e^-barrier should be capable of treating groundwater to these levels.

Energetic compound data in groundwater was monitored at sampling points upstream and downstream of the e^-barrier. Upstream concentrations provide background concentration levels. Downstream samples collected adjacent to the barrier face and at distances of 0.5, 2, and 4 meters provide a basis for performance assessment.

2.2 LONG TERM VIABILITY

Potential long-term viability concerns include loss of electrode surface reactivity or reduced groundwater flow through the barrier. Electrode surface reactivity could be impeded via loss of electrical properties, degradation of materials, or scaling effects. In a field demonstration, these would be made apparent through electrical monitoring (e.g., reduced current) or measured concentration reductions across the e^-barrier.

Electrical performance was monitored with data loggers. Aside from operational issues (discussed in Section 6.4), electrical performance data indicates no degradation of electrode materials. Groundwater data also indicated no decline in the treatment trend over the study's course.

Scaling or biofouling within the e^-barrier could decrease permeability and result in diminished groundwater flow through the barrier. This would be accompanied by an increase in pressure drop across the barrier. As such, piezometers were installed up- and downgradient of the e^-barrier. Pressure drops were relatively constant throughout the study, suggesting limited plugging of the formation and/or barrier panels.

The scope of this project did not include excavation of the e^-barrier to evaluate the electrode surface. However, our past experience indicates that electrode materials are stable under standard treatment conditions for at least three years, and modeling indicates that e^-barrier electrodes will remain stable for ten years or even longer (Gilbert 2009).

2.3 COST

A secondary objective of this demonstration was to evaluate the e^-barrier for its ability to cost-effectively remove energetic compounds from groundwater. Successful application of this performance objective includes a cost that is similar to or better than competing technologies, such as iron or mulch PRBs. A detailed cost analysis, including installation and operational costs, is included in Section 6. Results indicate that the cost per square foot of installing an e^-barrier is \$675. Annual operations and maintenance costs, including full replacement every 10 years, is $\$66/\text{ft}^2$/year.

2.4 IMPLEMENTABILITY

Another secondary objective of this project was to demonstrate that an e^-barrier could be successfully installed and operated in the field. Electrode panel design and installation methods used at the PCD demonstration showed improvement over those previously employed. Specific advances included:

- Use of four active electrodes (i.e., two sequential pairs of positive-negative electrodes, whereas all previous studies used a single electrode pair)
- Mounting electrodes on vinyl sheet pile sections with sealable interlocks
- Emplacing a cement-bentonite seal at the base of the barrier to prevent underflow
- Using cement/bentonite wing walls at each barrier to focus flow through the barrier
- Using a solar power supply to energize the electrodes

During the demonstration no major issues were encountered with implementability.

3.0 BACKGROUND FOR THE DEMONSTRATION LOCATION

The following provides background information regarding the site selected for the e$^-$barrier demonstration (SMW-17). This background includes the site location, historical land use, ongoing restoration activities, criteria used in selecting the site and site setting data that was available prior to initiating the field studies. Additional data describing the setting, collected during the demonstration, is presented in Section 5.

3.1 SITE LOCATION AND HISTORICAL LAND USE

Building of information presented on PCD's web site, PCD is located approximately 15 miles east of Pueblo, Colorado (Figure 2). Constructed during World War II, PCD was built to serve as an ammunition and material storage and shipping center. During the late 1950s, PCD became a major Army missile repair and maintenance facility. The facility operated at nearly full capacity during the Vietnam era. Pueblo's primary mission in the 1990s became the storage of chemical munitions.

Figure 2 - Location of Pueblo Chemical Depot near Pueblo, Colorado.

In 1988, PCD was identified for realignment. A Reuse Development Plan was generated to address the total reuse of the depot. PCD is undergoing environmental restoration to make it safe for future reuse. A primary restoration issue is the former holding ponds associated with munitions washout operations (SWMU-17). The ponds were active from 1948 to 1974. Unfortunately, releases from the ponds produced plumes several miles long that reached offsite into the Arkansas River alluvium. In 1998, sediments from the ponds were removed by excavation. Despite source excavation, the remaining soils are sustaining concentrations of

RDX, HMX, 2,4-DNT, 2,4,6-TNT, and 1,3,5-TNB in groundwater. Additionally, high levels of nitrate are present.

3.2 ONGOING RESTORATION ACTIVITIES

Relative to SWMU-17, the current site remedy at the facility boundary is pump-and-treat. Water produced is treated using activated carbon. The primary benefit of groundwater extraction and treatment is limiting further migration of site contaminant beyond the facility's boundary. Operation of the pump-and-treat system began in 1998. Unfortunately, operations and management of the pump-and-treat system have proven to be expensive (roughly $1 million/year).

With EarthTech Inc. as their lead consultant, PCD has been evaluating alternative restoration approaches through the 2000s,. This included a series of pilot tests involving *in situ* chemical oxidation and *in situ* biological reduction. Results of these efforts are documented by EarthTech (2007).

In 2008 a fixed price cleanup project was awarded to the Shaw Group for the PCD site. As of 2009, key elements of the restoration plans for SWMU-17 include:

- Excavation of additional soil adjacent to the former ponds
- Injection of a soluble carbon substrate (lactate) immediately downgradient of the former ponds
- Injection of additional emulsified vegetable oil in a series of 10-20 transects through the SWMU-17 plumes that extend to the site property boundary.

A desired outcome for the e^-barrier demonstration was to show that e^-barriers would be a promising treatment option at the source and in downgradient plumes. To date, our advocacy for this has been limited due to rebound of the target compounds immediately downgradient of the e^-barrier. While this is a limitation of the e^-barriers technology at PCD, it may equally well be a limitation for other technologies currently being considered for SWMU-17. The topics of e^-barrier performance and downgradient rebound are discussed in detail in Section 5.

3.3 SELECTION OF A DEMONSTRATION LOCATION

In 2004-2005, as part of SERDP CU-1234, several sites at PCD were screened as potential locations for the field demonstration. Selection criteria included:

1. Shallow depth to groundwater – to minimize project costs and simplify monitoring activities.

2. Energetic compound concentrations on the order of 100 µg/L – allowing performance to be evaluated over multiple orders of magnitude.

3. Groundwater seepage velocities greater than 0.2 feet/day – lower velocities would make it difficult to evaluate performance based on downgradient water quality during the limited demonstration period.

4. Basal aquitard – ideally, the barrier would be keyed into a low permeability unit with low groundwater and contaminant flux.

5. Low total dissolved solids (TDS) – locations with lower TDS are preferred in that they have lower potential for adverse fouling of the electrodes by inorganic precipitates.

6. Minimal interference with other site activities.

Based on the above criteria and permission from the base, a suitable location was identified as shown in Figure 3. A 180-degree photographic panorama of the site is presented in Figure 4.

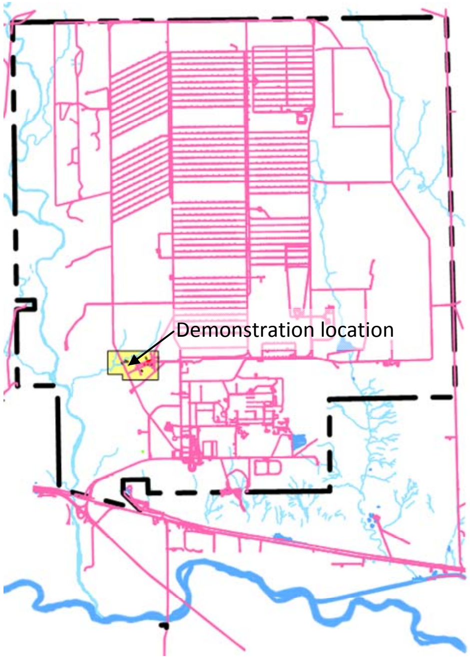


Figure 3 - Location of the e-barrier demonstration at the PCD site (base map from EarthTech 2007).

Figure 4 - Pre-installation photograph of location selected for e-barrier demonstration.

3.4 PRE-DEMONSTRATION SITE SETTING INFORMATION

The site is underlain by 10-15 feet of sandy alluvium. The alluvium is a fluvial terrace deposit associated with either the Arkansas River or Chico Creek. Groundwater occurs at approximately 8-10 feet below ground surface (bgs). The alluvium is underlain by the Pierre Shale, which is thousands of feet thick and areally extensive across the plains in south central Colorado.

Historic water level data from 2,4,6-TNTMW-02, a well near the demonstration site, is presented in Figure 5. This shows that seasonal water level fluctuation is on the order of 2 feet. Average annual precipitation at the site is 12 inches/year. Much of this comes in the form of summer thunderstorms. Average annual pan evaporation is 66 inches/year.

The primary contaminant of concern in the demonstration location is RDX. Maps illustrating the RDX plume emanating from SWMU-17 are presented in Figure 6 and Figure 7.

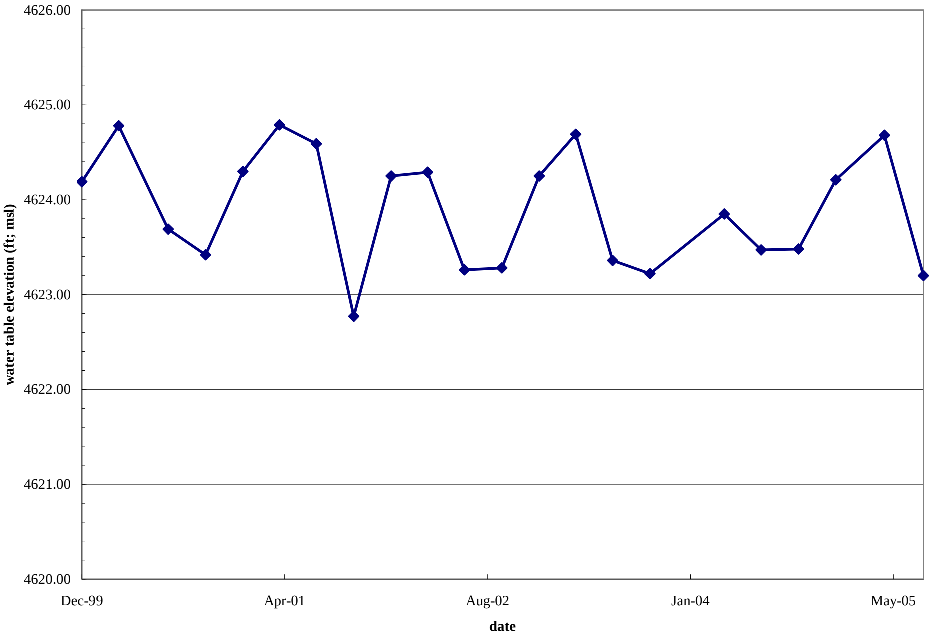


Figure 5 - 2,4,6-TNTMW 02 well hydrograph for the period of 1999-2005 (EarthTech).

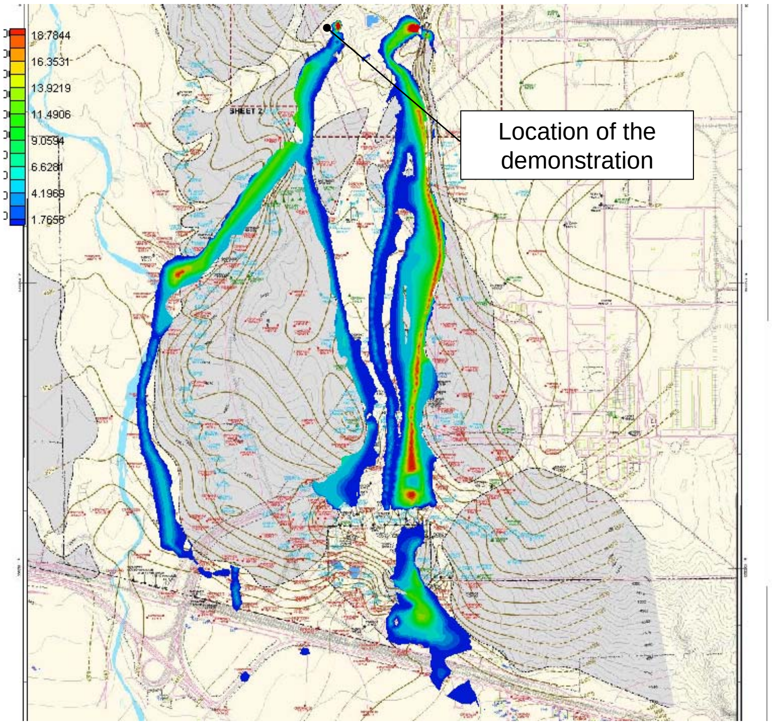


Figure 6 - PCD RDX plume map (provided by AECOM /EarthTech). Concentrations are presented in µg/L.

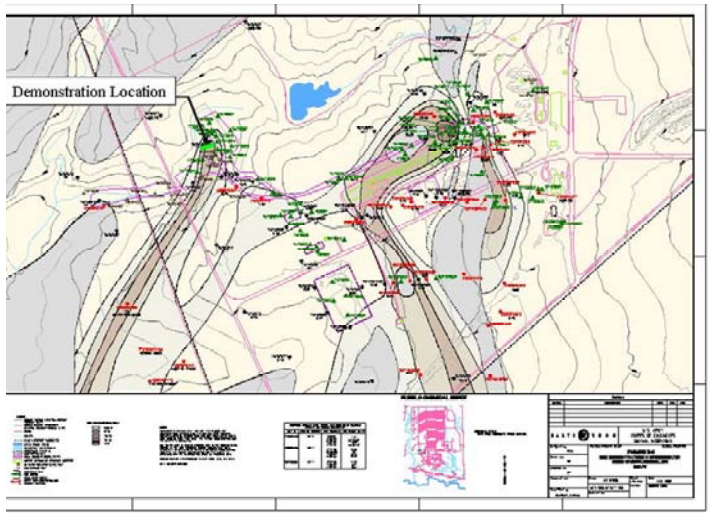


Figure 7 - PCD RDX plume map for SWMU-17 (provided by AECOM /EarthTech). Concentrations are presented in µg/L.

4.0 TEST DESIGN

The following describes the test design. This includes:

- Conceptual Design – An overview of the demonstration
- Baseline Characterization – Field data collected prior to installation of the e$^-$barrier
- Laboratory Testing – Pre-design studies conducted in the laboratory
- Design and Layout – An as-built description of the e$^-$barrier
- Field Testing – A description of applied voltages and related operational issues
- Sampling Methods – Methods employed in collecting critical data
- Complementary Studies – A description of complementary studies that were conducted concurrently with the field demonstration

4.1 CONCEPTUAL EXPERIMENTAL DESIGN

The primary objective of this project was to conduct a definitive demonstration of the e$^-$barrier technology for treatment of energetic compounds in groundwater. This included the goal of employing promising design enhancements, which had been identified through earlier e$^-$barrier studies. These included:

- Use of four active electrodes (i.e., two sequential pairs of positive-negative electrodes, whereas all previous studies used a single electrode pair)
- Mounting electrodes on vinyl sheet pile sections with sealable interlocks
- Emplacing a cement-bentonite seal at the base of the barrier to prevent underflow
- Using cement/bentonite wing walls at each barrier to focus flow through the barrier
- Using a solar power supply to energize the electrodes

As installed, the active portion of the e$^-$barrier was 35 feet in length and located immediately downgradient of a former washout pond. Over a period of 777 days, the barrier was operated at electrical potentials of 1.4, 2.3, 3.3, 4.3, 5.3, and 6.3 volts. At all of these except 1.4V, concentrations of RDX, 2,4,6-TNT, 2,4-DNT, and HMX were measured up- and downgradient of the barrier. Complementary data collected during the effort included:

- Voltage and amperage data describing the status of the system and the imposed conditions at the electrodes
- Water level data defining hydraulic gradients, groundwater flow directions, and saturated thicknesses at the barrier as a function of time
- Costs associated with installation and operations of the e$^-$barrier

Midway through the demonstration, the need for several complementary studies was recognized. These included:

- Detailed coring and analysis of energetic compounds through the alluvium shale in an effort to resolve the mechanisms driving rebound downgradient of the e$^-$barrier
- Sorption studies to resolve if sorption processes were in part responsible for the apparent downgradient rebound

- Additional column studies addressing the issue of competition for reactive sites on the electrode

4.2 BASELINE CHARACTERIZATION

Prior to installing the e^-barrier it was necessary to verify subsurface conditions at the chosen location and to collect data supporting design of the e^-barrier. Specific activities included test boring and monitoring well installation, water level measurement, and collection and measurement of water samples. Methods and observed conditions are described in the following section.

4.2.1 TEMPORARY MONITORING WELL INSTALLATION

On June 21, 2005 eleven borings (designated as ESTCP 1 through 11) were installed to characterize the area selected for the demonstration. Temporary monitoring wells were installed in ten of these locations (ESTCP 10 was dry, consequently no well was installed). Locations of the borings and wells are presented in Figure 9. Borings were completed by PSA Environmental (Lee’s Summit, Missouri) using GeoProbe^{TM} direct push drilling techniques (Figure 8). Soil cores were logged by Dr. Tom Sale (Wyoming PG-1954). Monitoring wells were constructed of 1-inch PVC pipe and 10-slot well screens. A 20-40 quartz filter sand was installed adjacent to the well screens. The annular space above the filter sand was filled with a bentonite seal. Following installation, wells were developed by surging and pumping. Well logs with completion diagrams are presented in Appendix A.

Figure 8 - Installation of temporary wells at the demonstration site.

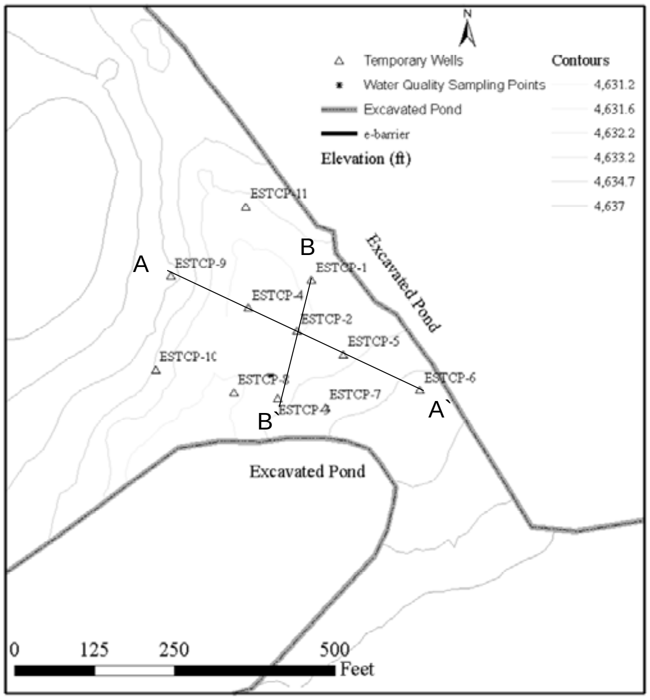


Figure 9 - Locations of borings, temporary monitoring wells, and geologic cross-sections.

4.2.2 GEOLOGY

Figure 10 presents geologic cross-sections through the demonstration location. The alignment of the cross-sections is presented in Figure 9. Sediment encountered consisted of a surficial silt layer ranging in depth from 1-2 feet. Underlying the surficial silt are well- and moderately-sorted coarse sands (Sand A and Sand B, respectively). The sands are unconsolidated and consist primarily of quartz and potassium feldspar. Within the sands, minor interbedded clay intervals were encountered in five of the eleven borings. The interbedded clays are unconsolidated and discontinuous. The Pierre Shale underlies the sediments at depths ranging from 12-15 feet bgs. Horizontal and vertical fractures are present in the shale. Fractures are attributed to near surface releases of overburden pressure. Figure 11 presents photographs of the primary geologic media encountered.

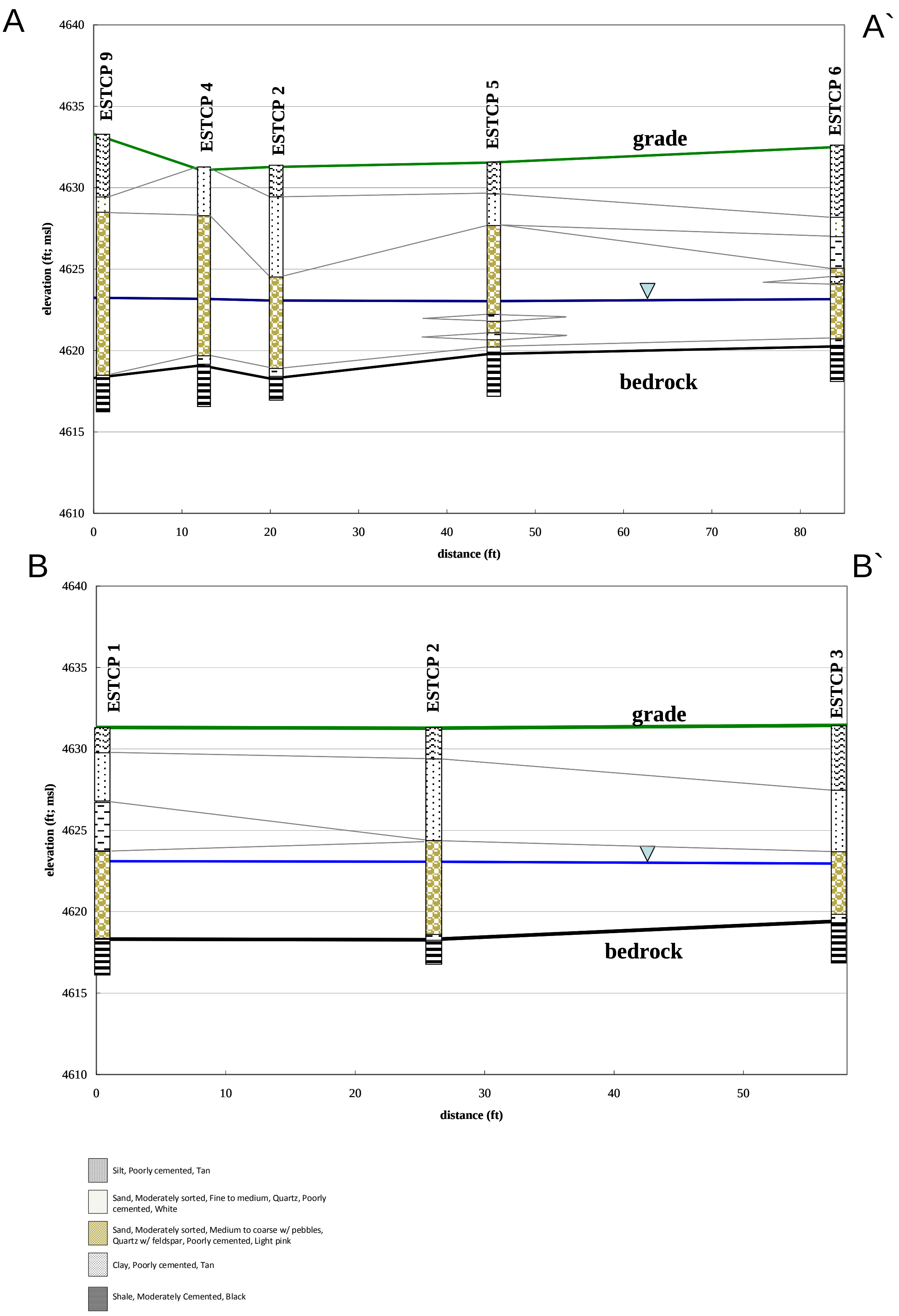


Figure 10 - Geologic cross-sections through the demonstration location.

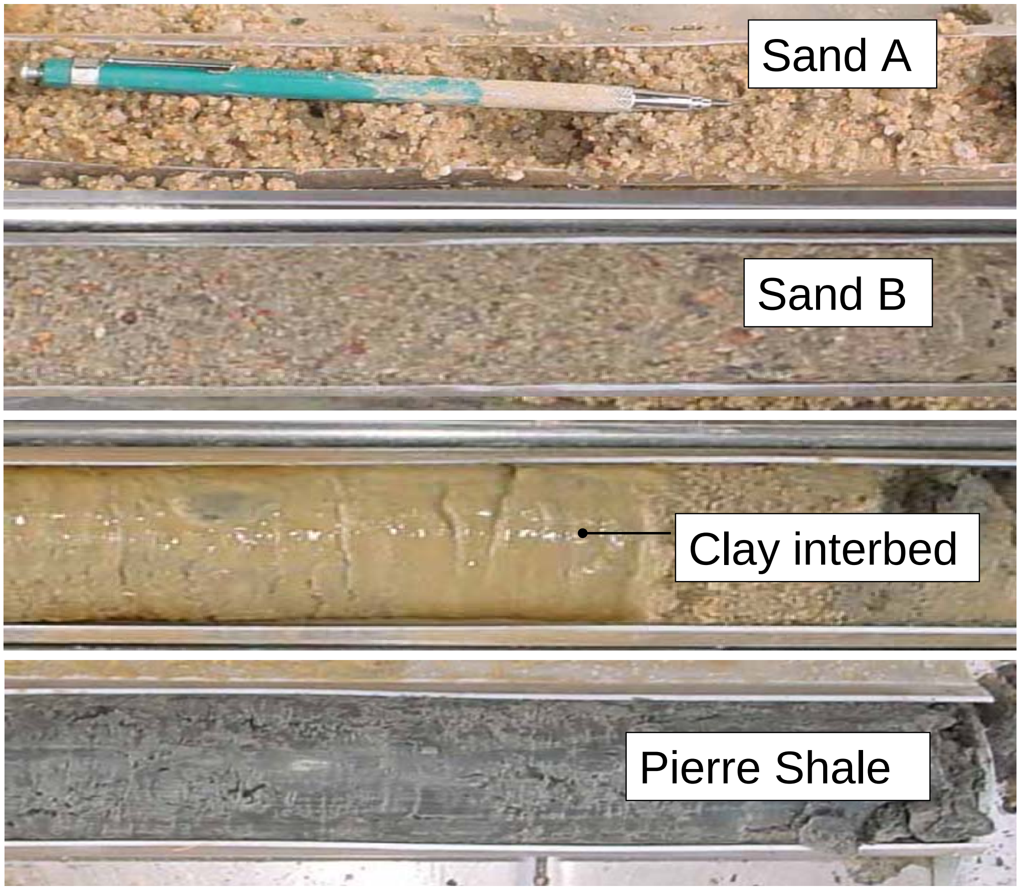


Figure 11 - Photographs of primary geologic media at PCD.

4.2.3 GROUNDWATER HYDROLOGY

Hydraulic Conductivity - The hydraulic conductivities of Sand A and Sand B were measured via laboratory permeameter studies. Sand A was collected from 10-15 feet and 15-20 feet bgs at ESTCP 9. Sand B was collected from 5-10 feet bgs at ESTCP 2 and 9. Soils from the borings were dried at 100°C for 24 hours and then homogenized. The materials were loaded into Plexiglas columns (5 cm ID × 30 cm L), in a continuous manner such that fine particles were not allowed to segregate. De-aired tap water was pumped through the columns using a peristaltic pump at five fixed flow rates. Hydraulic conductivity was measured via head loss across the columns. Resultant data and estimates of hydraulic conductivity are presented in Figure 12. The observed hydraulic conductivities of 5×10^{-2} cm/s and 1×10^{-2} cm/s for Sands A and B fall within the range of expected hydraulic conductivities for sands as reported by Domenico and Schwartz (1998). Based on typical values for clay and shale, it is anticipated that the hydraulic conductivities of the clay interbeds and Pierre Shale are many orders of magnitude lower then the sands' (e.g., 10^{-6} to 10^{-8} cm/sec).

Soil Type A

L	24 cm
r	2.5 cm
A	19.6 cm^2

Q mL/min	Dh cm	K cm/s
0.613	1.1	1.1E-02
0.633	0.4	3.2E-02
1.277	0.3	8.7E-02
1.284	0.7	3.7E-02
1.887	0.5	7.7E-02
	average K	4.9E-02

Soil Type B

L	22.5 cm
r	2.5 cm
A	19.6 cm^2

Q mL/min	Dh cm	K cm/s
0.547	1.9	5.5E-03
0.563	1	1.1E-02
1.126	1.6	1.3E-02
1.128	2.3	9.4E-03
1.67	1.9	1.7E-02
	average K	1.1E-02

Figure 12 - Column study data and estimates of hydraulic conductivity for Sands A and B (L = distance between piezometers, r = column radius, A = cross-sectional areas of the columns, Q = flow rate, Dh = observed head loss, K = hydraulic conductivity).

Water Levels – In July 2005, five data logging pressure transducers (Solinst Levelogger Model 3001) were installed in wells ESTCP 1-3, ESTCP 5 and ESTCP 11 to record water table elevation in the proposed footprint of the demonstration barrier. Barometric correction was conducted *a posteriori* using data collected from a Solinst Barologger Model 3001 installed under atmospheric conditions in ESTCP 11. Hydrographs are included in Figure 13.

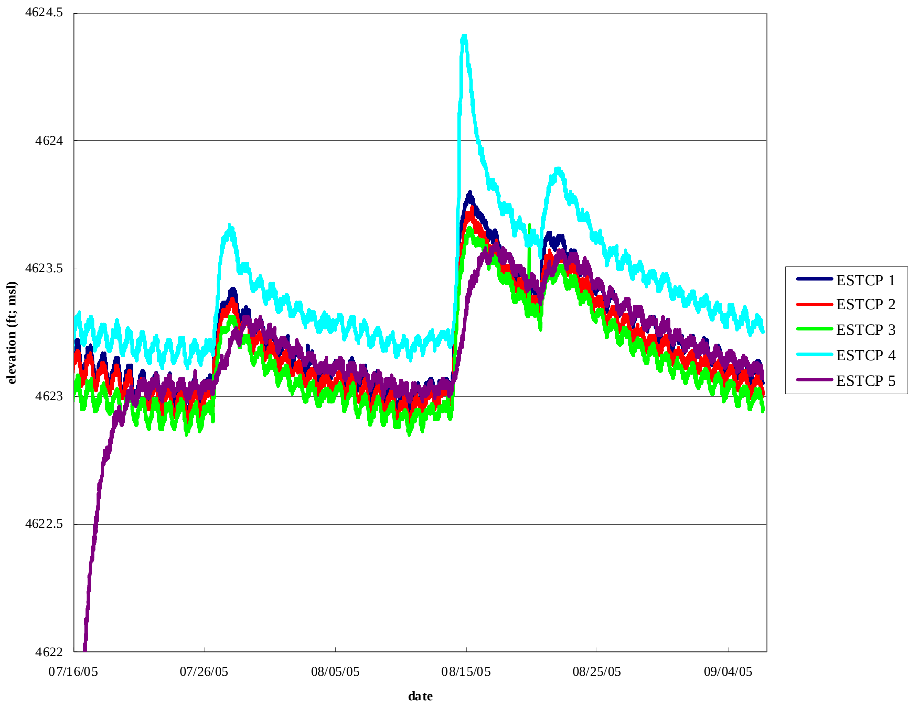


Figure 13 - Pre-demonstration hydrographs from temporary wells .

Observations from the pre-demonstration hydrographs indicate that:

- Periodic increases in water levels correspond with precipitation events
- Precipitation events cause brief periods when the gradient through the area increases
- The ordering of well elevations (high to low) and differences in water level elevations between wells generally remain the same, suggesting a constant flow direction gradient.

Figure 14 and Figure 15 present typical pre-demonstration potentiometric surface and saturated thickness maps for the alluvium. Additional hydrogeologic information collected during the demonstration, including estimates for groundwater flow rates, is presented in Section 5.4.3.

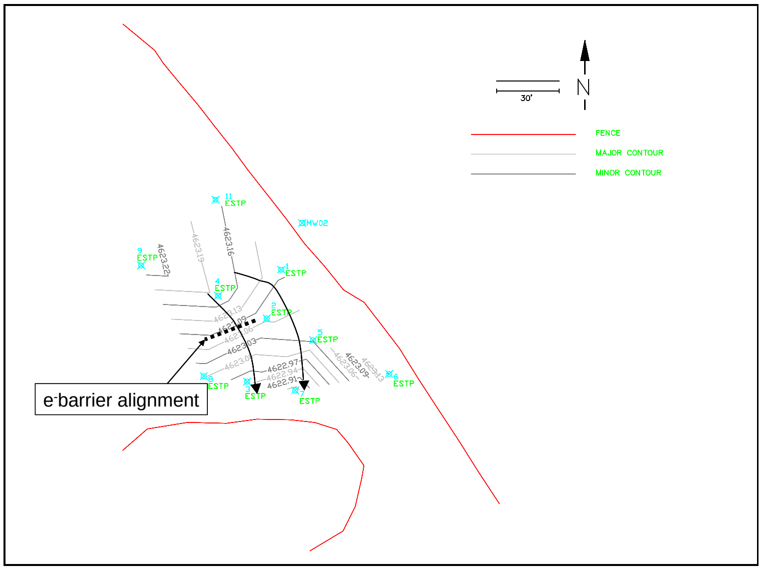


Figure 14 - Typical pre-demonstration potentiometric surface (7/15/05) with barrier alignment.

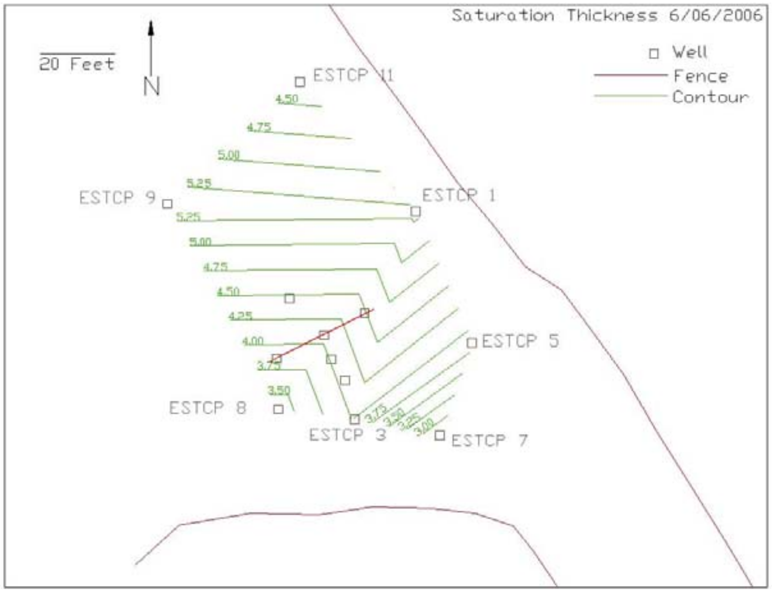


Figure 15 - Saturated thickness in the alluvium based on 6/6/06 water level data.

4.2.4 WATER QUALITY

The following presents pre-demonstration water quality data. Methods used to determine the noted parameters are presented in Section 4.6.

Energetic Compounds - Historic data from 2,4,6-TNTMW-02 indicates RDX concentrations as high as 400 µg/L. 2,4,6-TNT, 2,4-DNT, HMX, 1,3,5-trinitrobenzene and nitrate were also identified. As part of pre-demonstration baseline characterization, groundwater samples were collected from select temporary monitoring wells on July 15 and September 7, 2005. Figure 16 summarizes results from the September 7, 2005 data set. The highest RDX concentration measured was 12.0 µg/L (ESTCP 11). Concentrations of all energetic compounds are below historic levels. This is consistent with more recent results from 2,4,6-TNTMW-02 (e.g., 14.1 µg/L on 1/10/2006, EarthTech 2007). The highest 2,4,6-TNT concentration was 134 µg/L (ESTCP 9). It is also notable that the data indicates a high degree of spatial variability in concentrations of energetic compounds.

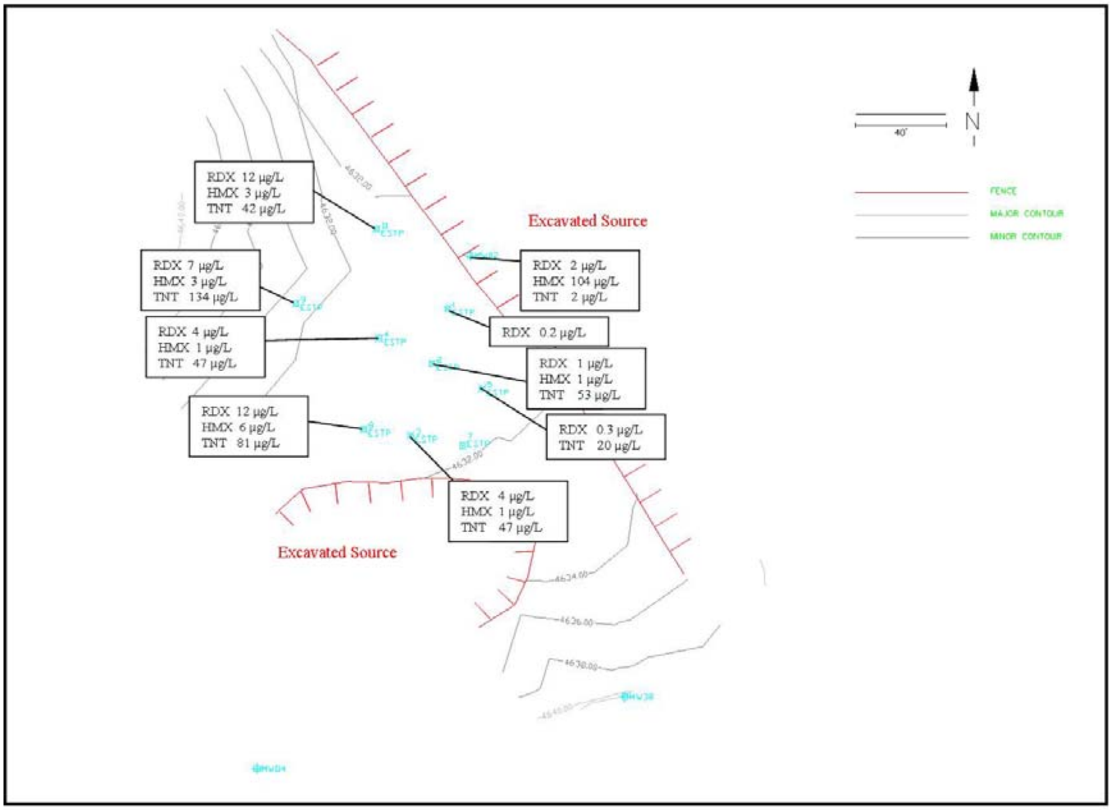


Figure 16 - Measured pre-demonstration energetic compounds in groundwater in temporary monitoring wells.

Field Parameters - Field parameters were measured in conjunction with collecting water samples for analysis of energetic compounds. Field parameters included pH, Eh (oxidation reduction potential), and specific conductivity. Results for field-measured parameters and inorganic parameters are presented in Table 3.

Table 3 - Field parameters from the demonstration site

Location	pH	Eh (SHE, mV)	SPECIFIC CONDUCTIVITY (µS/cm)
ESTCP 02	7.36	320	1,114
ESTCP 03	7.43	331	881
ESTCP 04	8.01	323	918
ESTCP 08	7.83	329	1,220
ESTCP 09	7.54	340	811
ESTCP 11	7.58	344	832
TNT MW-02	7.48	328	885

Inorganic Parameters - In addition, samples were collected and analyzed for inorganic parameters (i.e., major anions and cations). Results presented in Table 4 indicate sodium bicarbonate water with high sulfate. The water types in the three wells sampled are nearly identical, which suggests uniform inorganic water quality in the study area.

Table 4 - Baseline water quality: inorganic parameters

	ESTCP 3	ESTCP 11	TNT-MW 02
Anions (mg/L)			
Chloride	27	27	29
Fluoride	1.1	0.87	1.1
Bromide	0.22	0.25	0.32
Nitrate-N	4.1	1.7	1.5
Nitrite-N	0.21	<0.1	<0.1
Orthophosphate-P	<0.2	<0.2	<0.2
Sulfate	90	94	100
Carbonate (as $CaCO_3$)	<20	<20	<20
Bicarbonate (as $CaCO_3$)	260	240	260
Total Alkalinity (as $CaCO_3$)	260	240	260
Cations (mg/L)			
Aluminum	0.57	0.44	<0.2
Arsenic	<0.01	<0.01	<0.01
Cadmium	<0.005	<0.005	<0.005
Calcium	27	31	19
Chromium	<0.01	<0.01	<0.01
Copper	<0.01	<0.01	<0.01

Iron	0.52	0.37	<0.1
Lead	<0.003	<0.003	<0.003
Magnesium	5.5	7	4.6
Manganese	0.17	0.15	0.076
Mercury	<0.0002	<0.0002	<0.0002
Nickel	<0.02	<0.02	0.02
Potassium	3.4	3.2	2.5
Selenium	<0.005	0.0077	<0.005
Sodium	110	100	120
Thallium	<0.01	<0.01	<0.01
Vanadium	<0.01	<0.01	<0.01
Zinc	0.16	<0.02	<0.02
Ammonia-N	5.5	0.47	8.6

4.3 PREDESIGN LABORATORY TESTING

Laboratory testing was conducted in two phases. The first phase included 1-dimensional column studies and 2-dimensional tank studies. These were conducted prior to the field demonstration with the objective of resolving operational parameters. The second phase was conducted concurrently with the later stages of the field demonstration, with the objective of resolving mechanisms underlying the observed treatment patterns. Second phase laboratory study tasks included additional column reactor studies and adsorption studies. The focus of the second phase column reactor studies was to evaluate the effect of competition for electron transfer sites on the electrode surface.

4.3.1 COLUMN STUDIES

Pre-demonstration column studies were conducted using a Plexiglas column of 90-cm length and 10-cm I.D. (Figure 17). The column was loaded with PCD soils obtained from the former pond bottom located near 2,4,6-TNTMW-02. Four electrodes (two positive and two negative) were placed in the column, oriented perpendicular to flow and spanning the entire cross-section of the column. The electrodes consisted of expanded (70% open area) titanium-mixed metal oxide (Ti-mmo) of the same type to be used for the field portion of the demonstration. This material is commercially available (ELGARD™ 150 Anode Mesh). Electrode spacing was 2 cm within each positive/negative pair and 10 cm between pairs. Intervals around the electrodes were filled with silica glass beads to prevent the site soils from infiltrating and plugging the electrodes.

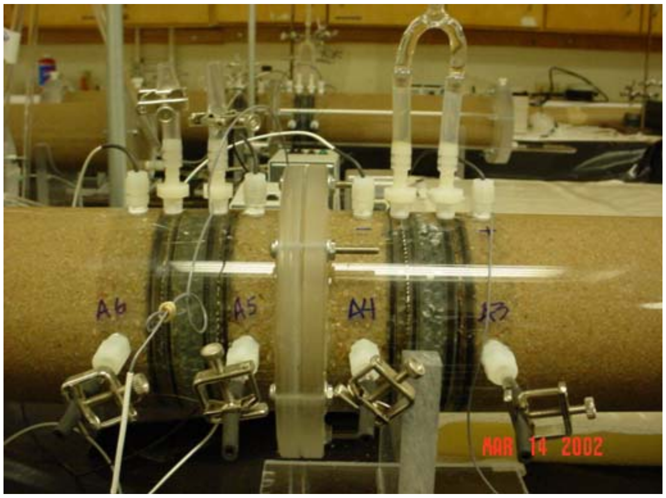


Figure 17 - Column study electrode set.

Experimental Conditions - The studies were conducted using a tiered approach to successively evaluate multiple variables. Table 5 outlines the experimental conditions evaluated. Site conditions at PCD indicate that the groundwater in the area also contains high nitrate which may interfere with the transformation efficacy of the e^-barrier. To evaluate potential nitrate interference, a similar column experiment was conducted with influent solutions spiked to 10 mg/L (as N) nitrate.

Table 5 - Column study experimental matrix

EXPERIMENT	CONTAMINANT	ELECTRODES	IONIC STRENGTH	OBJECTIVE
C1	RDX, HMX	Single set[1]	3.0 mM	Evaluate transformation of RDX using site soils
C2	RDX, HMX	Two sets	3.0 mM	Evaluate use of four electrode design
C3	RDX, HMX, NO_3	Two sets	4.5 mM	Evaluate influence of high nitrate on RDX transformation

1 The second electrode pair was installed, but no potential was applied for this portion of the study.

A constant potential of 5V was applied to both electrode sets using a DC power supply (GW Laboratory model GPS-3030D). Potentials of the anode and cathode were measured using DRIREF-5 (World Precision Instruments) reference electrodes placed 0.5 cm distal from the electrode pack along the center transect. This potential difference and electrode sequence was based on proof-of-concept experiments and likely operating voltages for the field demonstration.

Feedstock solution used in the pre-demonstration column studies consisted of calcium-carbonate water (Table 6) spiked to 100 mg/L each of RDX and HMX. For the final experiment (C3, per Table 5), the solution was spiked to 10 mg/L (as N) nitrate. The feedstock solution was pumped though the columns at a rate of 0.5 ml/min using a multi-channel variable speed peristaltic pump (Ismatec™) equipped with Viton™ tubing. The resultant seepage velocity was 1 ft/day. Elevated

RDX and HMX concentrations (as compared to field levels) were used to provide information regarding treatment efficacy and possible intermediate compounds.

Table 6 - Column study source water composition

CONSTITUENT	CONCENTRATION
pH	**7.8 std. units**
Alkalinity	**37.4 mg/L as $CaCO_3$**
Chloride	**2.1 mg/L**
Nitrate	**0.08 mg/L as N**
Silica	**7.1 mg/L**
Sulfate	**13.8 mg/L**
Aluminum	**62.9 µg/L**
Barium	**27 µg/L**
Calcium	**45.6 mg/L**
Copper	**1.7 µg/L**
Iron	**18.8 µg/L**
Magnesium	**1.8 mg/L**
Manganese	**2.5 µg/L**
Sodium	**2.8 mg/L**
Total Organic Carbon	**1.3 mg/L**

Sampling and Analysis - Glass sample ports were installed to monitor water quality and thermodynamic parameters. Eight sample ports were placed along the column: three upstream of the electrodes, three downstream, and two between the two electrode sets. Influent and effluent streams were also sampled. Samples from each port were analyzed for RDX, HMX and associated degradation products.

Analytical methods used are outlined in Section 4.6. Analytical standards for RDX, HMX, 2,4,6-TNT and 2,4-DNT were obtained from AccuStandard, Inc. (New Haven, CT). Analytical standards for RDX metabolites (MNX, DNX, TNX, and MEDINA) were obtained form SRI (Menlo Park, CA).

Column Study Results - Figure 18 presents normalized RDX and HMX concentration as a function of position in the column. Using a single electrode pair, approximately 85% of influent RDX and HMX were transformed. These results suggest that the e^-barrier can treat a mixed energetic plume that includes HMX. Using two electrode pairs, the second electrode set reduced concentrations by an additional 85 to 90%. Taken together, the two electrode pairs achieved an overall transformation approaching 99%. RDX and HMX were both transformed by each electrode pair. This result provides data supporting the use of two electrode pairs (i.e., four electrodes total) for the PCD field demonstration.

Results from the elevated nitrate study indicate minor influence of nitrate on the transformation of RDX or HMX (Figure 19). From these results, it seems likely that the threshold reduction voltage for nitrate is higher than that for RDX or HMX. Since nitrate is an end product of the electrolytic transformation of RDX and HMX it is not clear if nitrate itself is affected by sequential electrolytic oxidation-reduction.

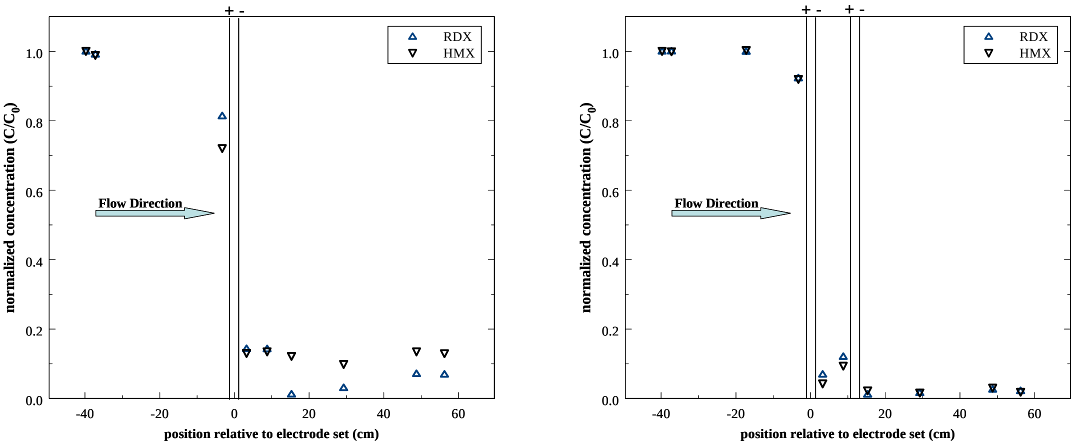


Figure 18 - Normalized RDX and HMX concentrations as a function of position in the test column: one electrode pair (left) and two electrode pairs (right).

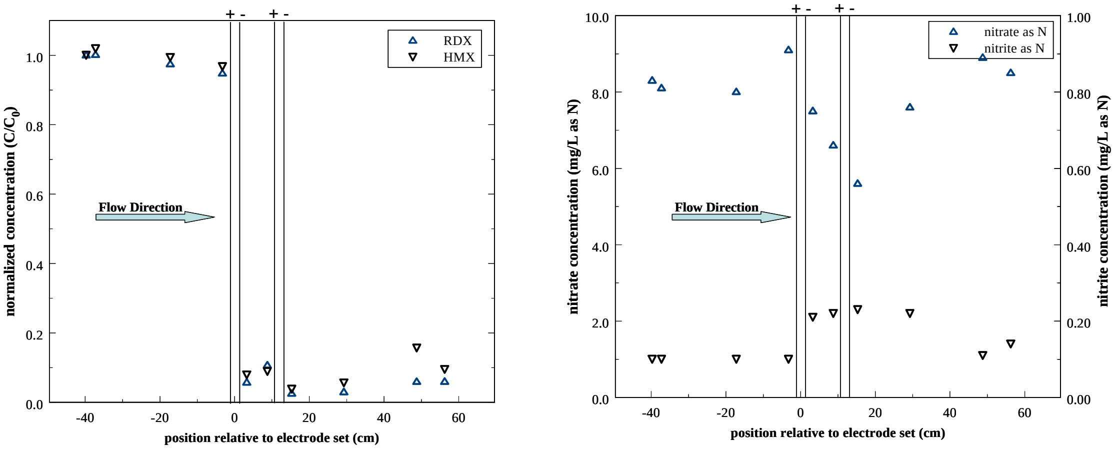


Figure 19 - Concentration as a function of position in the column studies using RDX and HMX with added nitrate (10 mg/L NO_3-N): influent-normalized RDX and HMX concentrations (left) and nitrate-N and nitrite-N measured during testing (right).

4.3.2 TWO DIMENSIONAL TANK DESIGN STUDIES

Column study results provided a basis for using two electrode pairs for the field application. Building on this, a two dimensional (2-D) tank study was conducted with the following objectives:

- To evaluate electrolytic transformation of energetic compounds in a 2-D system,
- To evaluate electrolytic treatment efficacy for a contaminant mixture of RDX (3 mg/L), 2,4,6-TNT (8 mg/L) and 2,4-DNT (3 mg/L) using the electrode configuration that will be used in the demonstration/validation,
- To evaluate polarity reversals to manage precipitate formation (e.g., calcium carbonate) on electrode surfaces, and
- To test automated data acquisition and communication systems.

The studies were conducted in a tiered approach (Table 7) similar to that used in the column treatability studies.

Table 7 – Two-dimensional tank study experimental matrix

EXPERIMENT	CONTAMINANT	ELECTRODES	IONIC STRENGTH	POLARITY REVERSAL
T-1	RDX	Two sets	3.0 mM	None
T-2	RDX, 2,4,6-TNT, 2,4-DNT, NO_3^-	Two sets	4.5 mM	None
T-3	RDX, 2,4,6-TNT, 2,4-DNT, NO_3^-	Two sets	4.5 mM	Every 4 hours

Experimental Conditions - The study was conducted in a glass-walled sand tank measuring 48 inches long, 36 inches tall, and 1 inch wide (inside thickness between glass panels). The tank was loaded with an ideal porous media (quartz feldspar sand) and an electrode pack that is an analog to the PCD demonstration e^-barrier, consisting of four electrodes separated by biplanar geonet (Figure 20).

The feedstock solution was prepared using the same source water as was used for the column study. Contaminant concentrations in the 2-D tank study included 3 mg/L RDX, 8 mg/L 2,4,6-TNT and 3 mg/L 2,4-DNT. The solution was pumped through the tank using a peristaltic pump (Ismatec™) equipped with Viton™ tubing. The groundwater seepage velocity was 2 ft/day (approximately twice that of the column experiments), which was selected based on preliminary estimates of field conditions at PCD. Prior to starting the 2-D experiments, a bromide tracer test verified this seepage velocity.

The electrode sets were operated at 5V DC applied potential difference (Hewlett Packard 6267B DC Power Supply) to simulate possible field operating conditions. Electrode polarity reversal testing (experiment T-3, per Table 7) was conducted using a programmable logic controller (Allen Bradley Pico 1760 L12DWD) attached to a 60-amp DC contactor array (Albright International DC66-1P).

Sampling and Analysis - Performance evaluation consisted of monitoring aqueous concentrations of energetic compounds. The monitoring array included 27 monitoring points comprising nine bundles with sampling points at three depths. The sampling points consisted of $^1/_8$-inch diameter Teflon™ tubing fitted with Nitex™ mesh to prevent sand infiltration. Water samples were collected using a glass syringe connected directly to the sample point tubing. Given the high contaminant concentrations used in the experiments, solid phase extraction and preconcentration was not necessary in the 2-D tank experiment.

Figure 20 - 2-D tank used in design testing studies.

Tank Study Results - Overall results from the 2-D tank studies are consistent with those observed in the column experiments. Overall conversions achieved for RDX, 2,4,6-TNT, and 2,4-DNT were 90, 96, and 93%, respectively. Two-dimensional concentration profiles are presented in Figure 21. Concentration distributions in two dimensions suggested that the barrier's height may have an influence on RDX concentrations upgradient of the e^-barrier. The hypothesis is that these low concentrations are the result of back mixing due to the formation of convection cells, which are formed by gas generation at the electrode surfaces. 2,4,6-TNT and 2,4-DNT do not appear to exhibit this effect. High nitrate levels did not appear to affect treatment performance either.

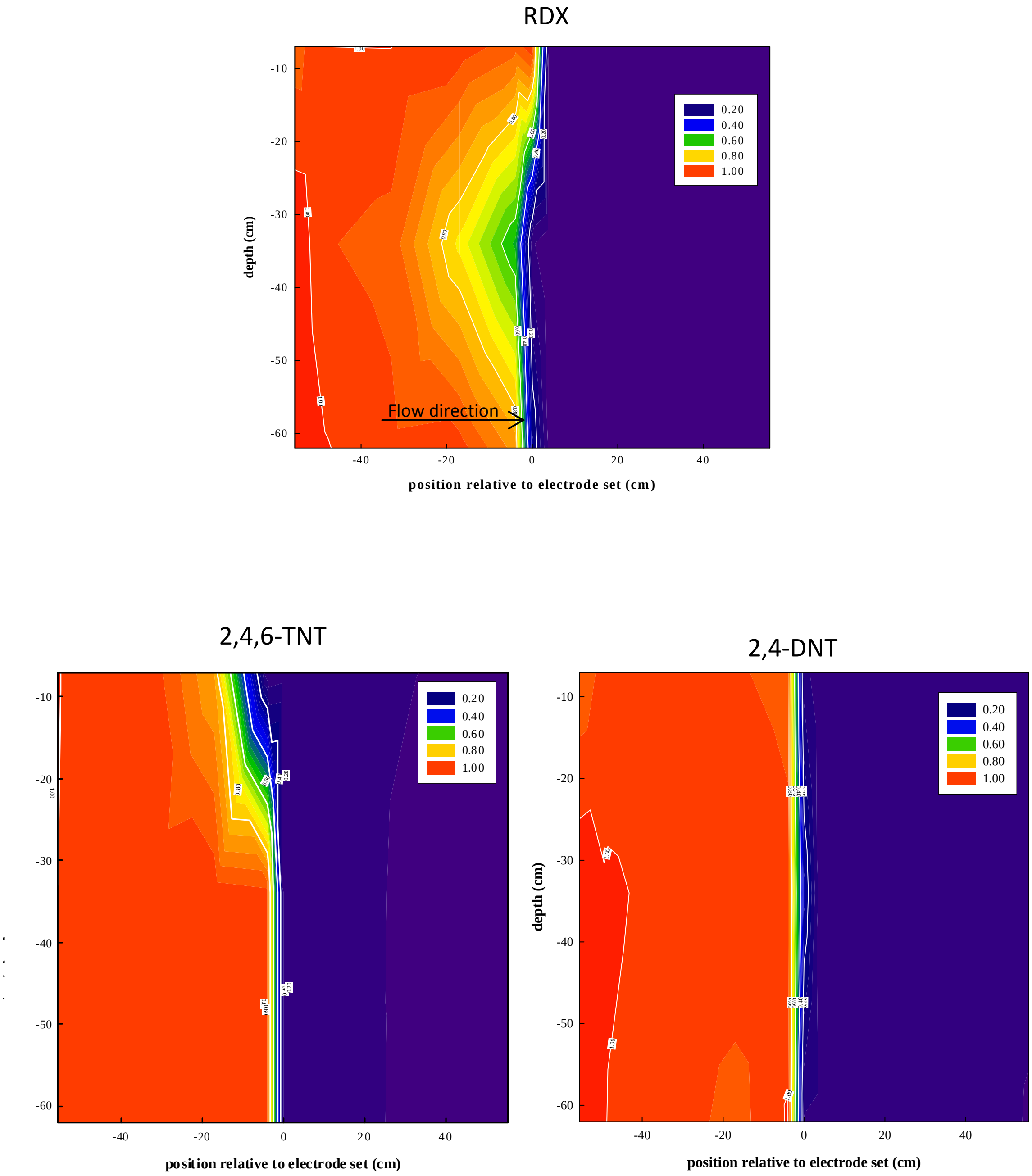


Figure 21 - Influent-normalized concentrations as a function of position in the 2-D tank study for RDX (upper), 2,4,6-TNT (lower left), and 2,4-DNT (lower right). Position 0 is the center of the electrode pack. Degradation of RDX is noted upgradient of the barrier.

4.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The following presents as-built details for the e^-barrier. Key components include e^-barrier panels, electrical systems, and performance monitoring components. Each is discussed in the following subsections.

4.4.1 E^-BARRIER PANELS – FABRICATION AND INSTALLATION

The e^-barrier panels were fabricated at CSU and transported to PCD for final assembly and installation. This section presents information on their fabrication and installed configuration.

Fabrication – The primary component of the e^-barrier is a composite panel containing four titanium mesh electrodes coated with mixed metal oxides (Ti-mmo) separated by HDPE geonet and bounded on the outside by a geotextile. The exterior geotextile limits sediment entry into the composite panel. A photograph of the components in the composite panel is presented in Figure 22. Information regarding the components is presented in Table 8.

The composite panels were mounted on vinyl sheet pile sections. Front and back views of three sheet pile sections with electrodes are shown in Figure 23. Methods employed in attaching the composite electrode panels to the vinyl sheet pile are shown in Figure 24.

A titanium distribution bar was welded to the side of each expanded mesh electrode in the composite panels. This provided the electrical connection to the individual electrodes. The distribution bar was extended 10 feet above the top of the electrodes. This extension was wrapped in heat shrink tubing that insulated the distribution bars, preventing short circuiting between the electrodes. The tops of the distribution bars provided the points for connecting the electrodes to the power supply.

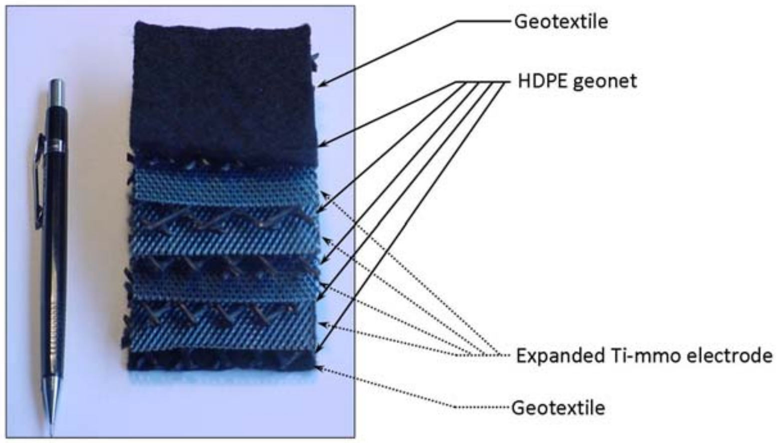


Figure 22 - Composite panel components.

Table 8 - Summary of primary material components for the e^{-}barrier

MATERIAL	SUPPLIER	PRODUCT DATA	QUANTITY
Vinyl Sheet Pile	Crane Materials International	CMI CL9000	24 panels (8' tall by 2' wide)
Ti-MMO Electrode	Corrpro Companies, Inc.	Expanded mesh Ti coated with mixed metal oxides	240 ft^2
Geonet	TENAX	DC 4100/TG600	300 ft^2
Geotextile	TENAX	DC 4100/TG600	120 ft^2

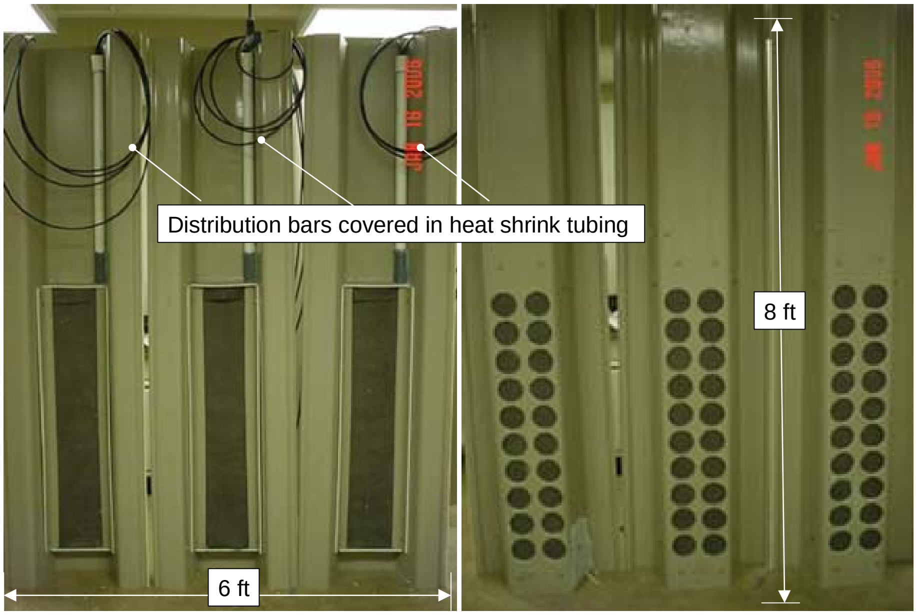


Figure 23 - Assembled e-barrier panels upstream side (front) and downstream (back).

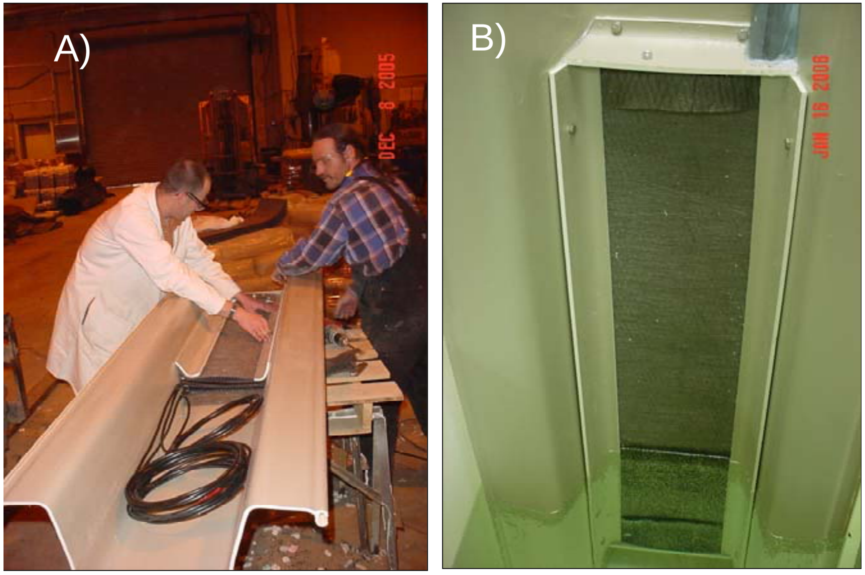


Figure 24 - A) Attaching composite electrode panels to the vinyl sheet pile and B) testing a fabricated section of the e-barrier in a water bath for electrical performance.

A total of 15 active electrode panels were constructed. Three blank sheet pile sections were placed at each end of the barrier. The blank portions were used to tie in the bentonite wing walls in the field. Figure 25 illustrates the e^-barrier in cross-section and the envisioned field installation. The role of the bentonite wing wall was to limit flow around the e^-barrier. Flow around the end of the barrier had been a limiting aspect of an earlier e^-barrier demonstration conducted at F.E. Warren AFB, WY (CU-0112).

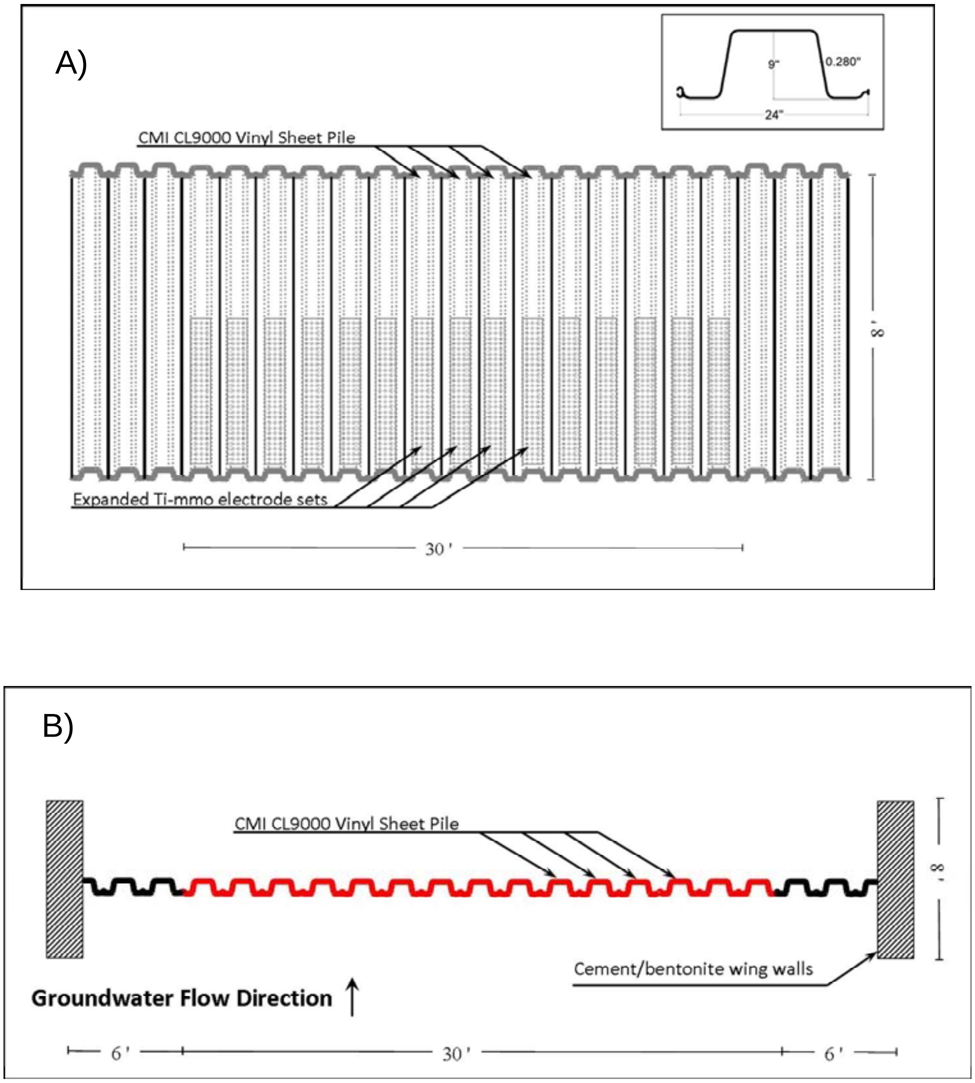


Figure 25 - A) Cross-section of e-barrier as fabricated and B) envisioned field installation in plan view.

Installation. – The e^-barrier was installed at PCD from January 30th through February 2nd, 2006. The construction contractor for the project was Metrix Inc., of Golden, Colorado, under the direction of Dale Evans. CSU students and faculty provided assistance with layout and handling of e^-barrier sections. Key activities included:

- Jan 30th – Layout of the components, setting flexible seals in the sheet pile interlocks, excavation, and setting a trench box to shore the excavation (Figure 26).

Figure 26 - A) Layout of barriers, B) sealing joints, and C) setting the trench box

- Jan 31st – Setting the panel through the alluvium along the selected alignment (Figure 27). The panels were set into the Pierre Shale and a cement/bentonite grout was placed at the base of the barrier to limit underflow.

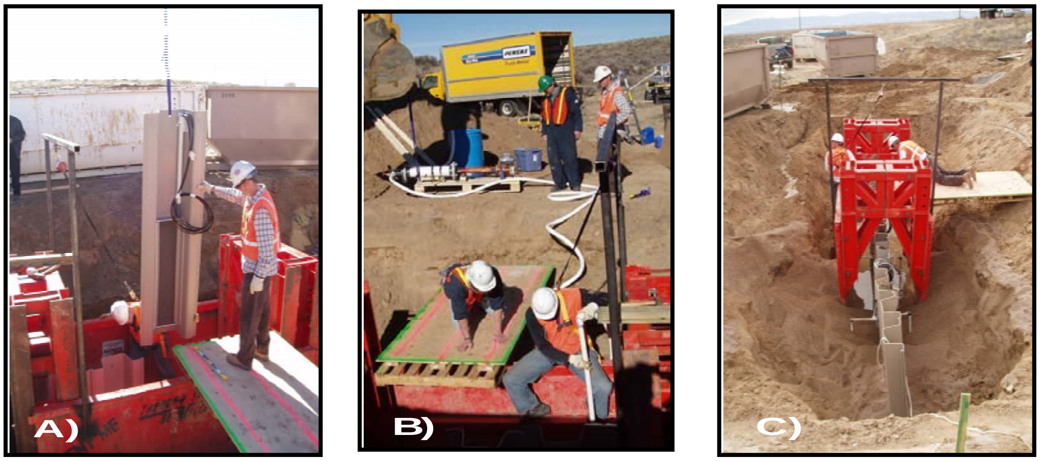


Figure 27 - A) Setting the panels inside the trench box to the top of the Pierre Shale, B) emplacing a cement-bentonite seal at the base of the barrier, and C) sheet pile prior to backfill with native sands.

- February 1st – Placing electrical system conduit and groundwater sampling systems to grade and backfilling (Figure 28). Backfill within the trench box consisted of a well-sorted coarse sand from a local sand and gravel operation. The backfill was similar to the formation sand but was largely free of fine sand and silt.

Figure 28. A) Setting conduit to grade for electrical and sampling systems and B) backfill.

- February 2nd – Excavated soils were taken to a local landfill per the requirements of the State of Colorado and PCD. All records associated with the disposal of the excavated materials were filed with PCD personnel.

The as-built alignment of the e$^-$barrier based on a post-installation survey is presented in Figure 29. A profile depicting the elevation of the individual sheet pile section is presented in Figure 30.

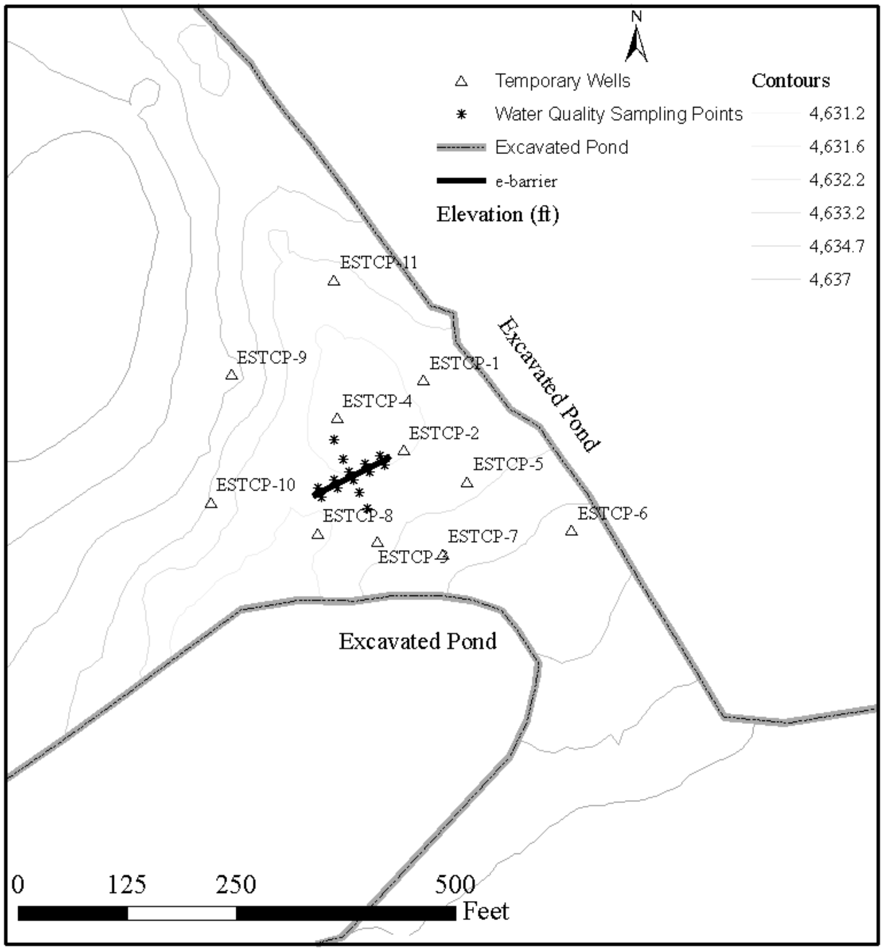


Figure 29 - As-built alignment of the e$^-$barrier.

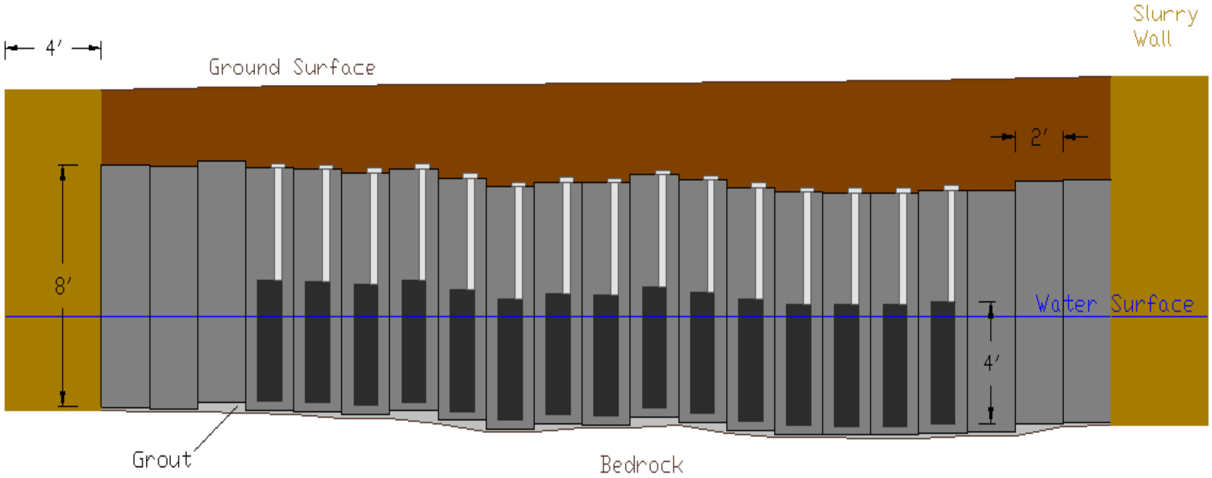


Figure 30 - As-built elevation profile of e⁻barrier panels.

4.4.2 ELECTRICAL SYSTEM

Treatment in the e⁻barrier is driven by imposing an electrical potential across the electrodes while contaminants move through via natural advective groundwater flow. The PCD e⁻barrier employed a four electrode sequence in which the primary operational mode (moving downgradient) was cathode (+), anode (-), cathode (+), and anode (-). On a daily basis, the polarity of each electrode was reversed for one hour to prevent formation of scale (inorganic precipitates) on the electrodes (Figure 31).

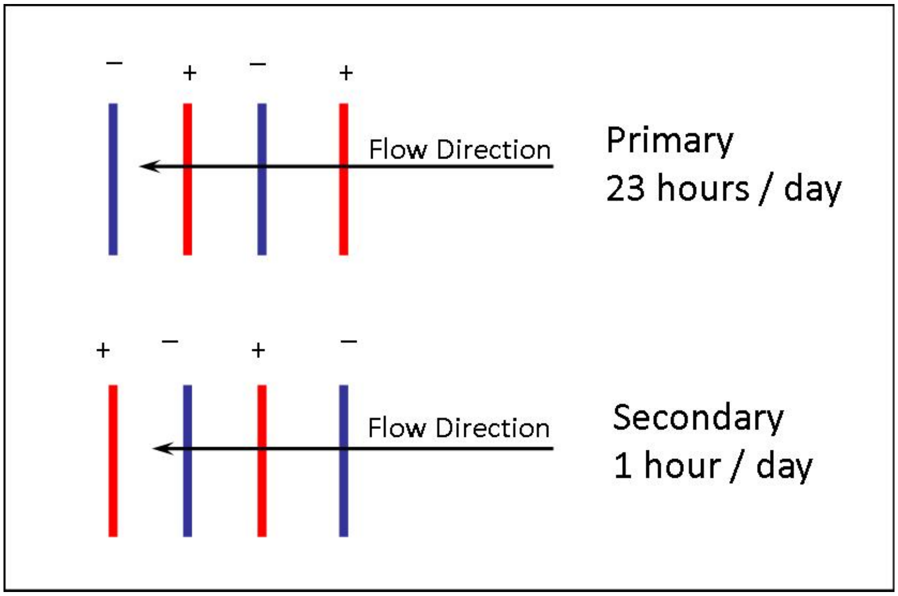


Figure 31 - Electrode polarities.

Key elements of the electrical systems included:

- A solar power supply capable of continuously delivering roughly 500 watts.
- Transformers to drop the applied voltage to the desired range of 3 to 6 V.
- A controller to manage daily 1-hour reversal in electrode polarity (Allen Bradley Automation, Milwaukee, WI).
- Reference electrodes used to measure the effect of the e^-barrier on redox conditions (Corrpro, Medina OH)
- Automated switches for polarity reversal (Albright International, Surrey, England).
- A data acquisition system to track imposed conditions (Campbell Scientific, Logan UT).
- A cell phone communications system allowing for remote tracking of system performance (Verizon).

The following describes these components to the best of our ability. Unfortunately, Dave Gilbert, our colleague who passed away in May of 2008 designed and operated these systems. With Dave's passing some details regarding design of these systems and some collected data were lost.

Solar Power – Due to the remote location of the e^-barrier, line power was prohibitively expensive. Furthermore, use of a solar power supply holds the promise of a "green" remedial technology. The solar power supply (Figure 32) included sixteen 125 W solar panels (BP Solar), sixteen 200 Amp-hour storage batteries (MK Battery, Anaheim, CA), and a control system (Morningstar Corp., Washington Crossing, PA). The output from the solar power supply was 48 V DC.

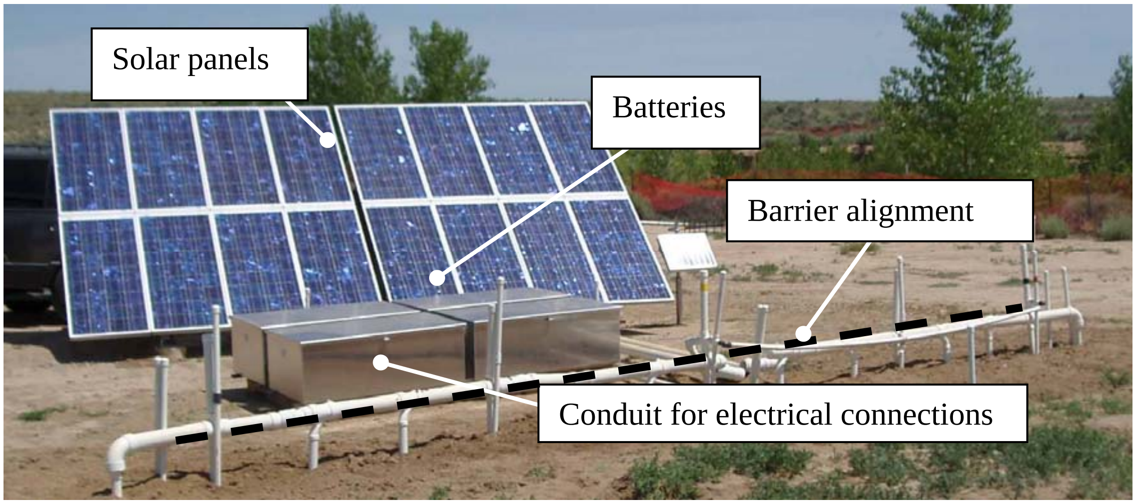


Figure 32 - Solar power supply.

Electrical Controls and Data Logging Systems - Figure 33 presents the control and data logging systems. In more detail:

- The three boxes on the far right-hand side control the solar power supply. These systems display status (e.g., barrier voltage and solar input), shut off solar charging at high voltage (above 13.3V), shut off all power discharge at low voltage (below 11.8V), and provide power supply to the breakers and fuses.

- The middle box contains voltage controllers. These were used to set the voltage applied to the electrodes. Two systems were employed during the demonstration. The first used the three identical boxes in the upper half of the box to separately control the applied voltage on the left (panels 1-5), center (panels 5-10) and right (panels 11-15) sections of the barrier. Unfortunately, two of the transformers failed during the first year of operations. This led to the use of the single controller at the bottom of the box. In June 2008 this system also failed (after the planned demonstration end date of April 2008). Future e^-barrier applications that rely on solar power will require better voltage transformers. It is, however, noteworthy that voltage controllers were not a problem on earlier e^-barrier applications (Canadian Forces Base Borden and F.E. Warren AFB, WY) that employed standard equipment to convert 120V AC power to low voltage DC power.

- Boxes in the lower left-hand corner contain switches and controllers for daily polarity reversals. These systems were reliable with the exception of the summer of 2008, when fatigue of an aluminum battery connector caused low power to the magnetic relays in the switches. Care should be used in employing aluminum wiring at connections due to its limited reliability.

- The box in the upper left-hand corner contains a multi-channel data recorder with wireless modem (Campbell Scientific, Logan UT). The system records applied voltage, resultant current to each active barrier module, and electrode potential relative to reference electrodes. The reference electrodes (Corrpro, Medina OH) were buried at the center panel adjacent to the up-and down-gradient faces of the e^-barrier. Data was collected in 15-minute intervals and downloaded to CSU via a wireless connection on a daily basis. This system operated reliably until December 2007. Applied voltage, reference electrode potential, and current are presented in Figure 35 and Figure 36. Although data was collected after this point, we have been unable to transform the data collected to the parameters of interest. The problems may have to do with the low power issue noted in the prior bullet.

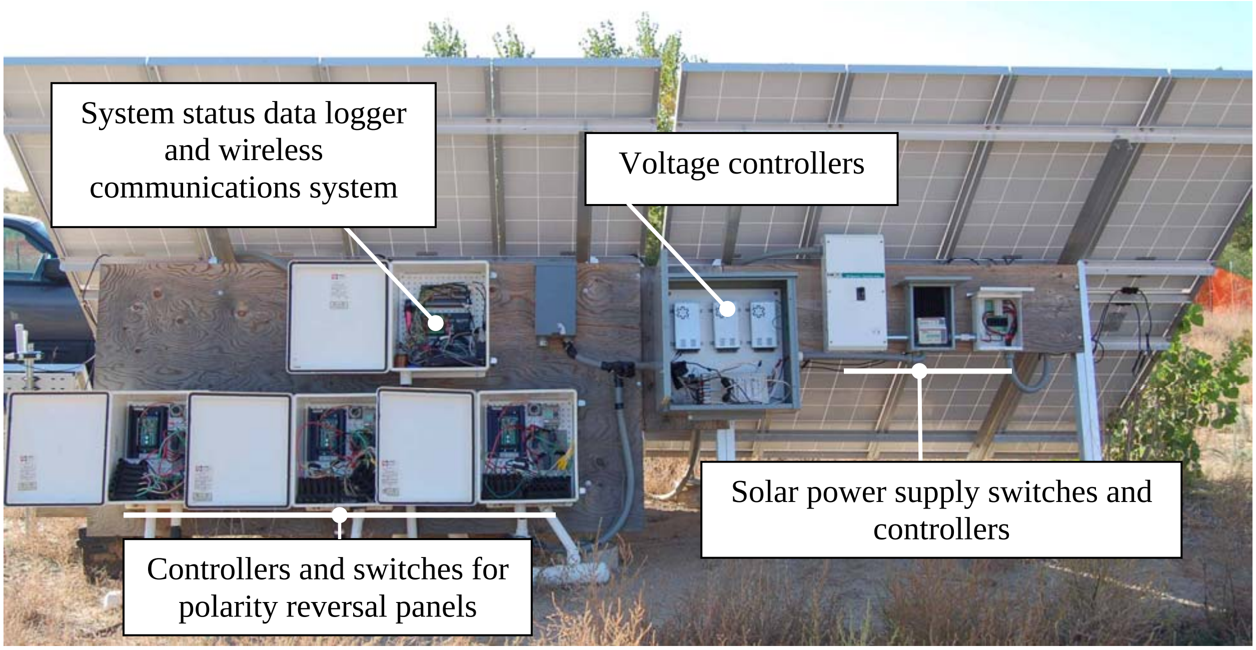


Figure 33 - Electrical controllers and data logging systems.

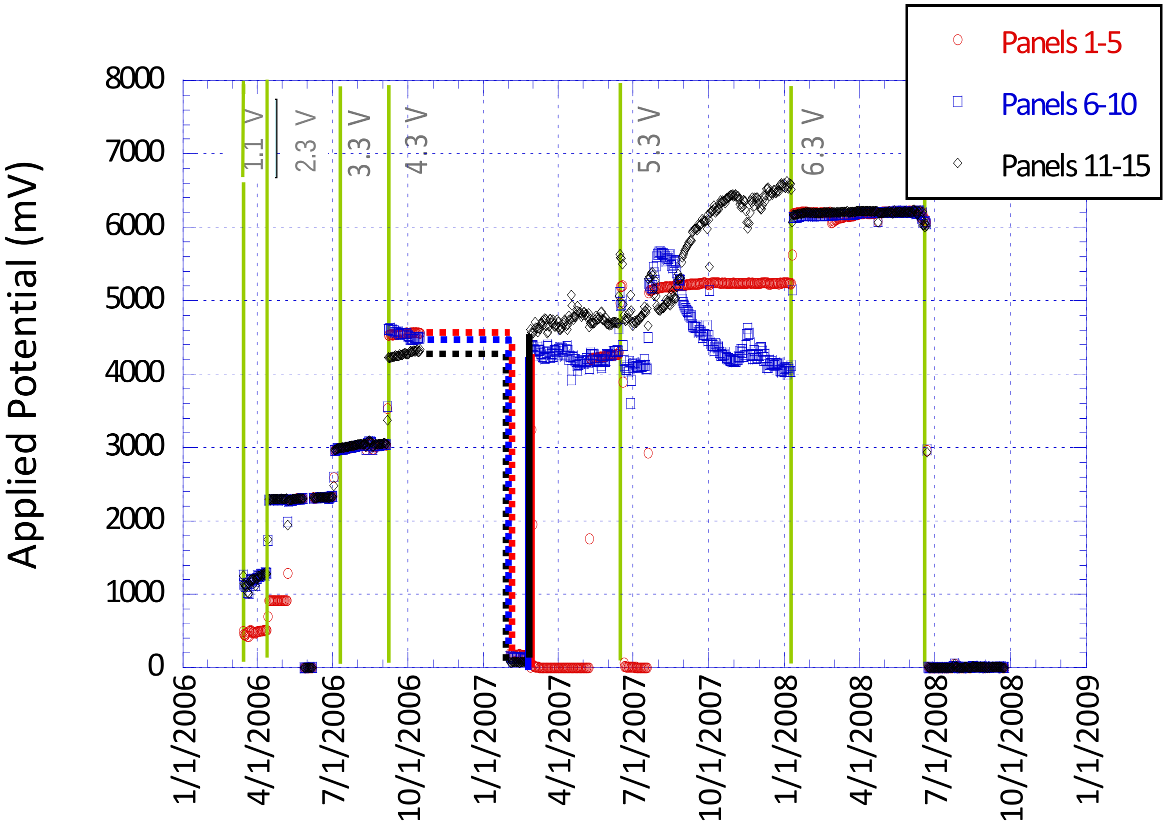


Figure 34 – Applied potential vs. time (dashed lines are estimated value from periods when the data logger was not working).

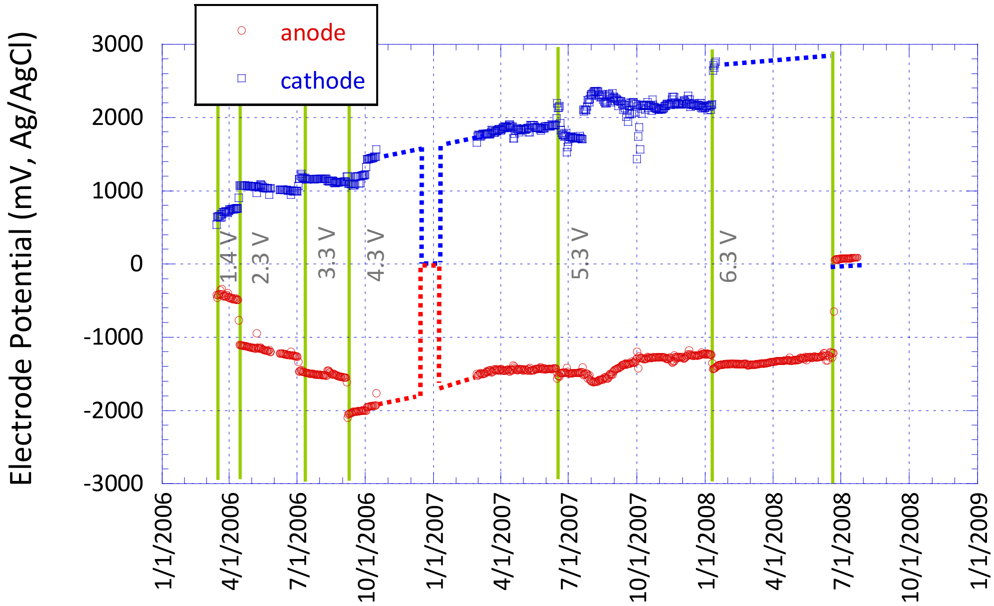


Figure 35. Reference electrode potential (mV).

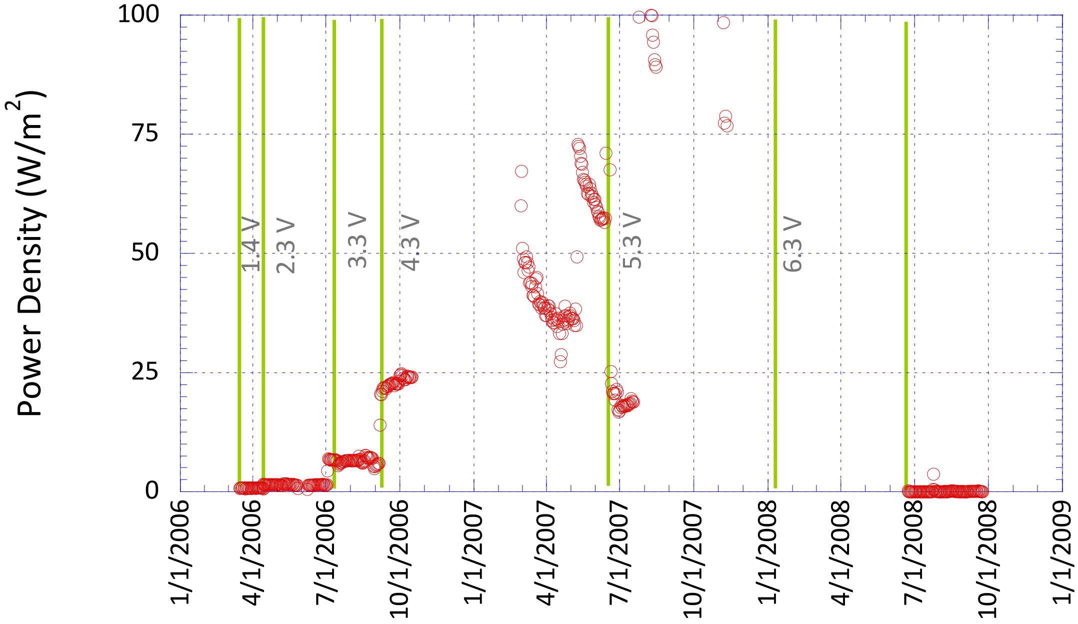


Figure 36. Power output in W/m^2.

4.4.3 GROUNDWATER MONITORING

Water Quality - Water quality monitoring was achieved using 24 monitoring locations including:

- Five point-water sampling systems on the upgradient face
- Five point-water sampling systems on the downgradient face
- Five 1-inch wells fixed to the e^-barrier at 0.5 m upgradient
- Five 1-inch wells fixed to the e^-barrier at 0.5 m downgradient
- Two 1-inch wells 2 and 4 m upgradient on the central transect
- Two 1-inch wells 2 and 4 m downgradient on the central transect

Photos of the on-face sampling points and the 0.5 m wells (attached to the barrier) are presented in Figure 37. The sampling points on the panel face were constructed of 6.35 mm ID Teflon tubing and a Nytex™ cloth screen. Samples were pulled from the 0.5 m wells via a 6.35 mm ID Teflon tube. The sample points attached to the e^-barrier panels (i.e., on-face and at 0.5 m, as shown in Figure 37) are located in backfill material (section 4.4). The wells at 2 and 4 m are located in the natural alluvial sands. Figure 38 illustrates the position of sampling points in cross-section and plan view.

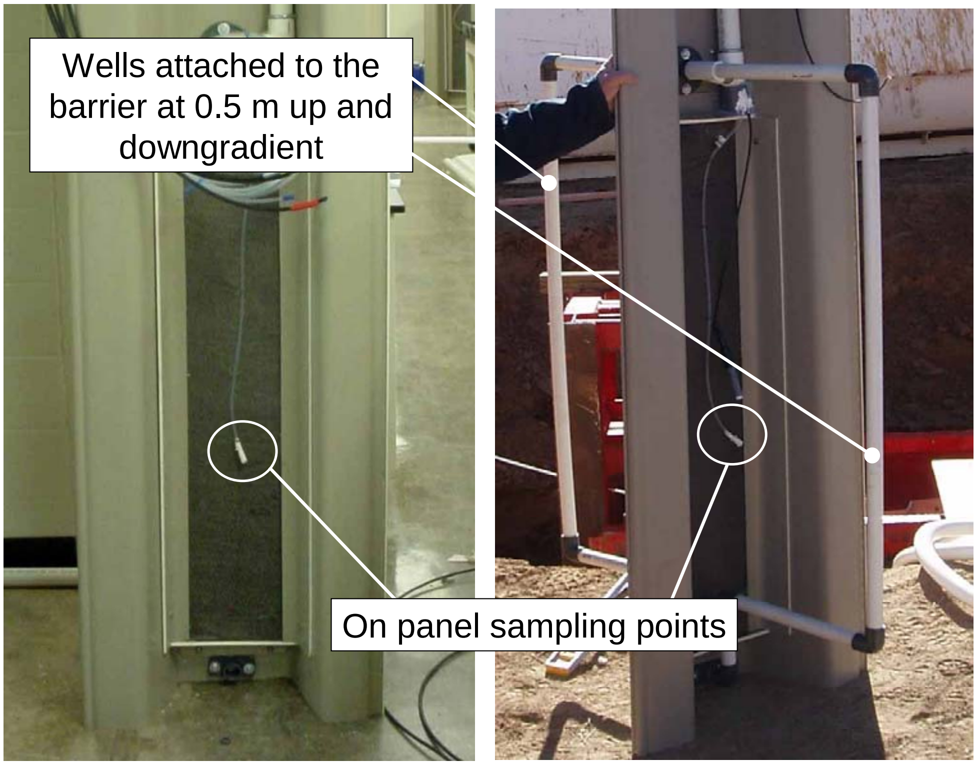


Figure 37 - Water quality sampling point attached to the e^-barrier.

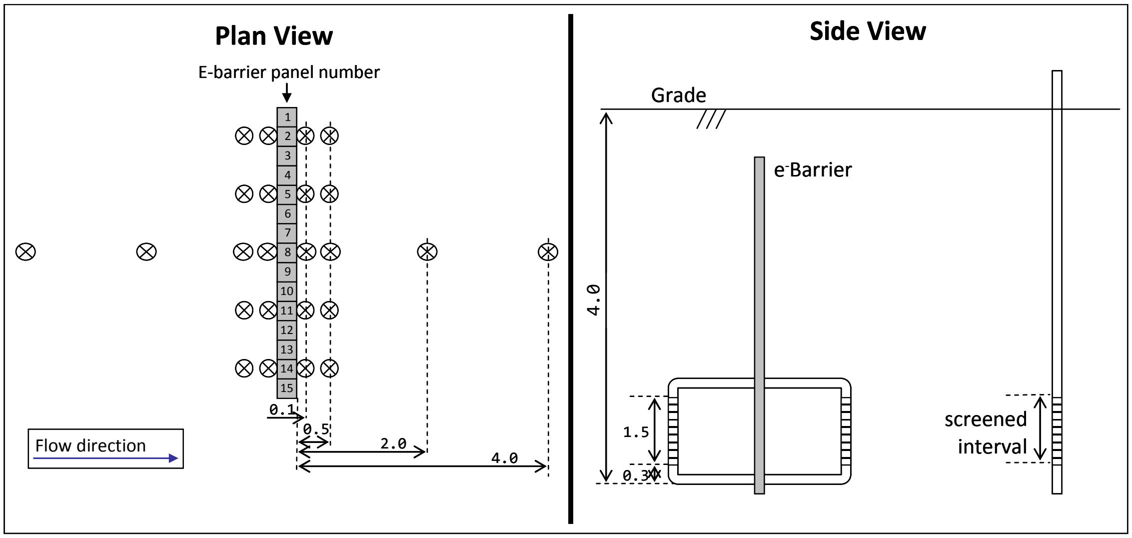


Figure 38 - Network of water quality sampling points. Distances are in meters.

Water Levels - Water level data were collected throughout the e-barrier demonstration at 15 minute intervals at ESTCP-3, ESTCP-6, ESTCP-8, ESTCP-9 and ESTCP-11 using data logging pressure transducers (Solinst, Inc. Level Loggers). In addition, manual water level measurements were collected in conjunction with each site sampling event using an electric water level sounder (Solinst, Inc.). Recorded water level data is presented in Figure 39. Key features include:

- Falling water levels during the growing season, attributed to transpiration by local cottonwood trees, and
- Sudden water level increases on the order of 0.5 to 1.5 feet attributed to high intensity summer thunderstorms.

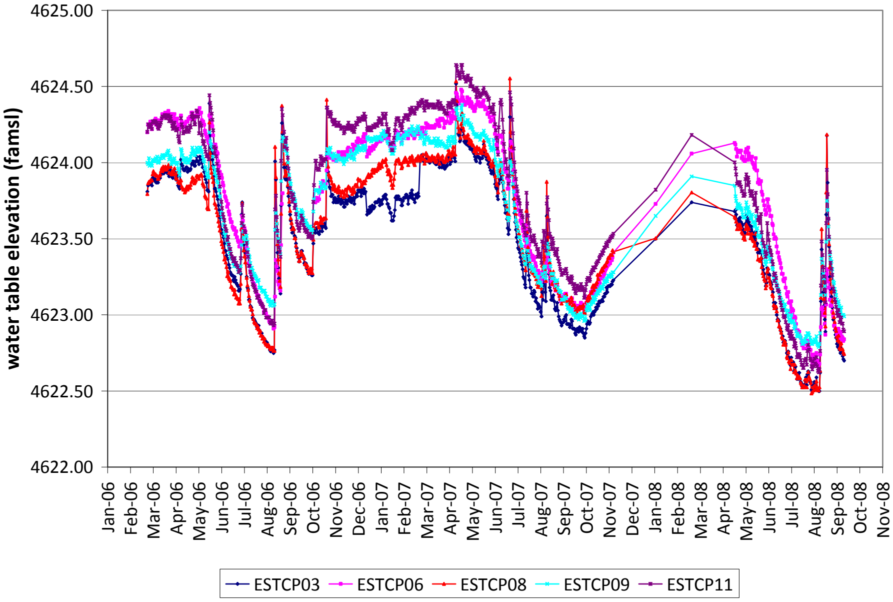


Figure 39 - Water level data collected during the e-barrier demonstration (Data from November 2007 to April 2008 is missing – data shown for this period comes from manual measurements of water levels).

Using the data from ESTCP 6, ESTCP 8, and ESTCP 11 (the wells that are farthest apart) the daily direction of groundwater flow and the magnitude of the hydraulic gradient were resolved for the available data sets. Figure 40 presents a vector plot illustrating magnitude and direction of groundwater flow. Figure 41 and Figure 42 plot the direction of flow and hydraulic gradient, respectively, as a function of time. During the recorded period, the mean direction of flow is to the southeast (36 degrees south of due east) with a standard deviation of 31 degrees. Using the same data, the mean gradient is 0.0041 with a standard deviation of 0.0015. Overall, the flow is largely perpendicular to the e^{-}barrier. Variance from the southeast flow direction is attributed to infiltration from high intensity summer thunderstorms. Using the high estimate of hydraulic conductivity from Section 5.1.3 of 0.015 cm/sec, a formation porosity of 0.25, and the observed gradients, the seepage velocity in the vicinity of the e^{-}barrier is 250±93 0.25.

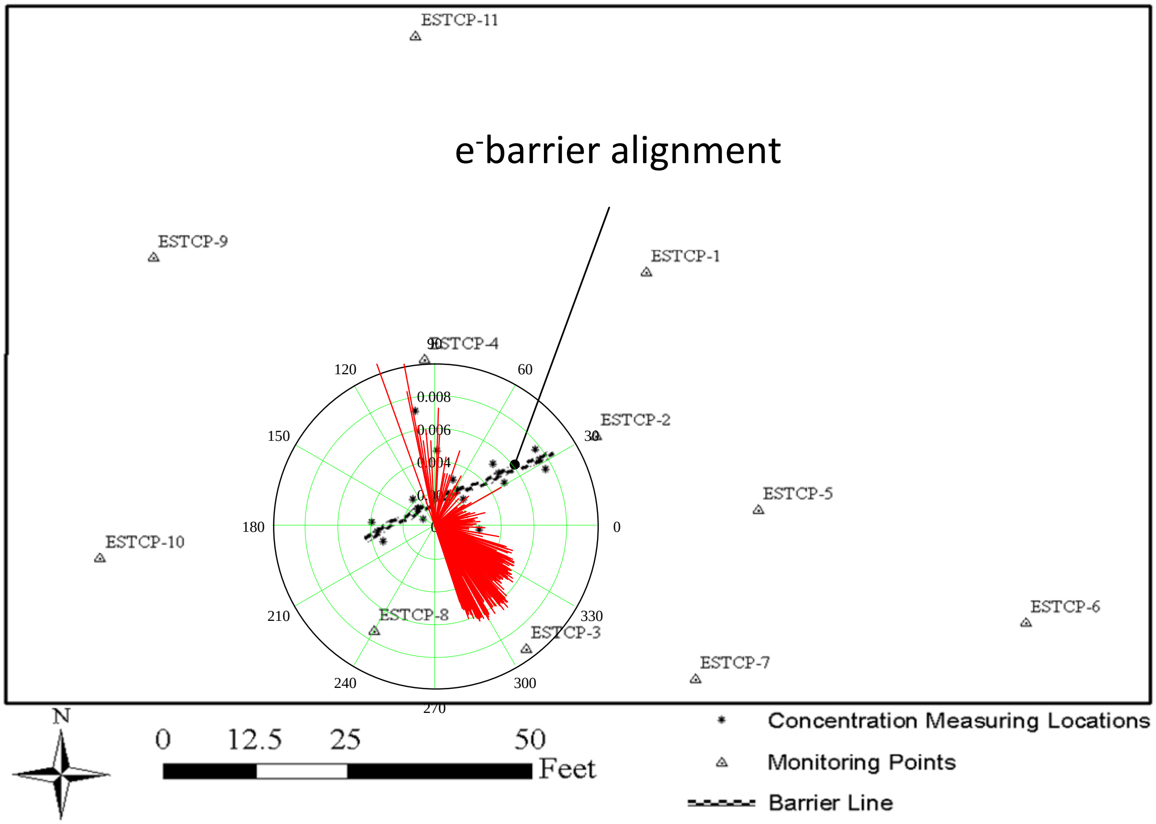


Figure 40 - Vector plot illustrating the direction of groundwater flow and the magnitude of the gradient for March 2006 through October 2008.

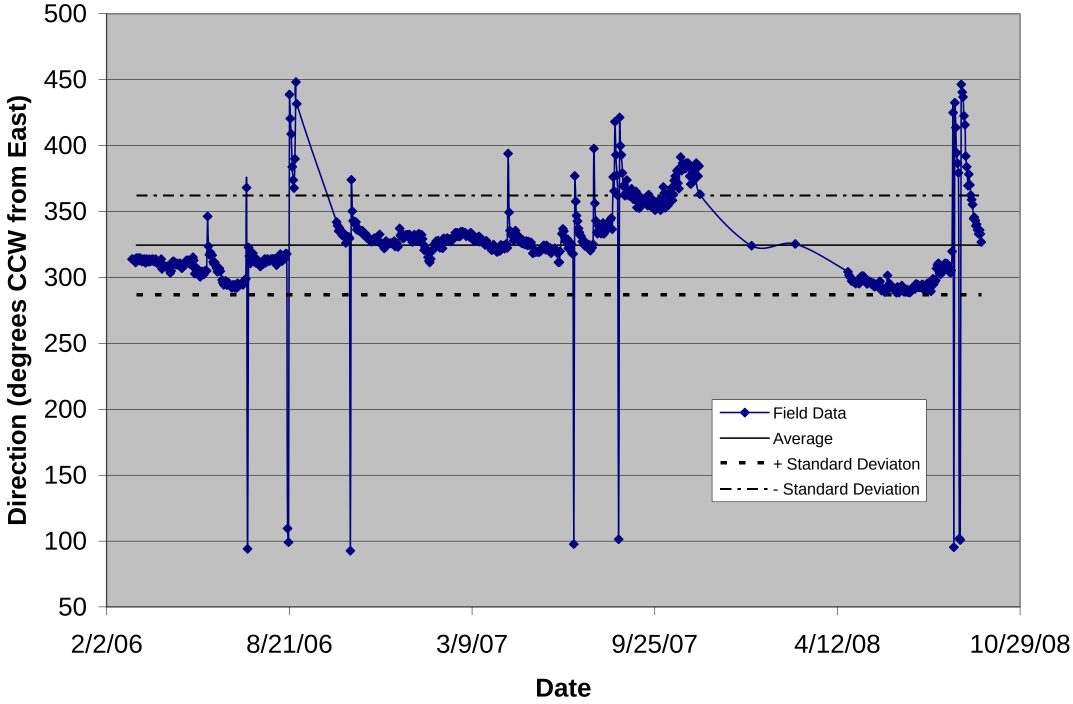


Figure 41 - Direction of groundwater flow as a function of time.

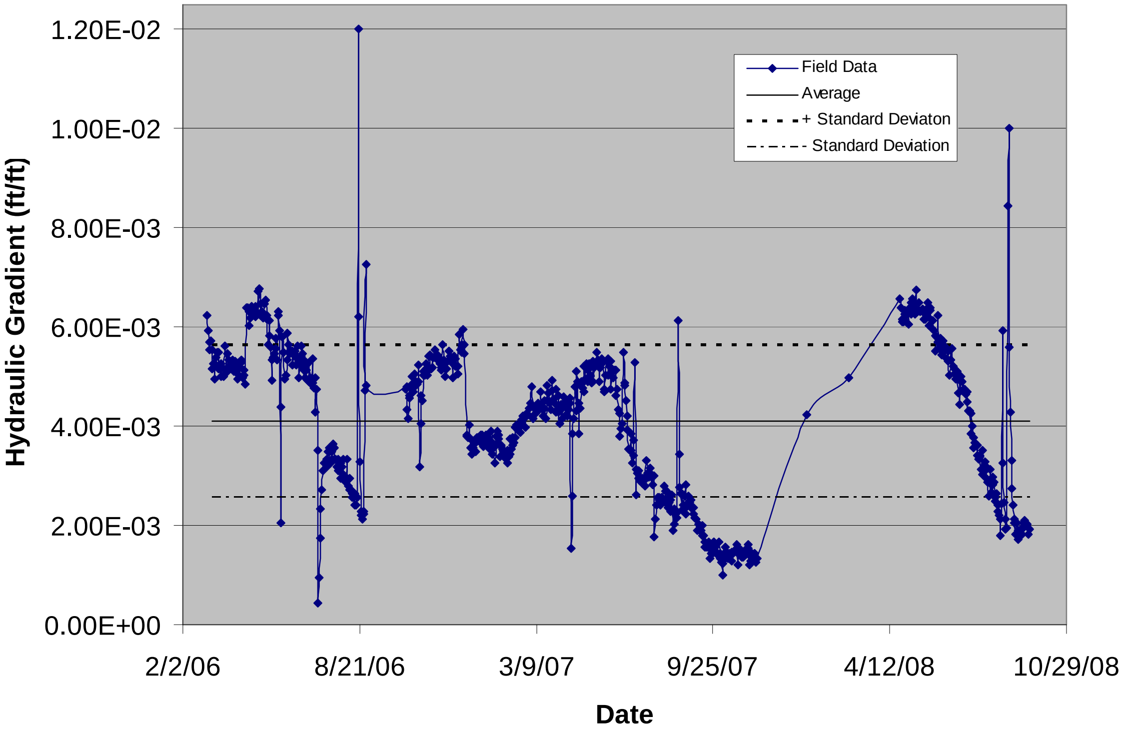


Figure 42 - Hydraulic gradient as a function of time.

4.5 FIELD TESTING

Field testing of the e^{-}barrier involved startup, operations, and demobilization. Each of these is described in the following sections. The status of the e-barrier as a function of time is documented in Figure 43.

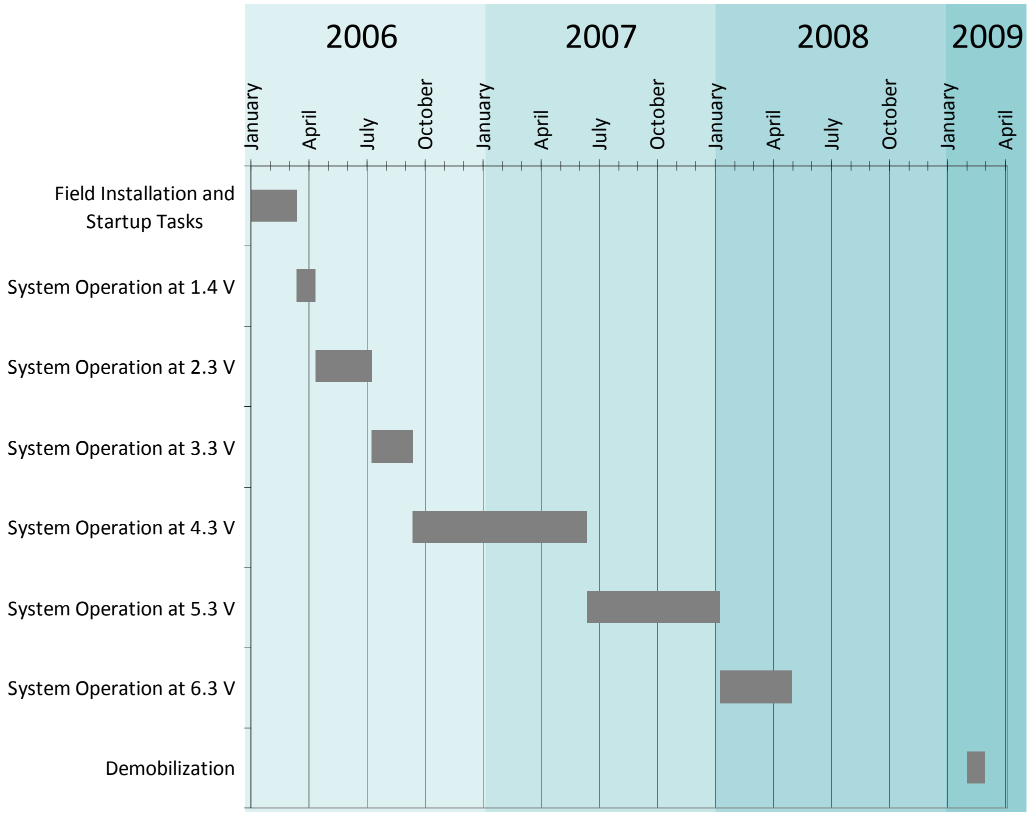


Figure 43 – Status as a function of time.

4.5.1 STARTUP AND OPERATIONS

The e^{-}barrier panels were installed at the end of January 2006. During February and early March the solar power supply, wiring, and control systems were installed and tested. On March 15, 2006 the e^{-}barrier panels were energized at 1.4V. All subsequent discussions reference March 15 as time zero. Over the course of the demonstration, six different voltages were applied (Table 9).

Table 9 - e^{-}Barrier Schedule of Operational Parameters

PROJECT PHASE	START DATE	ELAPSED DAYS
power applied: 1.4V	3/15/2006	0
power applied: 2.3V	4/13/2006	29
power applied: 3.3V	7/11/2006	118
power applied: 4.3V	9/13/2006	182
power applied: 5.3V	6/15/2007	457
power applied: 6.3V	1/9/2008	665
Power off	4/23/2008	770

4.5.2 SYSTEM SHUTDOWN

Per the January 8, 2008 project extension, the e^-barrier was operated through April 2008. Further efforts were made to extend operations through October 2008. Unfortunately, due to voltage transformer failure (June 22, 2008) and issues with power supply to the datalogger, no consequential data was collected after April 2008. In October 2008, the power from the solar power supply was shut off and all systems were de-energized.

4.5.3 DEMOBILIZATION

In February 2008, PCD notified CSU of their desire to have the e^-barrier removed. This was driven by PCD's plans to remove additional soils at the demonstration location. Demobilization activities were conducted in February 2009. All above-grade components were decommissioned and removed from the site. This included photovoltaic cells, batteries, control systems, wiring, conduit, and temporary monitoring wells. Well abandonment included removal of the 1-inch wells and backfilling the holes with bentonite. As approved by PCD, the e^-barrier, including vinyl sheet piles and electrode materials, was left in place.

Figure 44 - Former location of panels and power supply after removal of above ground facilities.

4.6 SAMPLING AND ANALYTICAL METHODS

The primary data set used to evaluate e^-barrier performance was water quality data. Parameters included:

- Energetic compounds (RDX, HMX 2,4,6-TNT, and 2,4-DNT)
- Inorganic compounds (nitrate, ammonia, major anions, major cations)
- Field parameters (pH, Eh, electrical conductivity)

Furthermore, as part of the complementary studies (which are described in the next section):

- Water samples were collected and analyzed to characterize microbial communities up- and downgradient of the barrier, and
- Soils were collected and analyzed to resolve the significance of site contaminants in low permeability zones (interbedded clay and the Pierre Shale).

The following describes sampling events and the methods employed in analyzing the samples. Interpretations of the data are presented in Section 5.0.

4.6.1 SAMPLES COLLECTED

Figure 45 shows a summary of field sampling events overlying project operational phases.

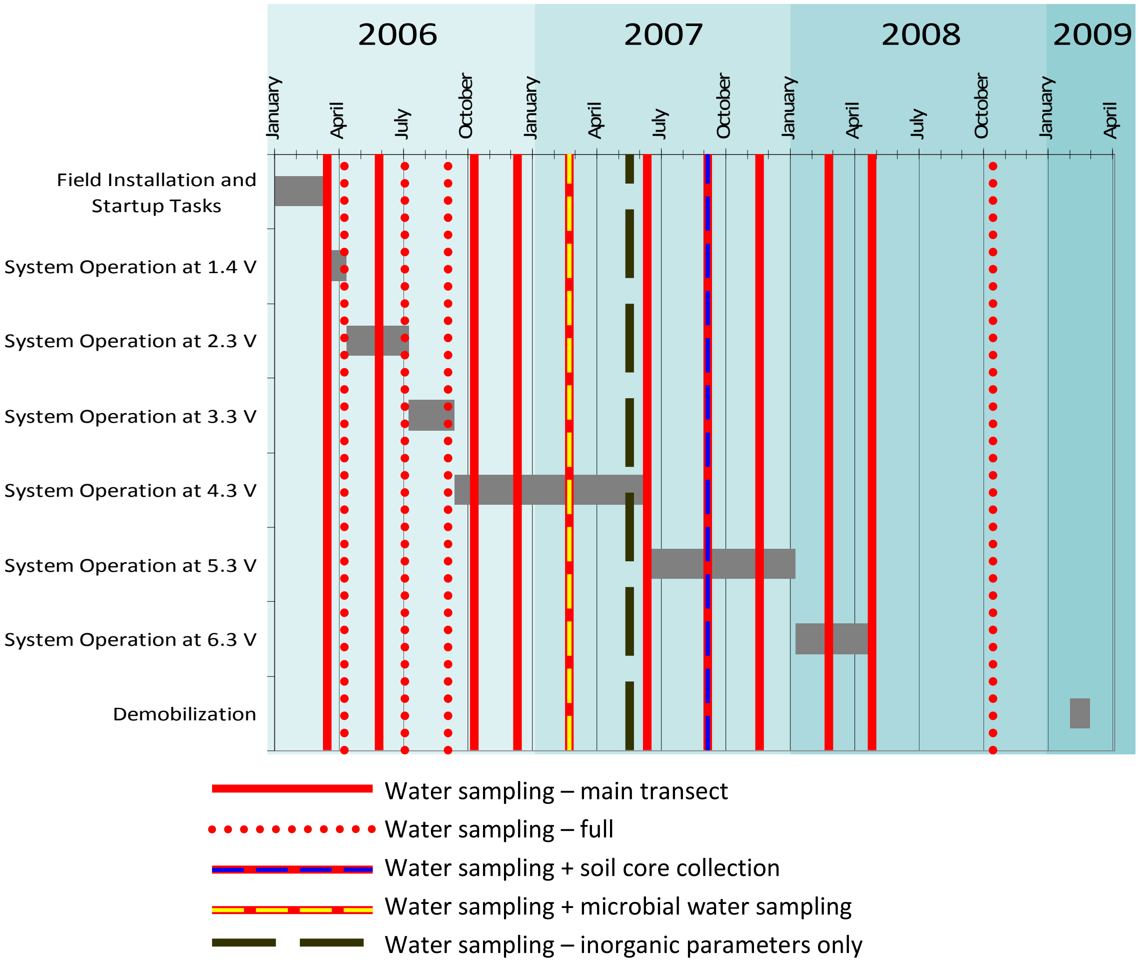


Figure 45 - Summary of field sampling efforts.

4.6.2 METHODS

Groundwater - Groundwater samples from wells and e^{-}barrier sampling points were collected with Teflon tubing and a peristaltic pump. All sampling hoses were used once and then taken back to the lab where they were rigorously cleaned by sequentially rinsing with acetonitrile, methanol, and DI water. Table 10 presents analytical methods, detection limits, sample preservation, holding times, and notes for groundwater parameters.

Soils – Soil samples used to resolve the distribution of contaminants were collected using CME-55 hollow stem auger drilling equipment (Drilling Engineers, Fort Collins, Colorado). After collection, cores were brought to CSU for extraction and analysis. At CSU, cores were divided in to 2-cm segments that were individually extracted and analyzed per the methods described in Table 10.

Table 10 - Analytical methods

MATRIX	ANALYTE	METHOD	DETECTION LIMIT OR ACCURACY	CONTAINER	PRESER-VATIVE	HOLDING TIME
Water	pH	EPA Method 150.1 - Denver Instruments AP25 and combination electrode (Ag/AgCl reference)	+- 0.01 pH units	None	None	Measured at collection
	Eh	Denver Instruments AP25 and Orion combination electrode (Ag/AgCl reference).	+- 0.1 mV	None	None	Measured at collection
	Conductivity	Orion 130 conductivity meter and cell	+- 1 uS/cm	None	None	Measured at collection
	Energetic compounds[1]	Modified EPA 8330[2]	Reported detection limit of 0.02 µg/L;. PQL determined by instrument calibration	1-liter amber glass bottle, unpreserved	None/ stored at 4ºC	14 days for extraction
	NO_3^-, NO_2^-	EPA Method 300.0[3]	Reported detection limit of 0.3 mg/L.; PQL determined by instrument calibration	1-liter amber glass bottle	None/ stored at 4ºC	48 hours
	Nitroaromatics and nitroamines	EPA 8330	var.	1-liter amber glass bottle, unpreserved	None/ stored at 4ºC	14 days for extraction
	Total metals	EPA 6010	var.	500-mL polypropylene, HNO_3 pres.	None/ stored at 4ºC	6 months
	Ammonia as N	MCAWW 350.1	0.10 mg/L	500-mL amber glass, H_2SO_4 pres.	7 days	28 days
	Anions including NO_3^- , NO_2^-, o-PO_4^{3-}	EPA 9056	var.	1-L polypropylene, unpreserved	None/ stored at 4ºC	48 hours
Soil	Lipid analysis	PLFA	NA	Glass jar	None/ stored at 4ºC	NA
	Energetic compounds[1]	EPA 8330	Reported detection limit of 1 µg/kg;. PQL determined by instrument calibration	Acetate sleeves	None	NA

Notes to Table 10:

1. RDX HMX, 2,4,6-TNT, 1,3,5-TNB, and 2,4-DNT
   2,4,6 2,4,6-TNT and degradation products (amino-DNT isomers, diamino-NT isomers, NT isomers)
   2,4-DNT and degradation products (amino-NT isomers, diamino-toluene isomers)
2. Analytical instrumentation consists of a Hewlett Packard 1100 Liquid Chromatograph (RP-C18 column, 50:50 H2O:methanol, isocratic) and Thermo Finnegan LCQ Duo Mass Spectrometer (Ion Trap, Electrospray, negative ion)
3. Analytical Instrumentation consists of a Metrohm 861 Advanced Compact Ion Chromatograph

4.7 COMPLEMENTARY STUDIES

During the November 6, 2006 In-Progress Review for Project ER-0519 it became apparent that the project would benefit from complementary studies not included in the original scope of work. These activities were funded based on a January 8, 2007 white paper. Complementary studies included:

- Extending operation through April 2008
- Direct measurement of groundwater seepage velocities using tracer dilution techniques
- Resolving the e^-barrier's impacts on microbial communities
- Resolving the significance of contaminant storage release from the Pierre Shale
- Evaluating adsorption of contaminants to materials of construction
- Evaluating competition for electron transfer sites and resolving the influence of groundwater redox state on the operation of the e^-barrier

In addition, a task that involved resolving the number of sites with shallow RDX plumes was appended to our original scope of work. This task is included in this section as a complementary study.

4.7.1 EXTENDED OPERATIONS

Funds for extended operations added an additional year of e^-barrier operation. Extended operations are described in Section 4.6.

4.7.2 DIRECT MEASUREMENT OF GROUNDWATER SEEPAGE VELOCITIES

In January and October of 2008, periodic tracer dilution tests were conducted at SMWU-17 to measure rates of groundwater flow at five wells located along the primary transect through the e^-barrier. The procedure involved:

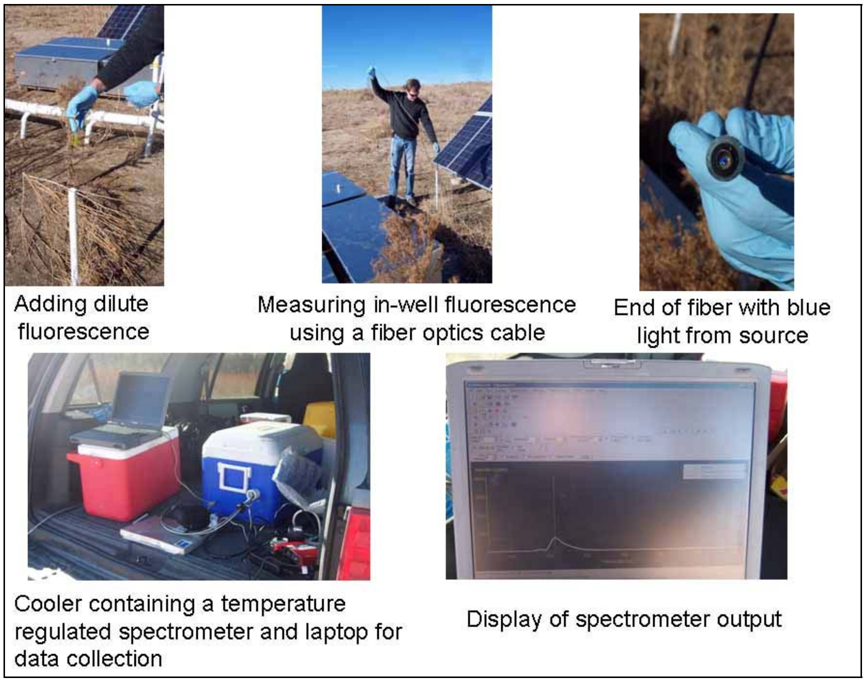
- Adding a dilute solution of fluorescein, an environmentally benign fluorescing dye, to the transect wells to achieve in-well fluorescein concentrations of ~10 mg/L.

- Over a two-day period, periodically mixing the fluids in the wells and measuring the intensity of fluorescence at 517 nm using an Ocean Optics USB-2000^{TM} spectrometer and an Ocean Optics^{TM} custom six-around-one fiber optics cable.

- Calibrating the spectrometer prior to each round of measurements using a single well with no tracer (zero concentration) and a well equipped with a ½ inch PVC pipe, plugged at the bottom, filled with formation water and spiked with fluorescein (100% control). In-well standards were used to keep the standards at the same temperature as the water in the wells, as the intensity of fluorescence is temperature dependent.

- Using the measured tracer losses over time to estimate groundwater flow rates per periodic tracer dilution techniques outlined in Smith (2008).

Photographs showing field methods are presented in Figure 46. Estimates of groundwater flow rates are presented in Figure 47. Results indicate average seepage velocities of 120 and 360 ft/year, respectively, in January and October 2008. These values are similar to prior estimates of seepage velocities based on measured hydraulic conductivity and observed gradients (Section 5.4.3).


Adding dilute fluorescence

Measuring in-well fluorescence using a fiber optics cable

End of fiber with blue light from source

Cooler containing a temperature regulated spectrometer and laptop for data collection

Display of spectrometer output

Figure 46. Field methods employed in conducting tracer dilution tests to estimate groundwater seepage velocities.

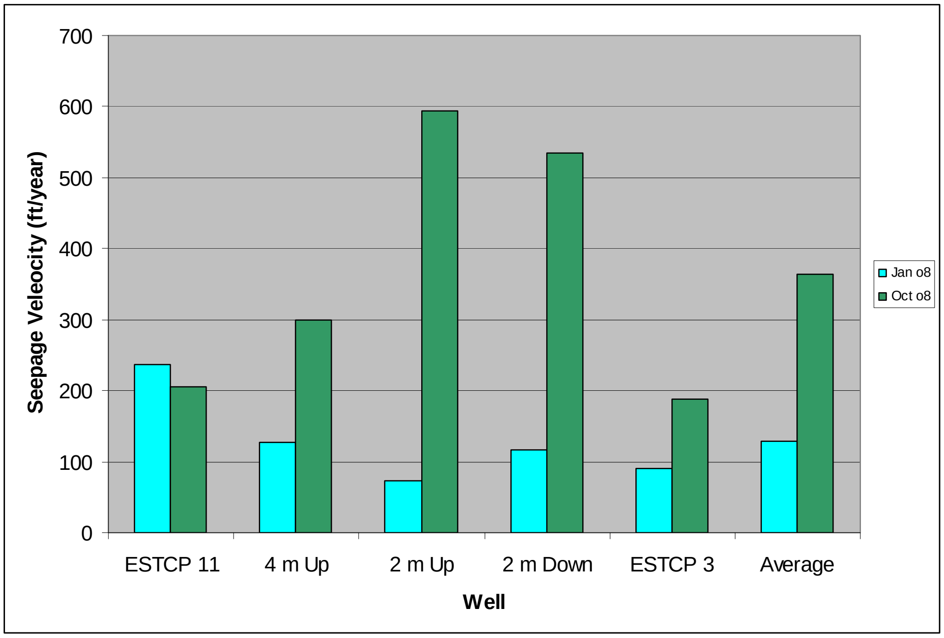


Figure 47 - Estimates of groundwater seepage velocities based on tracer dilution tests conducted in January and October of 2008.

4.7.3 IMPACTS OF THE e^-BARRIER ON MICROBIAL COMMUNITIES

An operating hypothesis has been that dissolved gases produced by an e^-barrier (e.g., hydrogen) will drift downgradient of the e^-barrier and drive microbially mediated degradation of target compounds. To test this hypothesis, water samples were collected in May 2007 from wells up- and downgradient of the e^-barrier. Subsequent analysis of the soils for biomass content and phospholipid fatty acids (PLFA) was performed by Microbial Insights Inc., Rockford, Tennessee. Results are documented in Figure 48 and Figure 49. With the exception of the total biomass at downgradient location 1, there appears to be little difference between the microbial communities up- and downgradient of the e^-barrier.

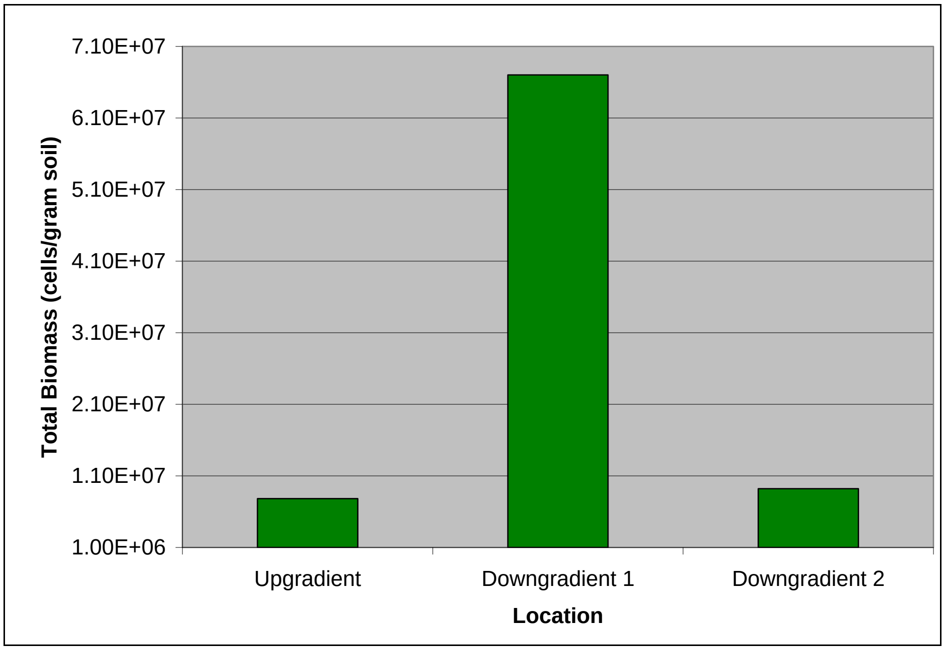


Figure 48 - Total biomass in soil up- and downgradient of the e-barrier.

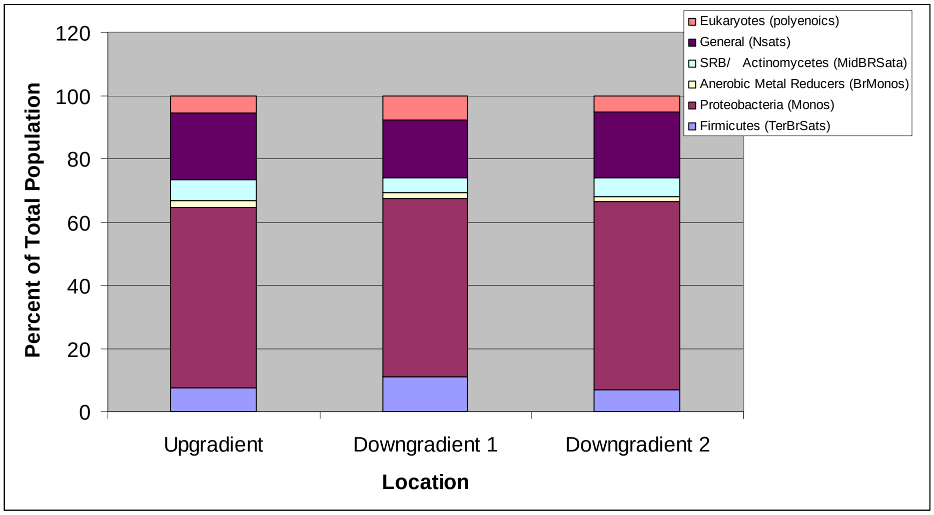


Figure 49 - Community structure up- and downgradient of the e-barrier.

4.7.4 CONTAMINANTS STORED IN LOW PERMEABILITY ZONES

Through early operations of the e^-barrier it became apparent that concentrations of energetic compounds were rebounding downgradient of the e^-barrier. The working hypothesis was that back diffusion of contaminants stored in low permeability zones was driving the observed rebound. To investigate, soil cores were collected adjacent to 2,4,6-TNTMW-02, 2 m downgradient of the e^-barrier (D2M), and at ESTCP 8. Drilling services were provided in May 2007 by Drilling Engineers, Inc. (Fort Collins, Colorado) using a CME 55 drill rig. Continuous core samples were collected using a five foot long barrel sampler containing a 4-inch I.D. butyl acetate liner. Core recovery was 83% from 2,4,6-TNTMW-02, 37% from ESTCP 8, and 32% from 2 m downgradient of the e^-barrier. Limited recovery from ESTCP 8 and D2M is attributed to the lack of cohesion in the soil above the water table. All down-hole sampling equipment was decontaminated between borings. Immediately after sample collection, boreholes were backfilled with bentonite. Sample collection activities are documented in Figure 50.

Figure 50 - Collection of soil cores to evaluate matrix diffusion.

Soil cores were brought to CSU for sub-sampling, extraction, and analysis. All cores were divided into 2-cm subsections for individual extraction and analysis. Each 2-cm segment was extracted and analyzed following methods based on EPA 8330. This involved a total of 366 samples. In addition, a sample of the Pierre Shale was analyzed to determine its fraction of organic carbon using a Shimadzu TMN1 TOC analyzer.

Concentrations of energetic compounds in cores collected from 2,4,6-TNTMW-02, D2M, and ESTCP 8 are presented in Figure 51, Figure 52, and Figure 53, respectively. In general, the highest concentrations of energetic compounds are found in the low permeability clay/silt layer or in the Pierre Shale. This supports the hypothesis that contaminants stored in low permeability zones are driving contaminant rebound downgradient of the e^-barrier.

The fraction of organic carbon (f_{oc}) in the Pierre Shale was determined to be 0.02 (2%). Figure 54 presents retardation coefficients for the contaminants of concern as a function of f_{oc} values ranging from 0.001 to 0.02. In combination, the observed contaminant distribution and retardation values reveal that much of the contaminant mass in the study area is sorbed or stored in low permeability zones. The retardation values were calculated using Koc values for 2,4,6-TNT, 2,3-DNT, RDX, and HMX of 1834, 363.8, 195.4, and 1853 mL/gm respectively (EpiSuite version, 3.20), and a porosity of 0.25.

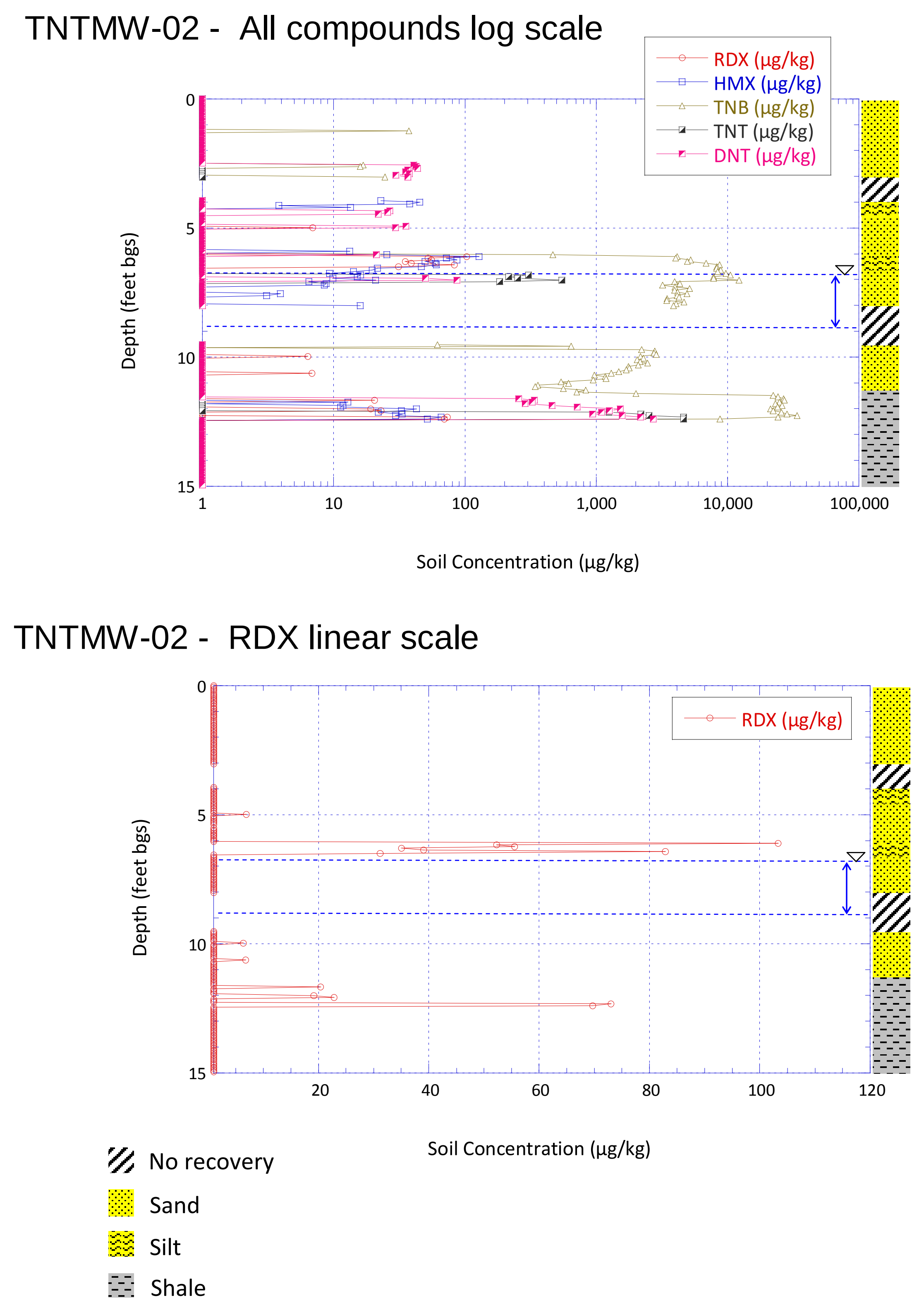


Figure 51 - Data from soil core 2,4,6-TNTMW-02: energetic compounds versus depth.

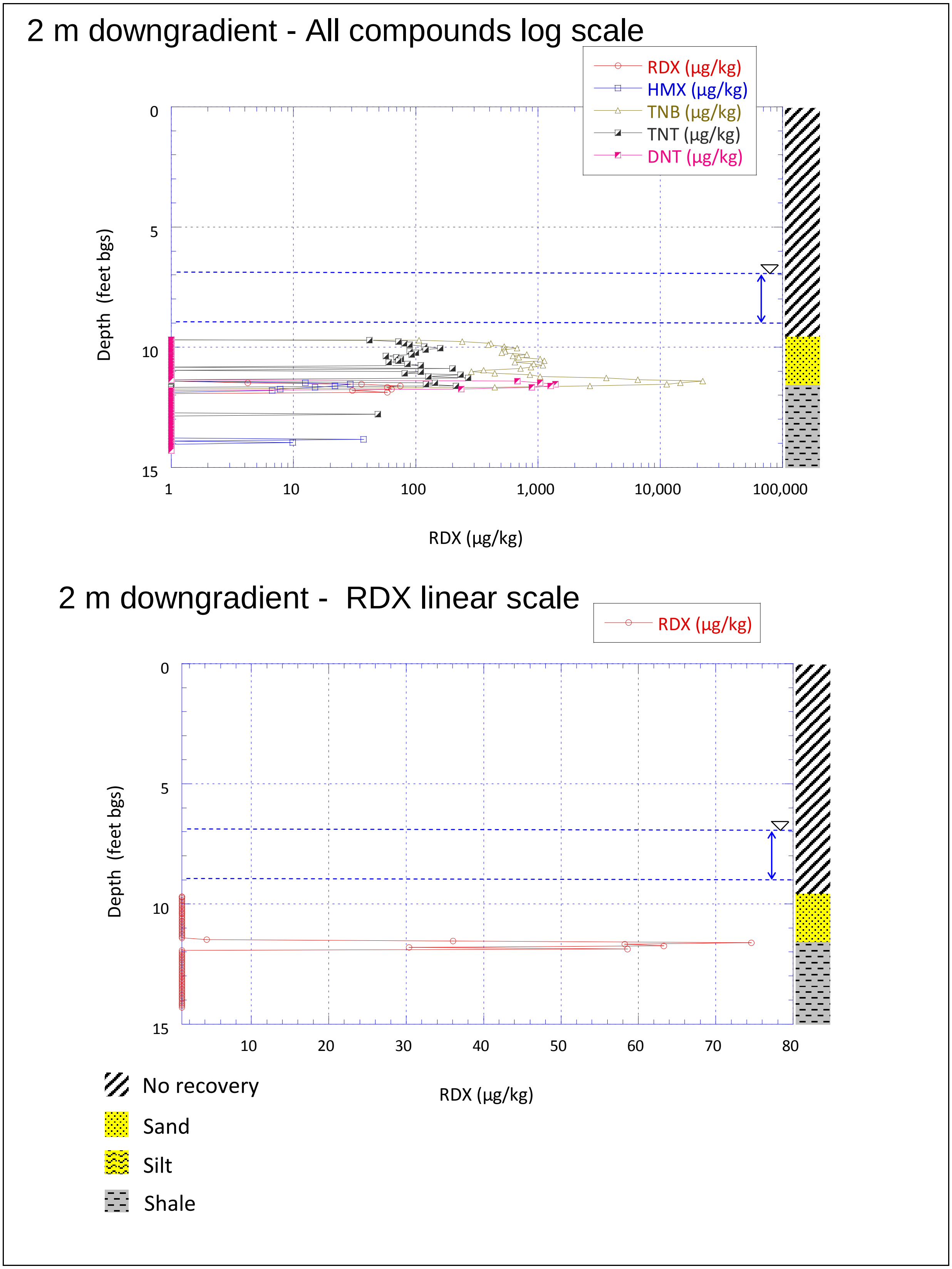


Figure 52 - Data from soil core collected 2 meters downgradient of e-barrier: energetic compounds versus depth.

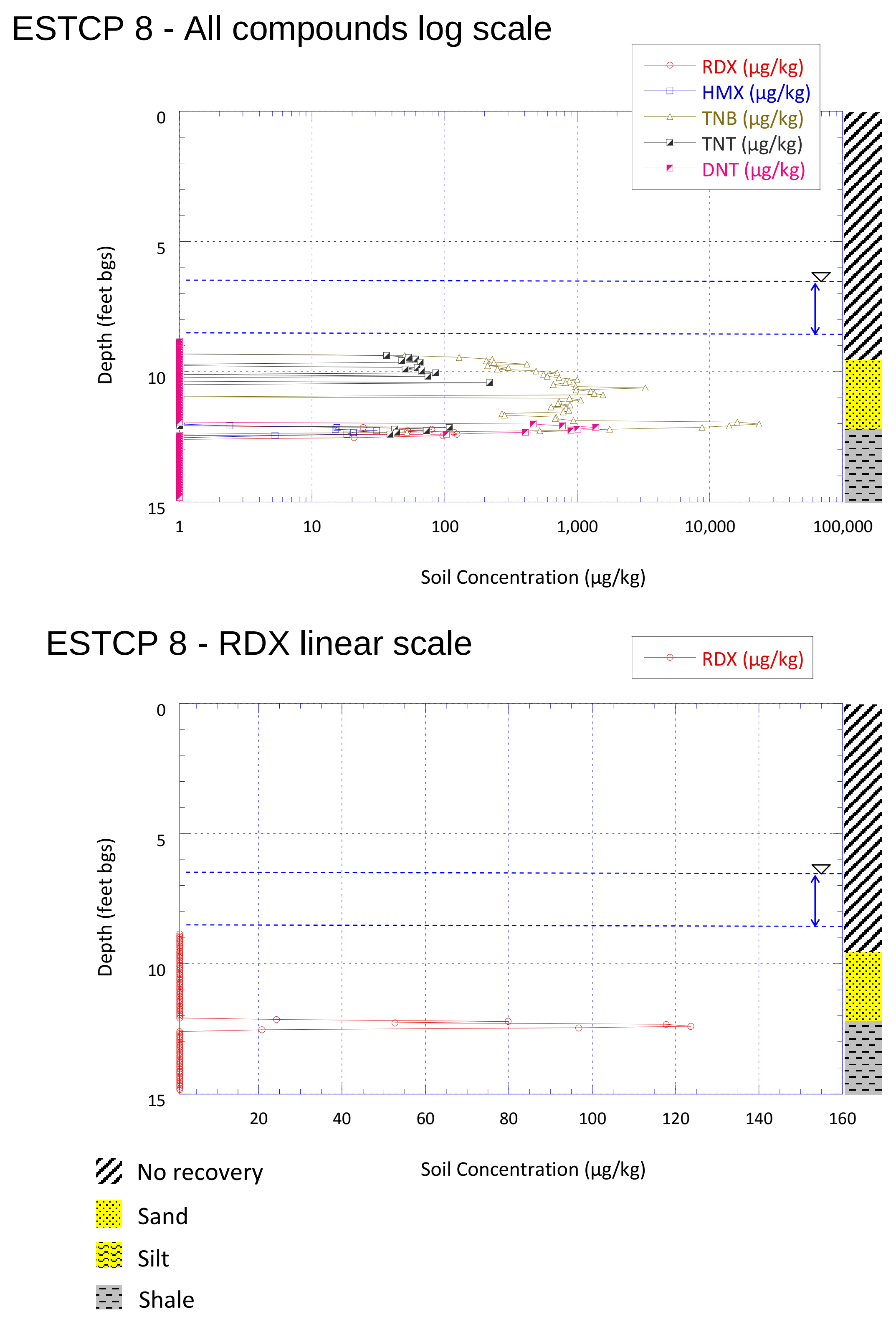


Figure 53 - Data from soil core ESTCP 8: energetic compounds versus depth.

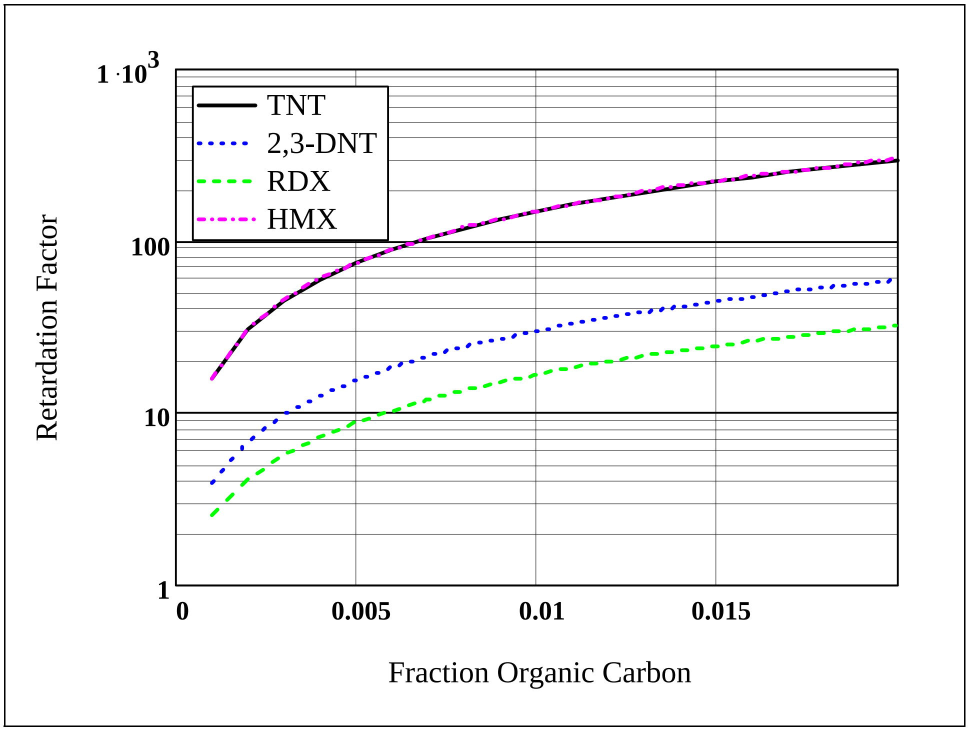


Figure 54 - Retardation factors for 2,4,6-TNT, 2,3-DNT, RDX, and HMX as a function of fraction organic carbon.

4.7.5 SORPTION TO e$^-$BARRIER MATERIALS

During the project's 2007 In-Progress Review, a concern was raised as to whether we would be able to differentiate between losses of contaminant at the barrier due to treatment and losses due to adsorption. Based on this, an adsorption study was undertaken. The study was conducted in 36 one-liter amber glass jars. The jars contained water collected from PCD that was spiked to varying concentrations of RDX, HMX, 2,4,6-TNT, TNB, and DNB. The experimental design is presented in Table 11.

Table 11 - Experimental design matrix for sorption study

TARGET INITIAL CONCENTRATION (mg/L)	CONTROL	GEONET	GEOTEXTILE	VINYL SHEET PILING
0		1	1	1
0.5		1	1	1
1		1	1	1
5		3	3	3
10	3	3	3	3
50		1	1	1
100		1	1	1

Samples were collected from the vials in March and October of 2009. The March samples were analyzed by CSU. The October samples were analyzed at a laboratory facility at PCD operated by EarthTech.

Figure 55 shows plots of sorbed concentration versus equilibrium aqueous concentration for RDX, HMX, 2,4,6-TNT, TNB, and 2,4-DNT. To analyze sorption study data, the sorbed concentration is calculated as follows:

$$\omega = \frac{(C_0 - C_e)V_l}{m_s}$$

where ω (mg/kg) is sorbed concentration (e.g., mass of sorbed contaminant per total mass of solid), C_0 (mg/L) is the initial aqueous concentration, C_e (mg/L) is the equilibrium aqueous concentration, V_l (L) is the volume of water, and m_s (kg) is the mass of solid adsorbent.

These results indicate that e^-barrier materials, especially the geotextile, are capable of sorbing considerable contaminant mass. This is not surprising, given the plastic nature of e^-barrier components such as geotextile and geonet, and hydrophobic nature of energetic compounds (e.g., the log K_{OC} for RDX is 2.291, per EpiSuite version 3.20). Nevertheless, for a field application, it could be expected that these materials would reach equilibrium, after which the influent of dissolved phase contaminants would be directly related to inlet groundwater levels.

Originally this study had a more comprehensive scope. Unfortunately, with the passing of Dave Gilbert, some the more detailed aspects of this study were lost. Further insights regarding the effects of sorption on apparent treatment using zero potential data from the end of the study are presented in Section 5.1.3.

4.7.6 COMPETITION FOR ELECTRON TRANSFER SITES

SWMU-17 has high background TDS and nitrate levels. The nitrate levels are attributed to natural degradation of nitro-aromatic compounds present at the site. This study was motivated by the concern that inorganic redox reactions might sorb preferentially. This could interfere with the desired redox reactions that involve the site energetic compounds. Unfortunately, due to the passing of Dave Gilbert this task was not completed. The challenges of picking up where Dave left off and larger issues discussed in the Performance section of this report forced us to decide to leave this incomplete. The portion of our budget allocated for this task was not spent.

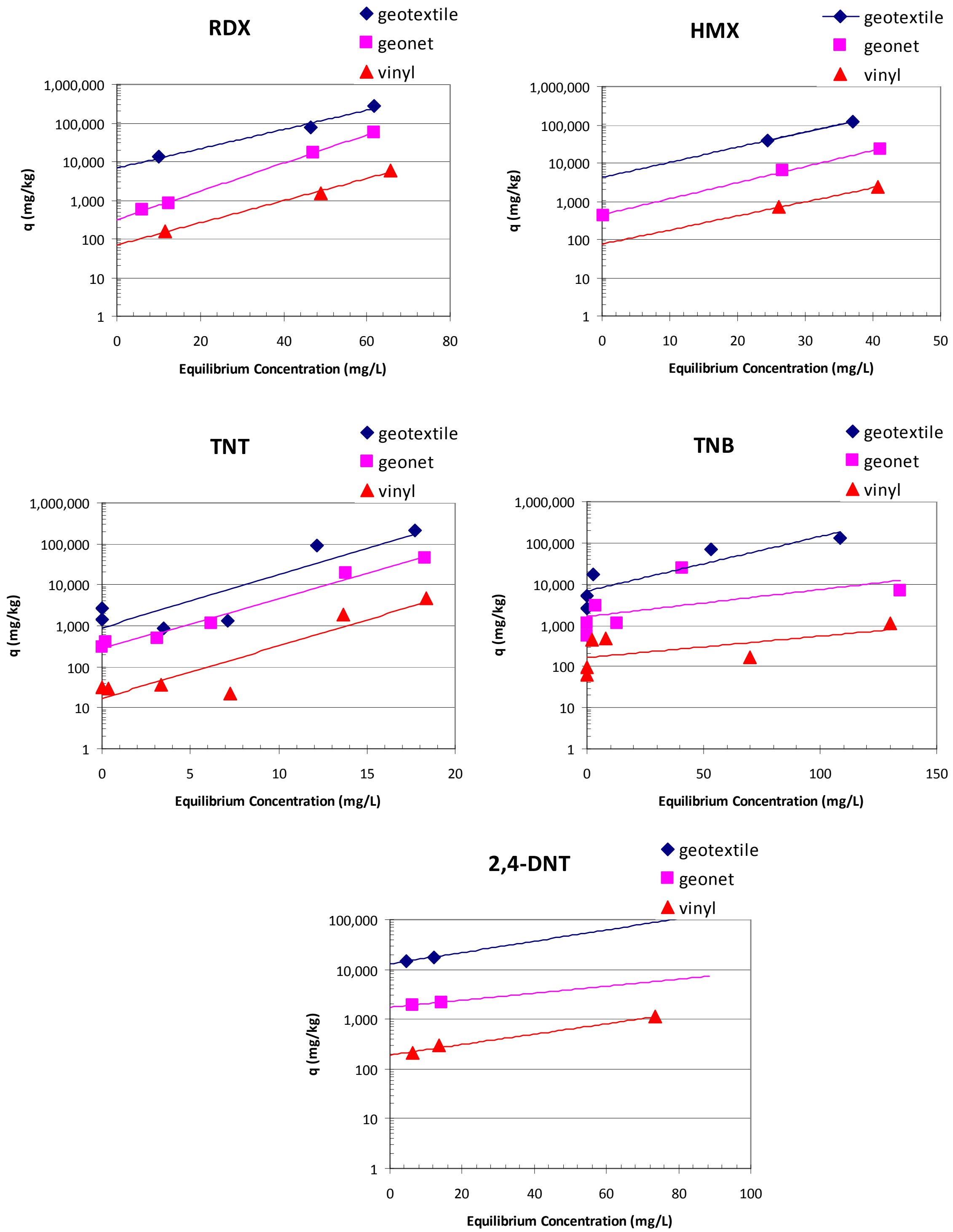


Figure 55 - Degree of contaminant sorption onto e^-barrier components.

4.7.7 RESOLVING THE NUMBER OF SITES HAVING SHALLOW RDX PLUMES

An early issue in this project was the question: How many sites exist where RDX is present in shallow groundwater that might be able to employ e^-barriers? In response, the following provides a list of Army sites where RDX has impacted soils and/or groundwater and our best understanding of the hydrogeology including the depths of RDX plumes. In addition, limited information regarding RDX in groundwater at “other” sites is presented. Other sites include Formerly Used Defense Sites (FUDS), Department of Energy (DoE) sites, and Navy sites.

Following NRC (2005), explosives sites can be categorized by “three generalized mechanisms of release: 1) production process discharges, 2) manufacturing processes discharges, and 3) military training and testing operations.” RDX has been widely employed in mixtures with other explosives (e.g., Comp B 60% RDX and 40% 2,4,6-TNT). RDX is also used in pressure-loaded projectiles, detonators, and blasting caps.

A primary activity driving release of RDX (and other energetic compounds) involves washing, using hot water or steam, following loading/assembly or as a primary step in demilitarization of expired munitions. As an example, washout operations at Umatilla Army Depot, OR (1955-1965) resulted in the discharge of 85 million gallons of wash water to two half-acre surface impoundments (NRC 2005). Similarly, large volumes of wash water were discharged to the SMWU-17 surface impoundment at PCD (EarthTech 2007).

Per personal communications with Ira May, U.S. Army Environmental Center (May 2009), concentrations of RDX in many plumes are declining. This can be attributed to:

- Practice of discharging wash waters to unlined ponds ended at most sites two or more decades ago
- Impacted sediment underlying many former washout ponds has been removed
- RDX can degrade naturally in groundwater under select conditions (e.g., Bradley and Dinicola, 2005)
- At many sites, either natural recharge or remedy-related activities are flushing clean water through the impacted area

From the above it appears that some RDX plumes are going away. A limitation of the following analysis is that much of the information is dated. As such, RDX may no longer be present in consequential concentrations at some of the listed sites. Per our observations at PCD, what remains at many sites may be RDX that is adsorbed to solids in transmissive zones and/or dissolved and sorbed phase RDX stored in low permeability zones.

Army Sites -Table 12 presents a list of 17 U.S. Army sites where RDX has been encountered in groundwater. Of these sites, 15 have shallow RDX plumes (< 40 feet) and consequently, are sites where e^{-}barriers could be deployed. Sources of information include 2001 Installation Action Plans, regulatory web pages, and personal communications with Ira May (May 2009).

Table 12 – List of US Army sites where RDX has been identified in groundwater

SITE	OPERATIONS/ IMPACTED UNIT	HYDRO-GEOLOGY	GENERAL DEPTH TO RDX IMPACTED GROUNDWATER	INFORMATION SOURCES
Holston Army Ammunition Plant, TN	Produced most of the RDX/HMX consumed in the U.S.	Holston River alluvium	Shallow	NRC (2005) *http://www.globalsecurity.org/military/facility*
Newport Chemical Depot, IN	Founded during World War II to produce RDX	Glacial till overlying limestone	Shallow	*http://www.globalsecurity.org/wmd/facility/newport.htm*
Redford Army Ammunitions Plant, VA	Production facility	New River alluvium overlying karst	Shallow	Installation Action Plan for Radford, Army Ammunition Plant 2001 *http://www.globalsecurity.org/military/library/report/enviro/RFAAP_IAP.pdf*
Picatinny Arsenal, NJ	RDX manufacturing	Glacial outwash	Shallow	*http://www.epa.gov/region02/superfund/npl/0201168c.pdf*
Cornhusker Army Ammunitions Plant, NE	Loading, assembly, and packaging	Platte River alluvium	Shallow	Johnson and Tratnyek (2008), Installation Action Plan for Cornhusker Army Ammunition Plant 2001
Louisiana Army Ammunitions Plant , LA	RDX handling and packaging	Red River Alluvium, low permeability	Shallow	Installation Action Plan for Louisiana Army Ammunitions Plant 2001 *www.atsdr.cdc.gov/toxprofiles/tp78-c5.pdf*
Lake City Army Amunitions Plant, MO	Building 139 - Manufacturing small caliber ammunitions	Missouri River alluvium	Shallow to deep	Installation Action Plan for LCAAP March 2001
Iowa Army Ammunition Plant, IA	Loading, assembly and packaging	Mississippi River alluvium	Shallow	Installation Action Plan for LCAAP March 2001 Army 1986e *www.atsdr.cdc.gov/toxprofiles/tp78-c5.pdf*
Lone Star Army Ammunition Plant, TX	Shell loading plant, RDX handling and packaging	Red River alluvium, low permeability	Shallow	Installation Action Plan for LCAAP March 2001 *www.atsdr.cdc.gov/toxprofiles/tp78-c5.pdf*
Ravenna Army Ammunitions Plant, OH	Loading, assembly, packaging and demilitarization	Glacial till	Shallow	Installation Action Plan for RVAAP March 2001
Milan Army Ammunition Plant, TN	Demilitarization (washout) - packing large caliber ammunitions	Upper Mississippi River Embayment of the Gulf Coastal	Shallow	Installation Action Plan for LCAAP March 2001 *www.atsdr.cdc.gov/toxprofiles/tp78-c5.pdf*
Badger Army Ammunition Plant, WI	Loading, assembly and packaging	Glacial terminal moraine and outwash plain	Shallow to deep	Installation Action Plan for BAAP March 2001
Joliet Army Ammunition Plant, IL	Loading, assembly and packaging	Alluvium of the Des Plaines and Kankakee Rivers	Shallow	Installation Action Plan for JAAP March 2001
Massachusetts Military Reserve	Training range and Research and Development	Glacial kame and terminal moraines	Shallow to deep	*www.globalsecurity.org/military/facility/mmr.htm*
Pueblo Chemical Depot, CO	Demilitarization (washout)	Alluvium	Shallow to deep	EarthTech Inc. (2007)
Umatilla Army Depot, OR	Demilitarization (washout)	Basalt	Deep (>50 feet)	NRC (2005) Installation Action Plan for UAAP March 2001
Hawthorne Army Depot, NV	HWAAP-B30 wastewater	Alluvial basin fill	Deep	Installation Action Plan for LCAAP March 2001

Other Sites - Other sites where RDX has been identified in groundwater include FUDS, DoE sites and U.S. Navy sites.

FUDS – Within the U.S. there are thousands of properties that were formerly owned, leased, possessed, or operated by the DoD or its components. Figure 56 presents the distribution of 9,171 FUDS by state. Following GAO (2001), "Unexploded ordnance and other explosive wastes were believed to contaminate over 1,600 FUDS properties, of which 753 were associated with former training ranges according to a recent DoD survey." Given the ages of many of these former sites and a large number of training sites (where RDX impacts can be limited) it seems likely that the number of FUDS where e$^-$barrier might be appropriate is limited. Two possible FUDS sites where RDX may be present are Nebraska Ordnance Works, NB and Hastings Ordnance Works, NB. No definitive information was found regarding either of these sites.

DoE - Per verbal communications with Ira May, U.S. Army Environmental Center, (May 2009), RDX was used in manufacturing triggers for nuclear weapons. Considering this information, it is possible that RDX plumes may be present at select DoE facilities. One such location is DoE's Pantex Plant in Texas. This site is underlain by the Ogallala Formation. Available data suggests groundwater depth and cemented sandstones would limit the applicability of e$^-$barriers (Adams et al., 2006).

U.S. NAVY – The U.S. Navy's use of RDX is limited compared to that of the U.S. Army. Based on Web searches, U.S. Navy sites that have RDX in groundwater include Crane Naval Depot, IN; Naval Weapons Station-Yorktown, VA; and Bangor Naval Submarine Base, WA. No additional information has been acquired regarding RDX plumes at these sites.

Figure 5: Distribution of 9,171 Potential FUDS Properties

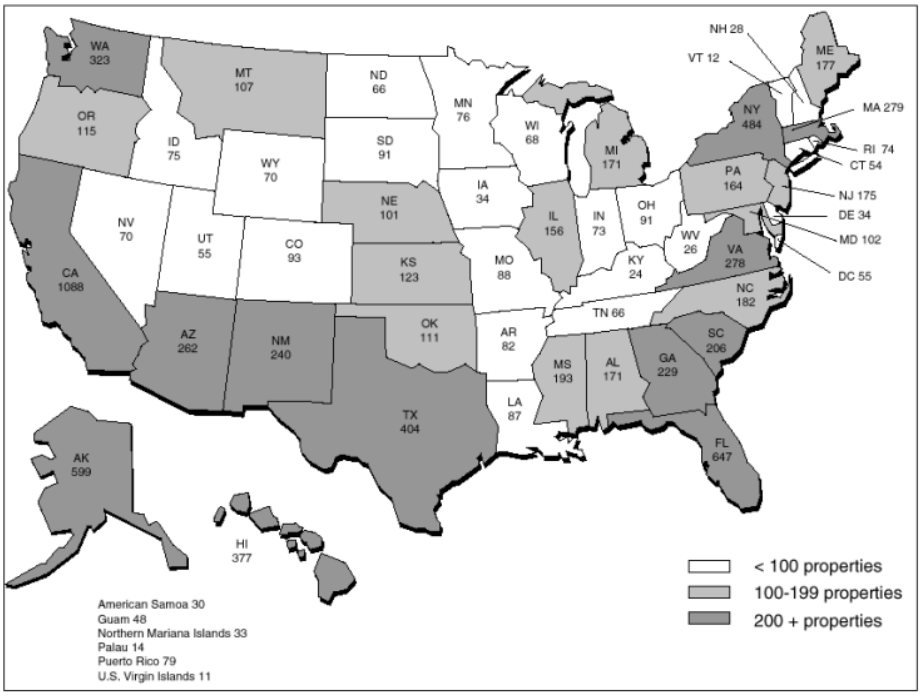


Figure 56 – FUDS from GAO 2001.

5.0 PERFORMANCE ASSESSMENT

The following presents our assessment of the e^-barrier's performance including:

- Contaminant removal
- Long-term viability
- Implementability

Related performance objectives (previously presented in Table 2) and a summary of results are shown in Table 13. The text that follows provides the basis for Table 13.

Table 13 – Objectives, data requirements, success criteria and results

PERFORMANCE OBJECTIVE	DATA REQUIREMENTS	SUCCESS CRITERIA	RESULT
Contaminant removal	Concentrations of energetic compounds in groundwater immediately downgradient of the e^-barrier.	Concentrations less than site cleanup goals.	Unfortunately, results from the demonstration failed to show large improvement in water quality downgradient of the e^-barrier. In general, site cleanup goals were not achieved. Falling upgradient contaminant concentrations during operations complicates analysis of the results.
Long-term viability	Sustained contaminant removal as above, with no measurable increases in head loss through the impacted interval, loss in electrical properties of the e^-barrier, or degradation of physical properties of e^-barrier components.	Low concentrations maintained throughout study; steady electrical demand.	The solar power supply and electrodes were reliable. Problems were encountered with voltage regulators and data logging systems. Similar problem are likely avoidable in future systems. Desired shifts in redox potential through the e^-barrier were sustained for 120 out of 123 weeks. The three-week down period was associated with the failure of a voltage regulator.
Implementability	Documentation of construction and operation experience in the final reports. This will include insight regarding the optimal niche for e^-barriers.	Installation of a functional system.	No major issues were encountered with implementability. The most significant limitation is that deep installations (> 30 feet) will likely be challenging.

5.1 CONTAMINANT REMOVAL

Contaminant removal is illustrated through the review of initial conditions and the depiction of concentrations of contaminants of concern in plan view and along the primary sampling transect through the center of the e^-barrier.

5.1.1 INITIAL CONDITION

Figure 57, Figure 58, and Figure 59 present initial concentrations of RDX, 2,4,6-TNT, and HMX in the vicinity of the e^-barrier. RDX is observed in the low single digits of µg/L. This is an order of magnitude lower than the concentration observed a year earlier during pre-demonstration studies (Figure 16). Falling concentrations may be due to removal of impacted sediment from the upgradient washout pond in 1998 and/or ongoing natural attenuation of RDX. 2,4,6-TNT is observed in the tens of µg/L (Figure 58) and HMX is observed in the single digits of µg/L (Figure 59). Available data indicates that concentrations of 2,4,6-TNT and HMX have been stable over the past decade.

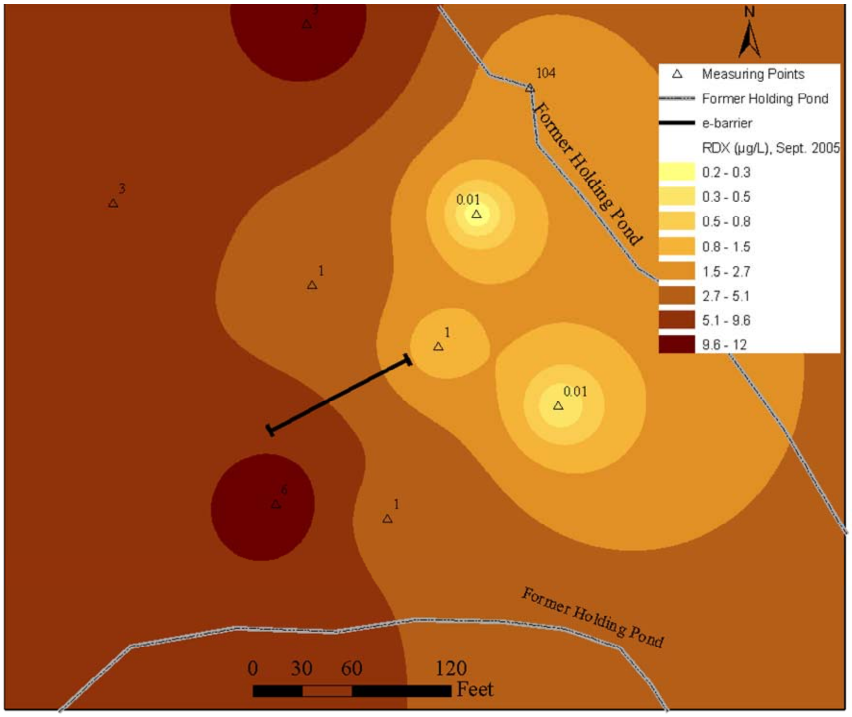


Figure 57 – Initial concentrations of RDX in groundwater.

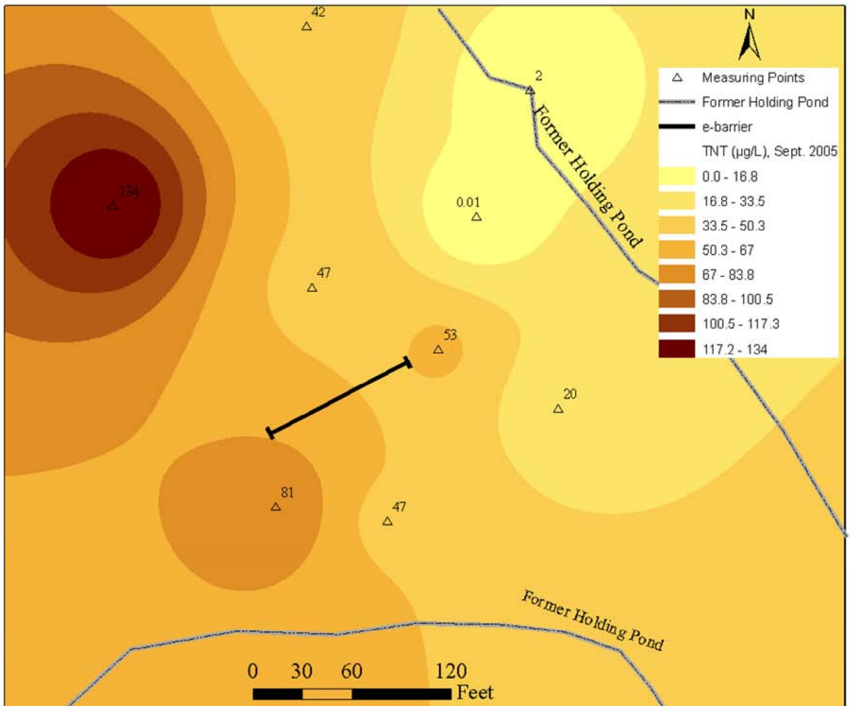


Figure 58 – Initial concentrations of 2,4,6-TNT in groundwater.

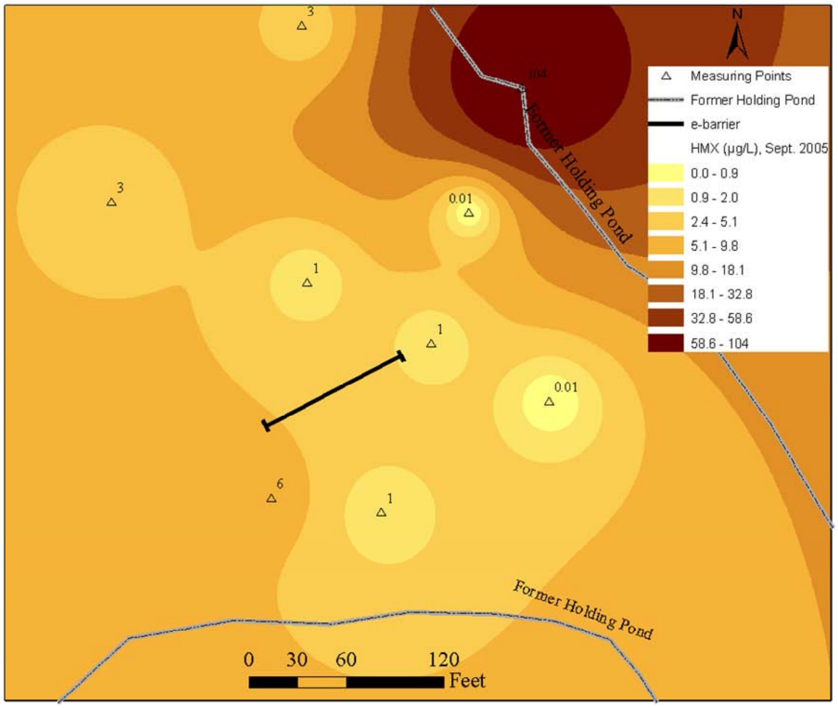


Figure 59 - Initial concentrations of HMX in groundwater.

5.1.2 CONCENTRATIONS IN PLAN VIEW

The following presents a plan view of contaminant distribution during operation of the e^{-}barrier (September 2006 at 3.3 V) and after shutdown (October 2008 at 0V). The e^{-}barrier performance at 3.3 V was similar that that observed at other voltages. Analysis of treatment as a function of applied voltage is presented in Section 6.1.3.

During Operations – Figure 60 through Figure 64 present concentrations of site contaminants of concern from the samples collected in September of 2006. At this time, the e^{-}barrier had been in operation for a total of 7 months and had been set at 3.3 V for 2 months. Disappointingly, concentrations downgradient of the barrier are only 40 to 82% lower than concentrations upgradient of the barrier. A more rigorous analysis of percent removal is presented using data from the primary transect through the e^{-}barrier in Section 6.1.3.

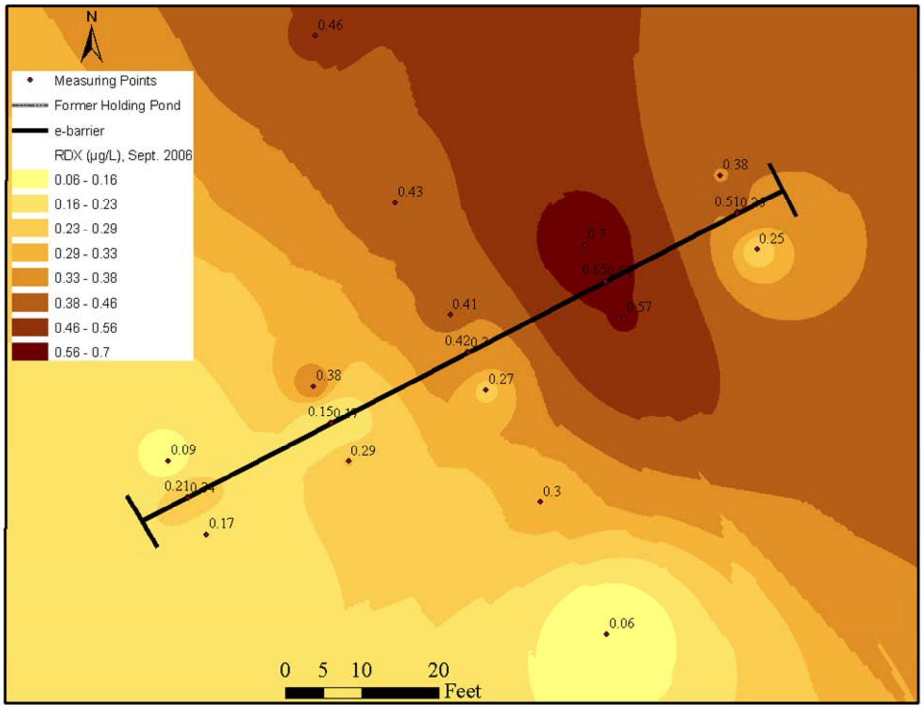


Figure 60 – RDX concentrations in groundwater during operations (September 2006, 3.3V).

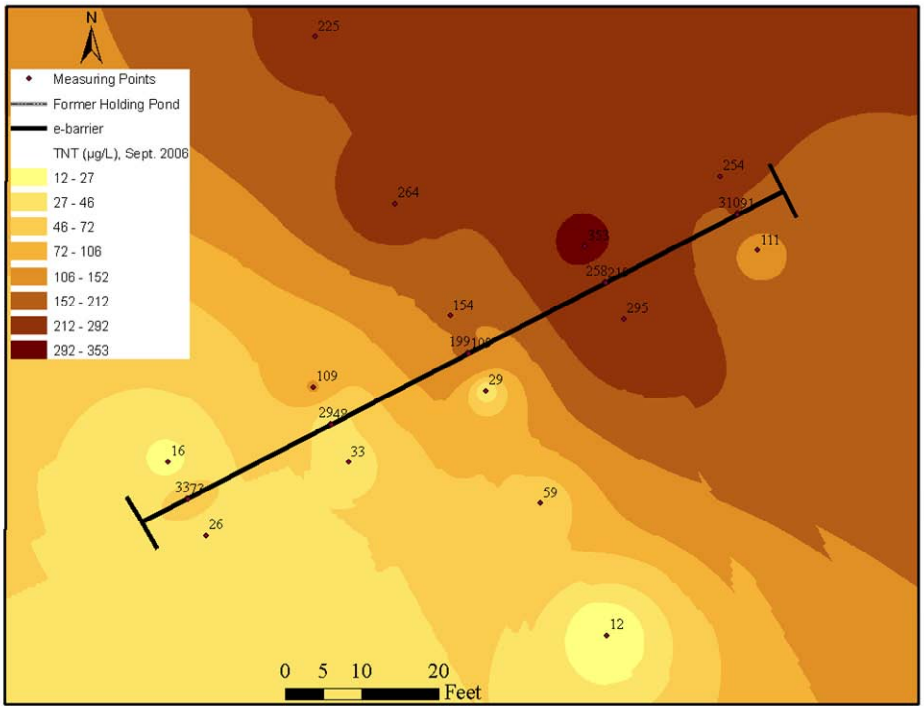


Figure 61 – 2,4,6-TNT concentrations in groundwater during operations (September 2006, 3.3V).

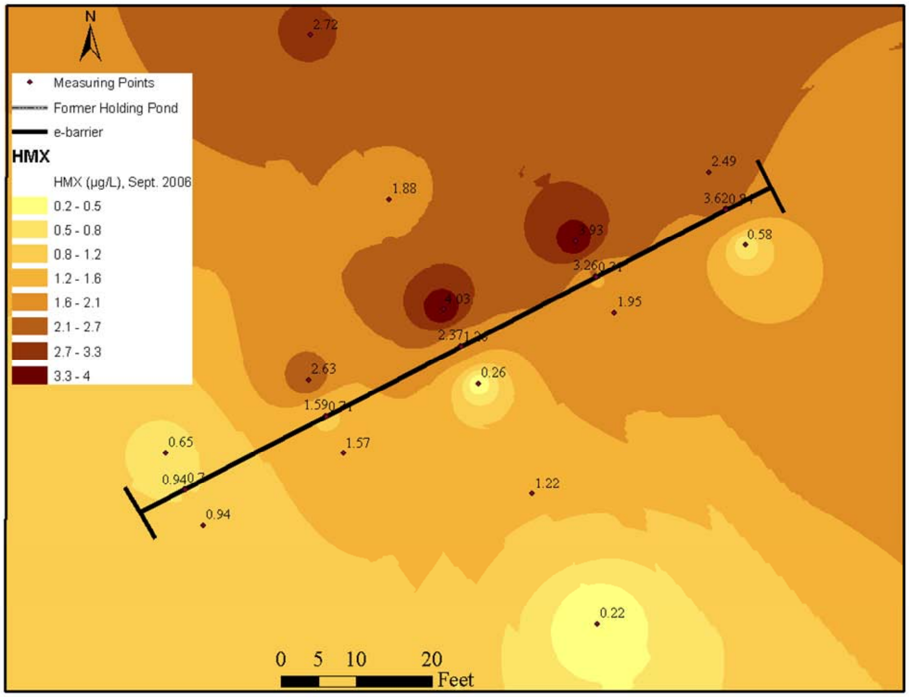


Figure 62 – HMX concentrations in groundwater during operations (September 2006, 3.3V).

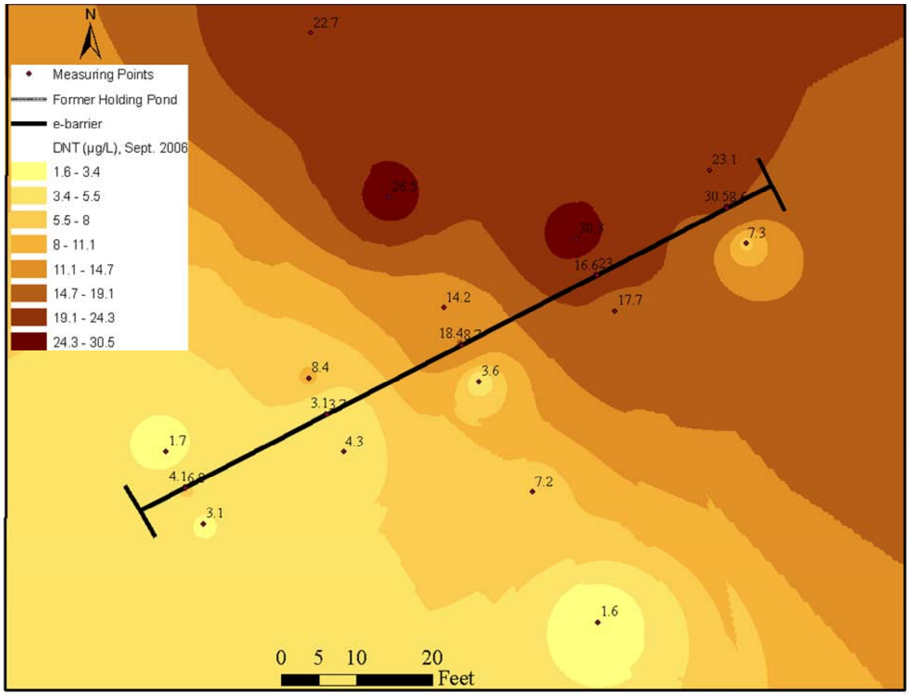


Figure 63 – 2,4-DNT concentrations in groundwater during operations (September 2006, 3.3V).

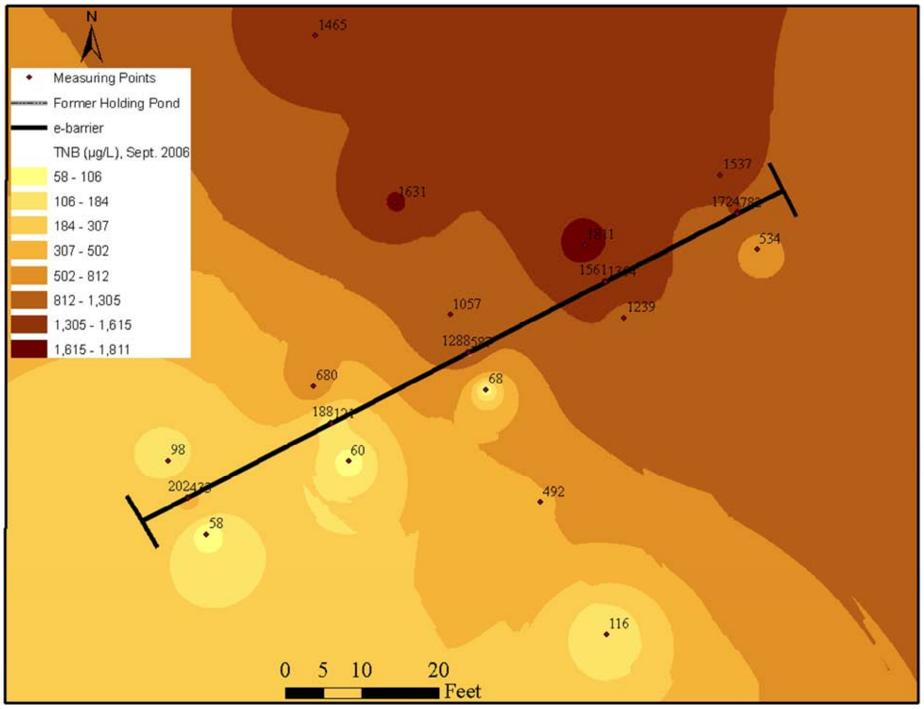


Figure 64 – TNB concentrations in groundwater during operations (September 2006, 3.3V).

After Shutdown - Figure 65 through Figure 69 present concentrations four months after shutdown of the e$^-$barrier (October 2008). This data was collected to see if:

- e^{-}barrier operation might modify the soil matrix downgradient of the barrier in a way that sustains treatment

- Sorption of site contaminant of concern is a primary factor driving the observed treatment when the barrier was active

In general, pre-treatment data (Figure 57 through Figure 59) and post-treatment data (Figure 65 through Figure 67) indicate similar concentration patterns. With this, it appears that e^{-}barrier operations have not modified the soil matrix in a way that sustains treatment and that sorption to the e^{-}barrier components was not a primary factor driving the observed treatment when the e^{-}barrier was energized.

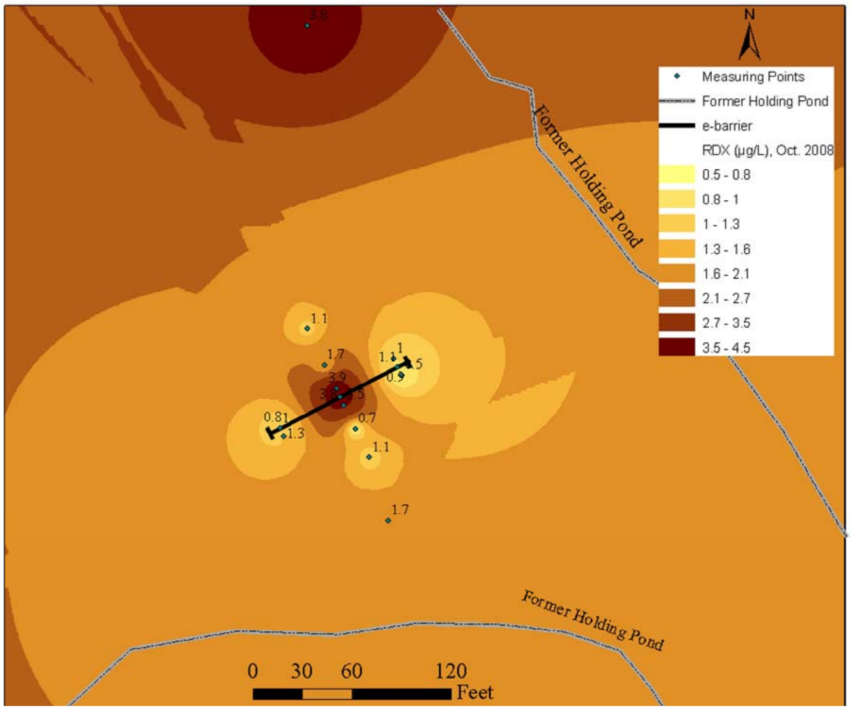


Figure 65 – RDX concentrations in groundwater 3 months after shutdown (October 2008, 0V).

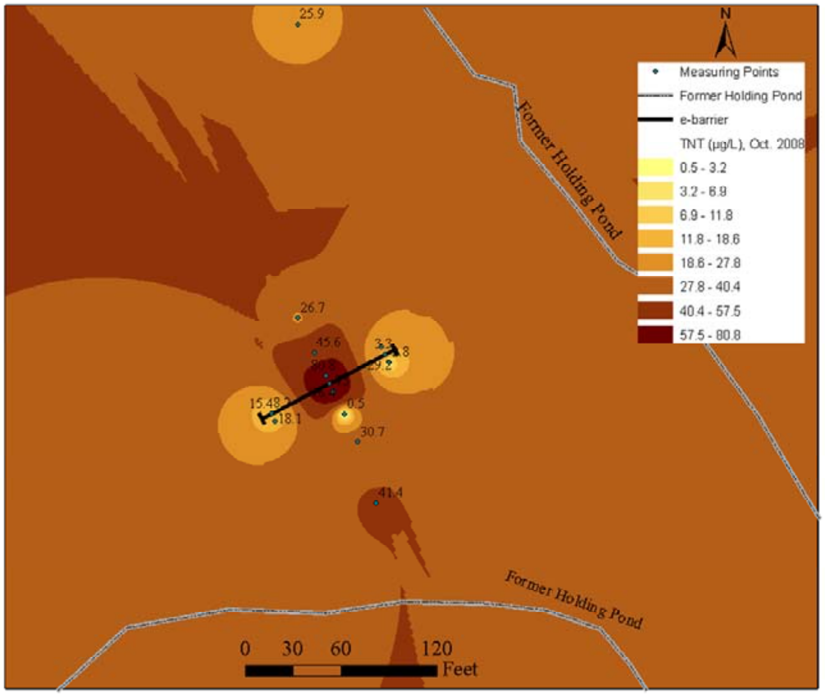


Figure 66 – 2,4,6-TNT concentrations in groundwater 3 months after shutdown (October 2008, 0V).

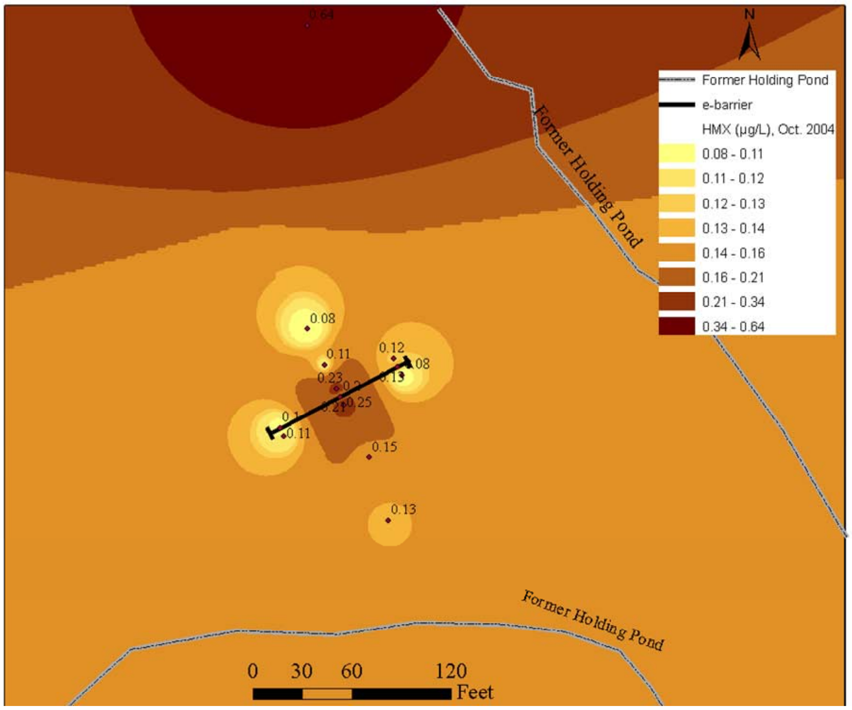


Figure 67 – HMX concentrations in groundwater 3 months after shutdown (October 2008, 0V).

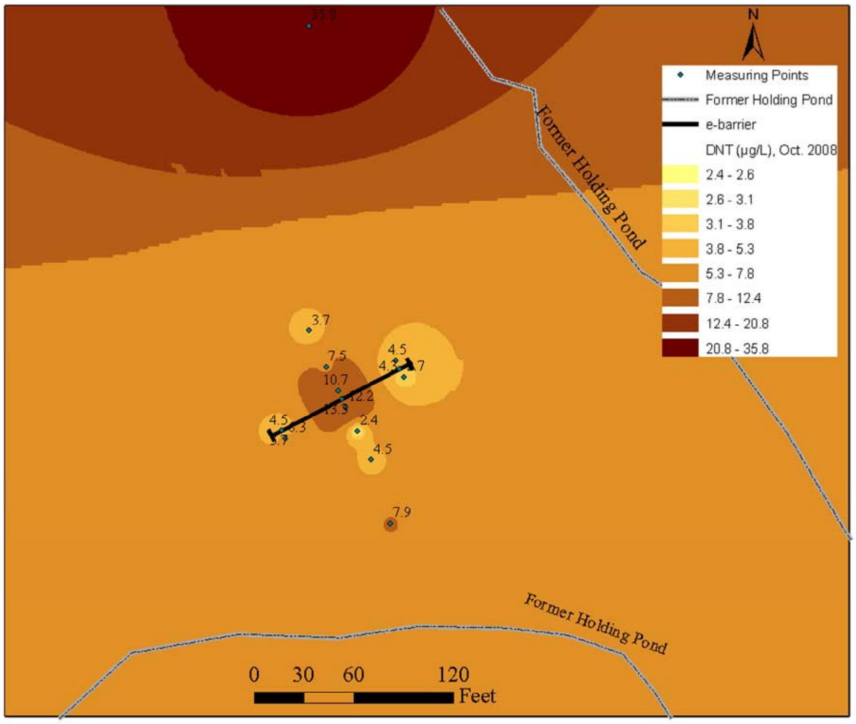


Figure 68 – 2,4-DNT concentrations in groundwater 3 months after shutdown (October 2008, 0V).

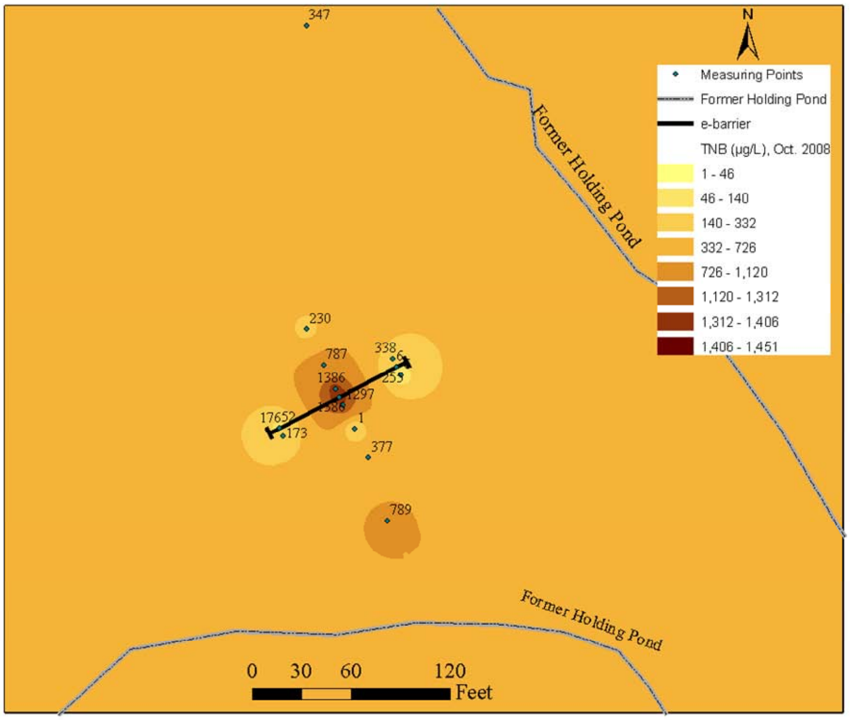


Figure 69 – TNB concentrations in groundwater 3 months after shutdown (October 2008, 0V).

5.1.3 CONCENTRATION ALONG THE PRIMARY TRANSECT

A more rigorous analysis of contaminant removal is provided by reviewing concentration data collected along the primary sampling transect passing through the e^-barrier (4 m upgradient ➔ 2 m upgradient ➔ 0.5 m upgradient ➔ 0.1 m upgradient ➔ 0.1 m downgradient ➔ 0.5 m downgradient ➔ 2 m downgradient ➔ 4 m downgradient ➔ ESTCP-3). This provides a basis for estimated treatment as a function of position and applied voltage.

For each contaminant, plots of concentration as a function of position and applied voltage are presented. Posted concentrations are the averages of all concentration measurements made at each location at the specified voltages. The position of the e^-barrier is set at zero, with negative positions upgradient and positive positions downgradient of the e^-barrier.

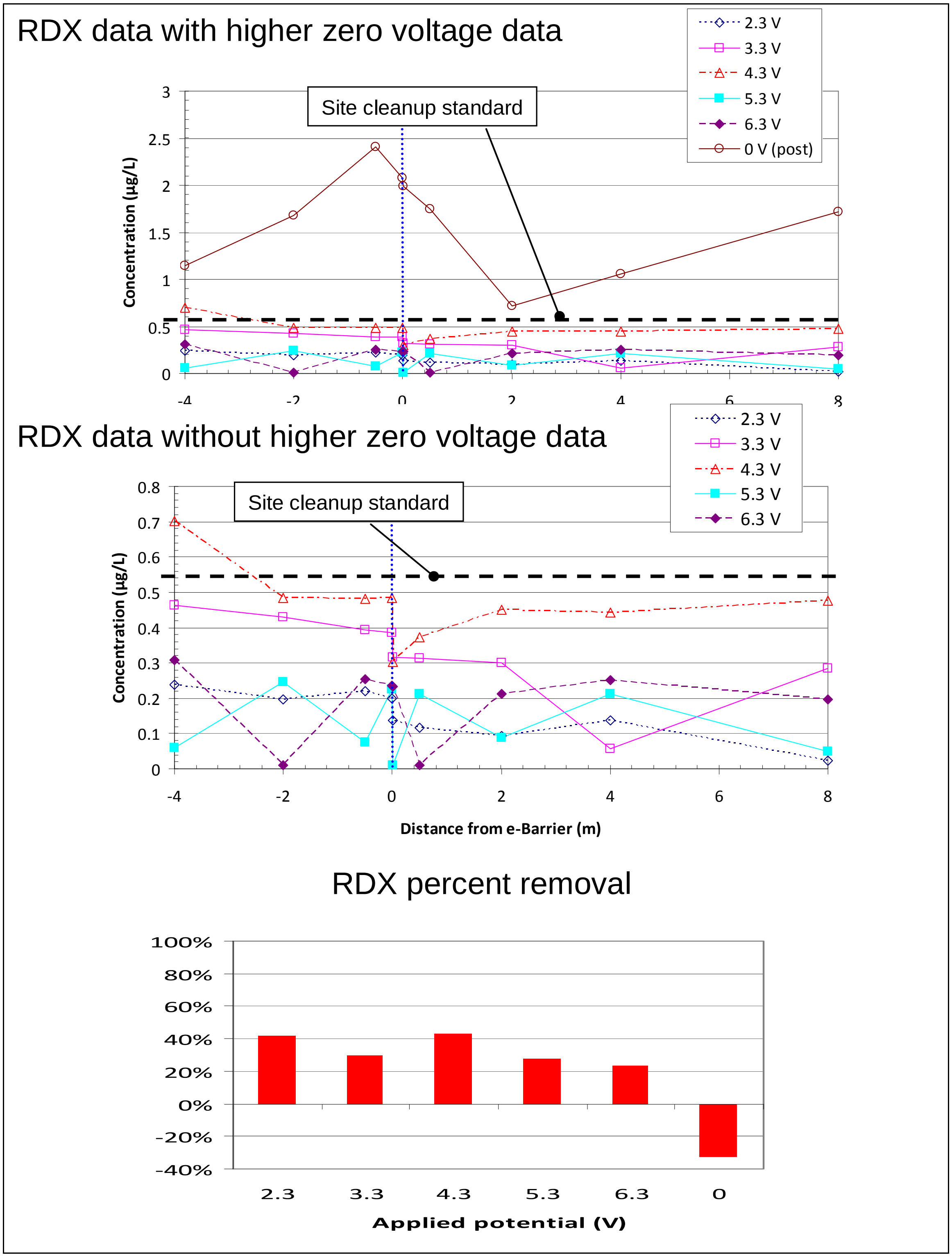
For each contaminant, percent removal is estimated based on comparisons of the average upgradient concentrations at -4 and -2 m for each voltage to the average downgradient concentrations at 0.1 and 0.5 m using

$$Percent\_Removal = \frac{[upgradient] - [downgradient]}{[upgradient]} 100$$

Samples from -4 and -2 m provide the best estimate of concentrations upgradient of the e^-barrier due to their greater distance from the e^-barrier. Samples from 0.1 and 0.5 m provide the best estimate of downgradient concentrations due to reduced biases associated with downgradient desorption of contaminant from the soils and/or back diffusion of contaminants from low permeability zones (e.g., the interbedded silt layers and underlying Pierre Shale). Also presented in this section are observed pH and Eh conditions observed along the primary transect.

Treatment of RDX - Figure 70 shows RDX concentrations as a function of position and percent removal for each applied voltage plus the post treatment (0V) condition. Concentrations of RDX range from non-detect (<0.02 µg/L) at 2m/6.5V to 2.4 µg/L at -0.5m/0V. The variability of the upgradient RDX concentrations makes it difficult to rigorously resolve the performance of the e^- barrier. On one hand, the 6.3 V RDX data everywhere is an order of magnitude lower than the post-treatment 0V data. On the other hand, the percent removal analysis suggests RDX removal in the range of 20-40%, largely independent of voltage. This compares to laboratory column study RDX removal of 99% (Section 5.3.1). The best available explanations for the limited removal of RDX and other compounds are presented in Section 5.4.

A curious note is that while the barrier was active, all but one data point is below the site cleanup standard of 0.55 µg/L for RDX. With the power off, all RDX concentrations are above the site cleanup standard. This raises the peculiar question of whether the e^-barrier was having an impact on both up- and downgradient concentrations of RDX. As described in the following text, this trend is also seen for HMX but not for 2,4,6-TNT, 2,4-DNT, or TNB.


RDX data with higher zero voltage data

RDX data without higher zero voltage data

RDX percent removal

Figure 70 – RDX concentration as a function of position, and percent removal as a function of applied voltage.

Treatment of 2,4,6-TNT. Figure 71 shows 2,4,6-TNT concentrations as a function of position and percent removal for each of the applied voltages. Concentrations of 2,4,6-TNT range from non-detect at 2m/0V to 1200 µg/L at -2m/4.3V. 2,4,6-TNT removal ranges from 10 to 60% with no clear trend relative to applied voltage. Again, data analysis is complicated by the variability of upgradient concentrations over time. The site cleanup criterion for 2,4,6-TNT is 2.01 µg/L. Oddly, this standard was only approached after the e^-barrier was shut off.

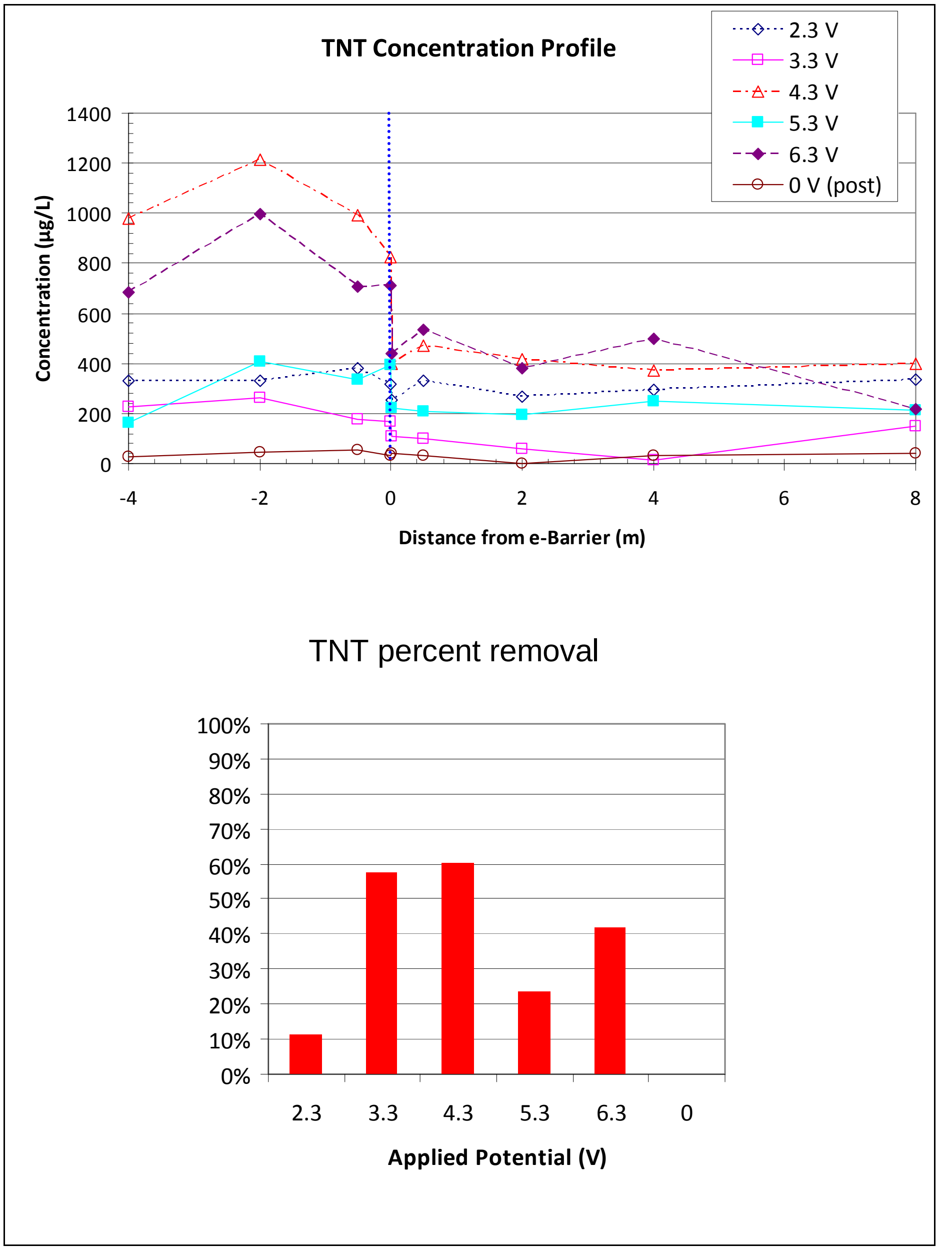


Figure 71 - 2,4,6-TNT concentrations as a function of position, and percent removal as a function of applied voltage.

Treatment of HMX - Figure 72 shows HMX concentration as function of position and percent removal for each of the applied voltages. Concentrations of HMX range from non-detect (<0.02 µg/L) at select points at 4.3 V and 6.3 V to 12.4 µg/L at 2m/4.3 V. Percent removal increases with applied voltage up to 82% at 4.3 V. Above 4.3 V, upgradient concentrations of HMX drop below detection limits and estimates of percent removal can not be developed. As with RDX, the curious phenomenon of upgradient concentrations dropping at higher voltages is observed. The site cleanup criterion for HMX is 602 µg/L. This standard is well above any of the concentrations observed in the immediate vicinity of the demonstration.

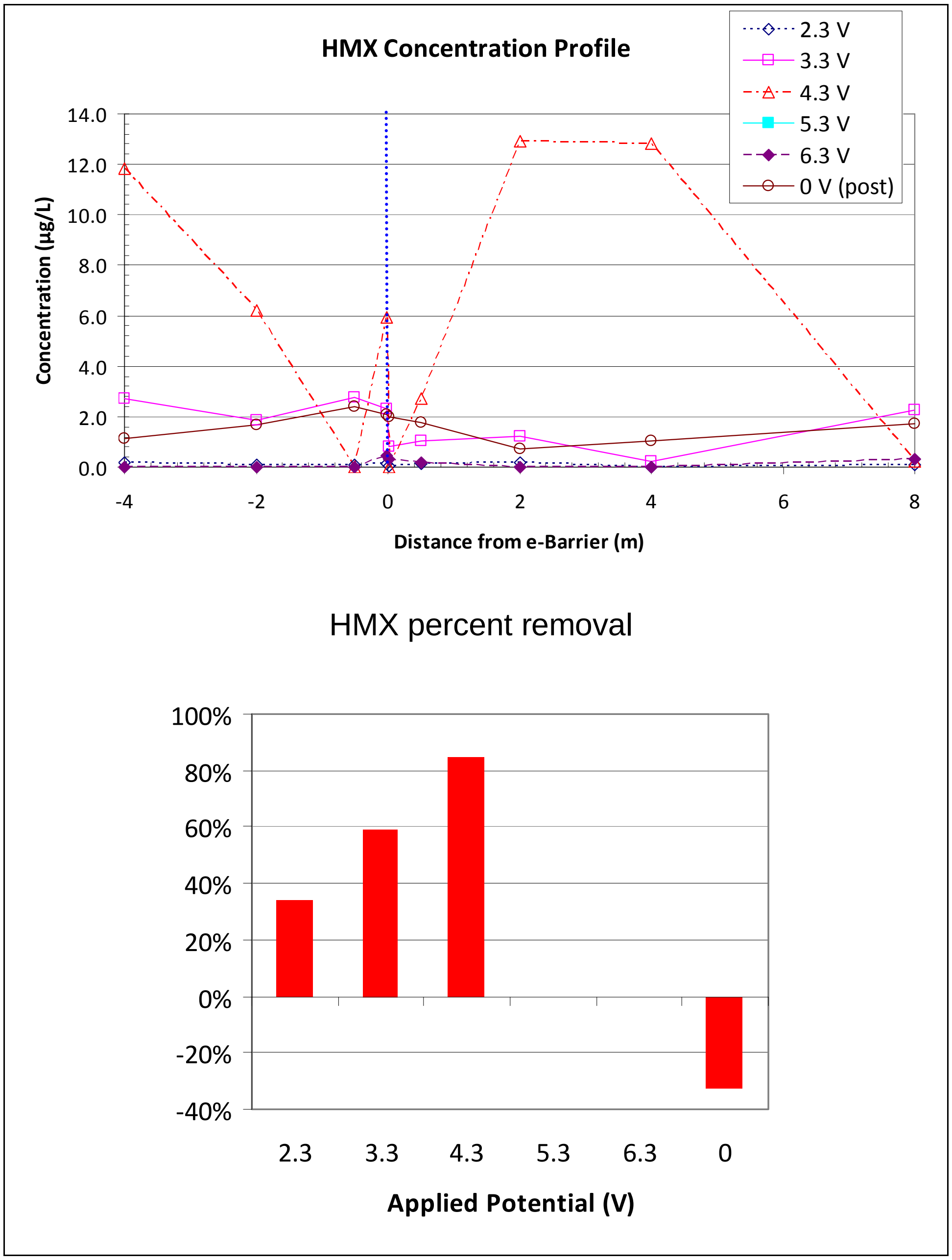


Figure 72 - HMX concentration as a function of position, and percent removal as a function of applied voltage.

Treatment of 2,4-DNT. Figure 73 shows 2,4-DNT concentration as function of position and percent removal for each of the applied voltages. Concentrations of 2,4-DNT range from non-detect (<0.02 µg/L) at -2m/0V to 50 µg/L at -4m/2.3V. 2,4-DNT removal ranged from 10 to 60% with no clear trends relative to applied voltage. The site cleanup criteria for 2,4-DNT is 0.0885 µg/L. Operation of the e^{-}barrier failed to meet this cleanup goal.

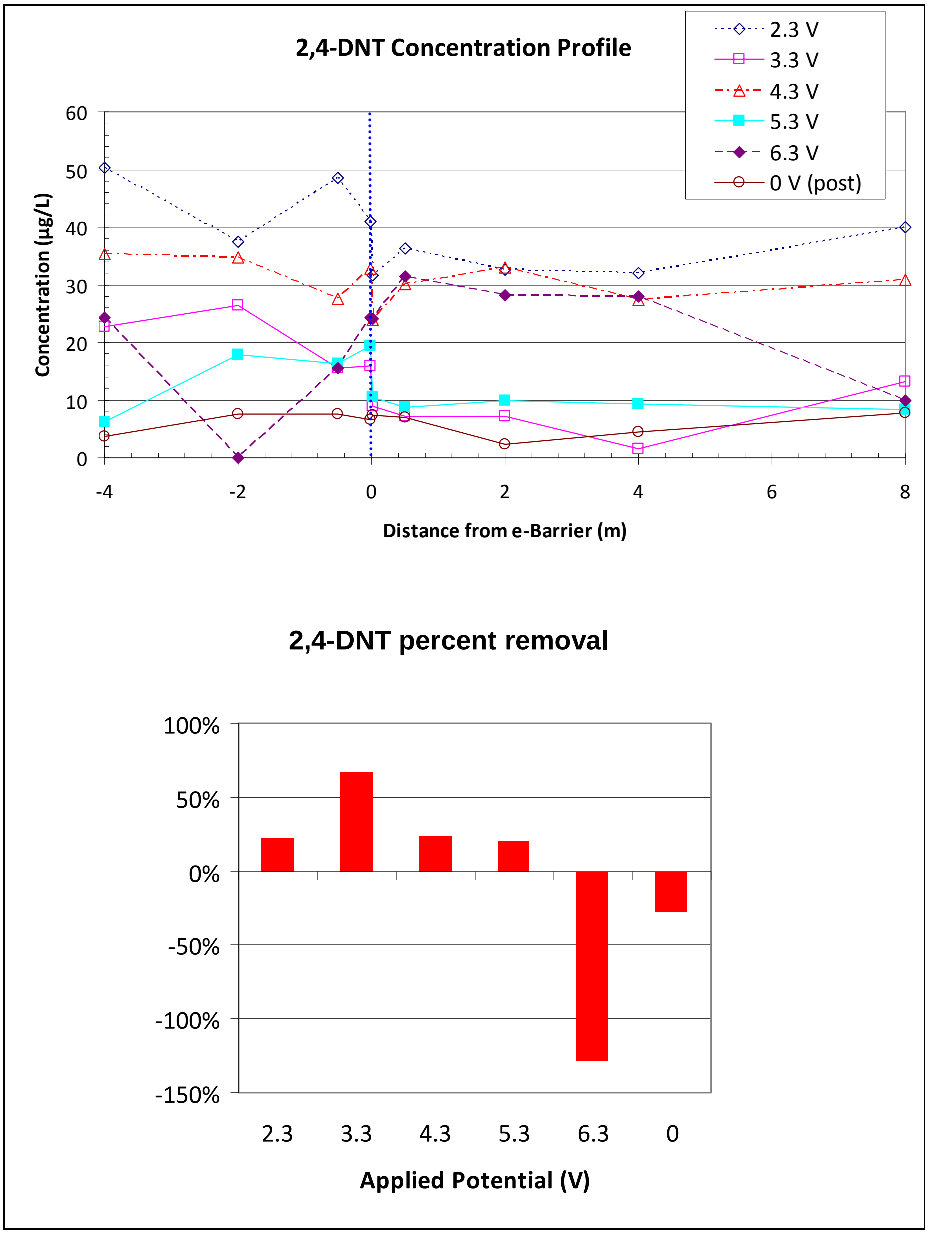


Figure 73 – 2,4-DNT concentration as a function of position, and percent removal as a function of applied voltage.

Treatment of 1,3,5-TNB. Figure 74 shows 1,3,5-TNB concentration as function of position and percent removal for each of the applied voltages. Concentrations range from less than detection limits at 2m/0V to 2,950 µg/L -2m/2.3V. The site cleanup criteria for 1,3,5-TNB is 361 µg/L. While the e^{-}barrier was active, this concentration was achieved only at 4m/3.3V.

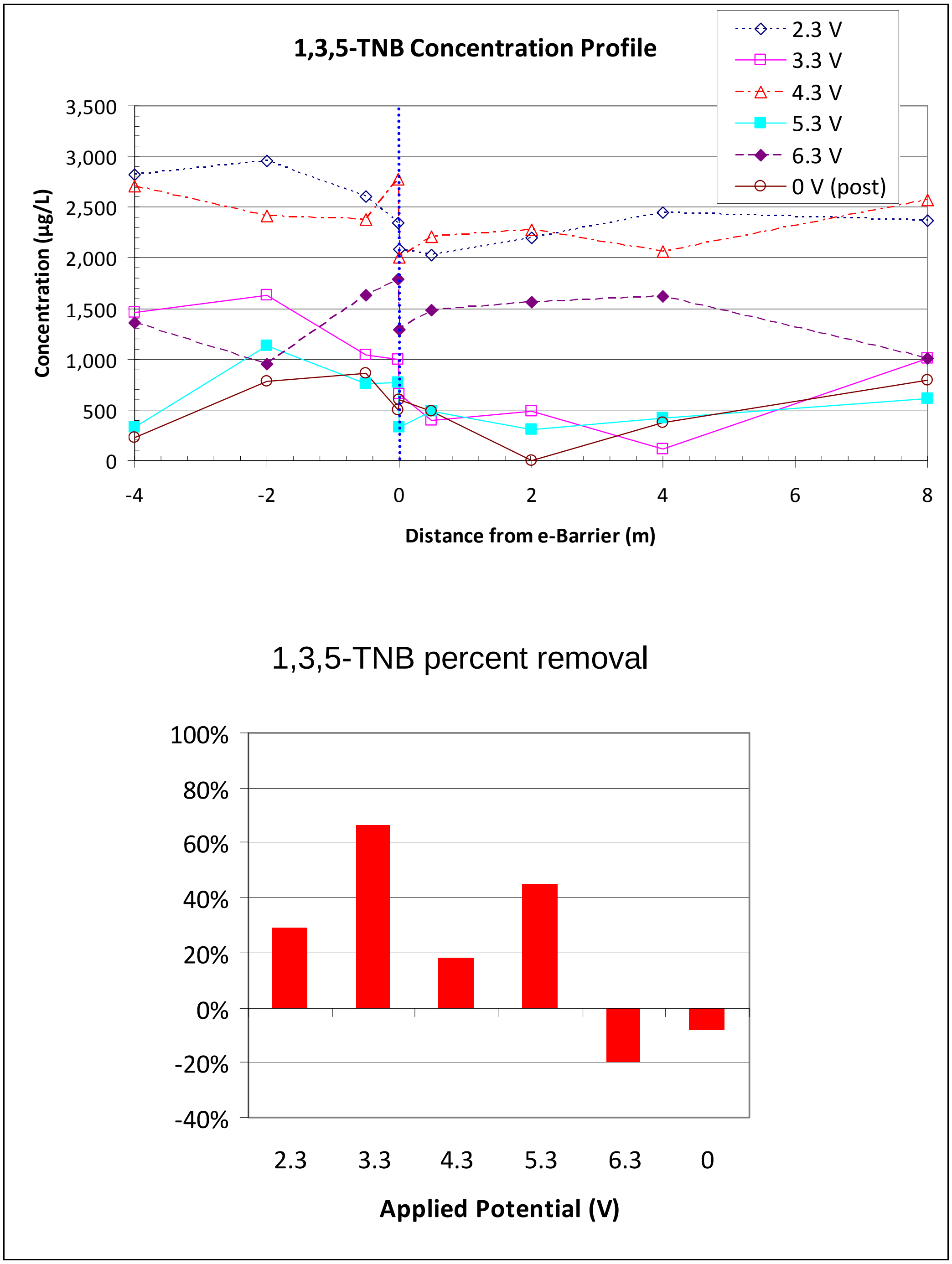


Figure 74 - 1,3,5-TNB concentration as a function of position, and percent removal as a function of applied voltage.

5.1.4 REDUCTIONS IN CONTAMINANT FLUX AT THE E-BARRIER

A primary objective for this project was to resolve the reduction in contaminant flux achieved at the e$^-$barrier. Unfortunately, rigorous analysis of flux reduction is complicated by time variant:

- Upgradient concentrations of target compounds
- Groundwater seepage velocities
- Percent removal of target compounds

Given these complicating factors, Table 14 presents high and low estimates of contaminant flux reduction based on observed high and low upgradient concentrations, the high values of percent removal, the average seepage velocity, the observed porosity of 0.25, and the cross-sectional area of the e$^-$barrier. Results indicate a maximum flux reduction for all contaminants of 1.125 kg/year.

Table 14 – Estimates of high and low contaminant flux reduction

Contaminant	High Upgradient Conc. (ug/L)	Low Upgradient Conc. (ug/L)	High % removal	Seepage Velocity (ft/year)	Cross-sectional Area (ft2)	High Flux Reduction (gm/year)	Low Flux reduction (gm/year)
RDX	2.4	0.02	40	250	240	0.41	0.0034
2,4,6-TNT	1200	0.02	60	250	240	306	0.0051
HMX	12.4	0.02	82	250	240	4.3	0.0070
2,4-DNT	50	0.02	60	250	240	12.7	0.0051
1,3,5-TNB	2950	0.02	64	250	240	802	0.0054
Total						**1125**	**0.0260**

5.1.5 IMPOSED REDOX CONDITIONS

Treatment in the e$^-$barrier is driven by electrically induced shifts in redox conditions. Herein redox conditions are described in terms of Eh referenced to a standard hydrogen electrode (SHE). The following documents redox data acquired using a reference electrode and inorganic redox couples.

Reference Electrode (Denver Instruments AP25 and Orion platinum combination electrode) - Figure 75 presents Eh measurements made at 2.3, 3.3, and 4.3 V. Background values of Eh made prior to startup (Table 3) fall in the range of 323 to 344 mV. At 2.2 V, Eh is reduced below background levels by as much as 200 mV in the immediate vicinity of the e$^-$barrier. At higher voltages Eh becomes elevated above background levels up- and downgradient of the e$^-$barrier by as much as 200 mV while remaining near background levels at the barrier. A clear trend of higher oxidization potential conditions is observed with higher voltages. Interestingly, the elevated Eh values upgradient of the e$^-$barrier may provide an explanation for the disappearance of RDX and HMX upgradient of the e-barrier at higher voltages (see Figure 70 and Figure 72). Unfortunately, Eh values for 5.3 and 6.3 V are not available.

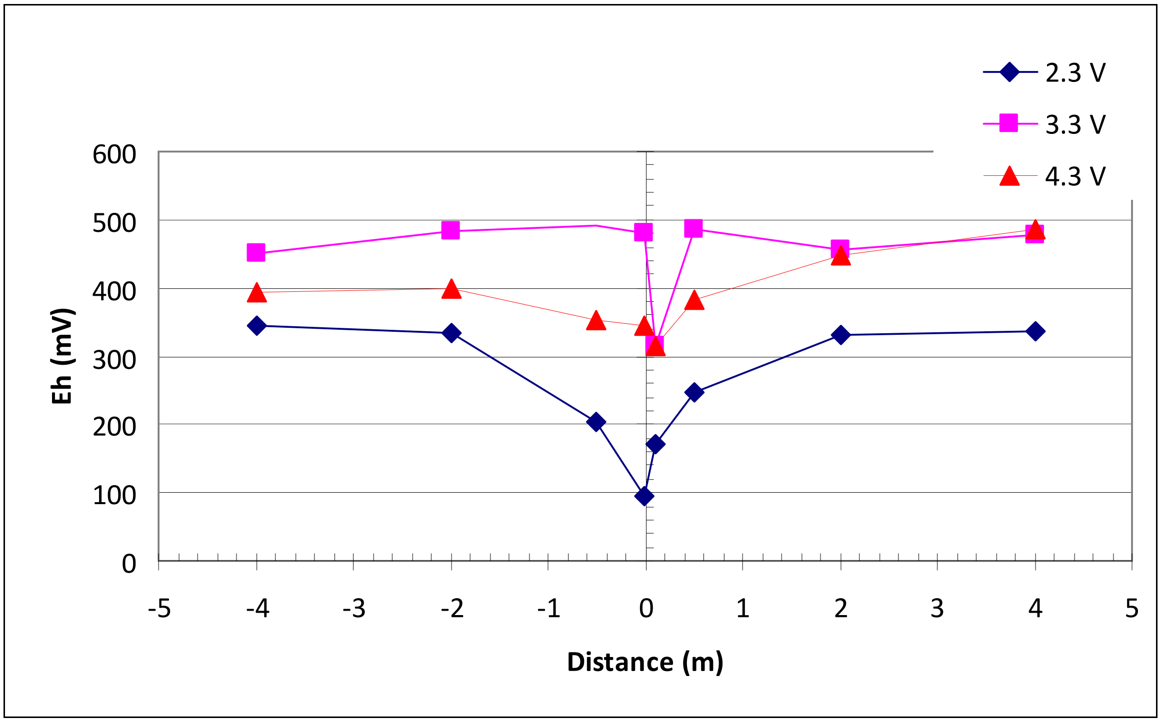


Figure 75 – Eh (SHE) measured on 4/13/2006 (2.3V), 8/29/2006 (3.3V), and 10/10/2006 (4.3V).

Typically, electrically driven shifts in Eh in e^-barriers coincide with shifts in pH. Figure 76 presents pH measurements made at 2.3, 3.3, and 4.3 V. Background values of pH made prior to startup (Table 3) fall in the range of 7.3 to 7.6 with an outlier of 8.0. A primary attribute of the pH data is that it decreases downgradient of the barrier at higher applied voltages.

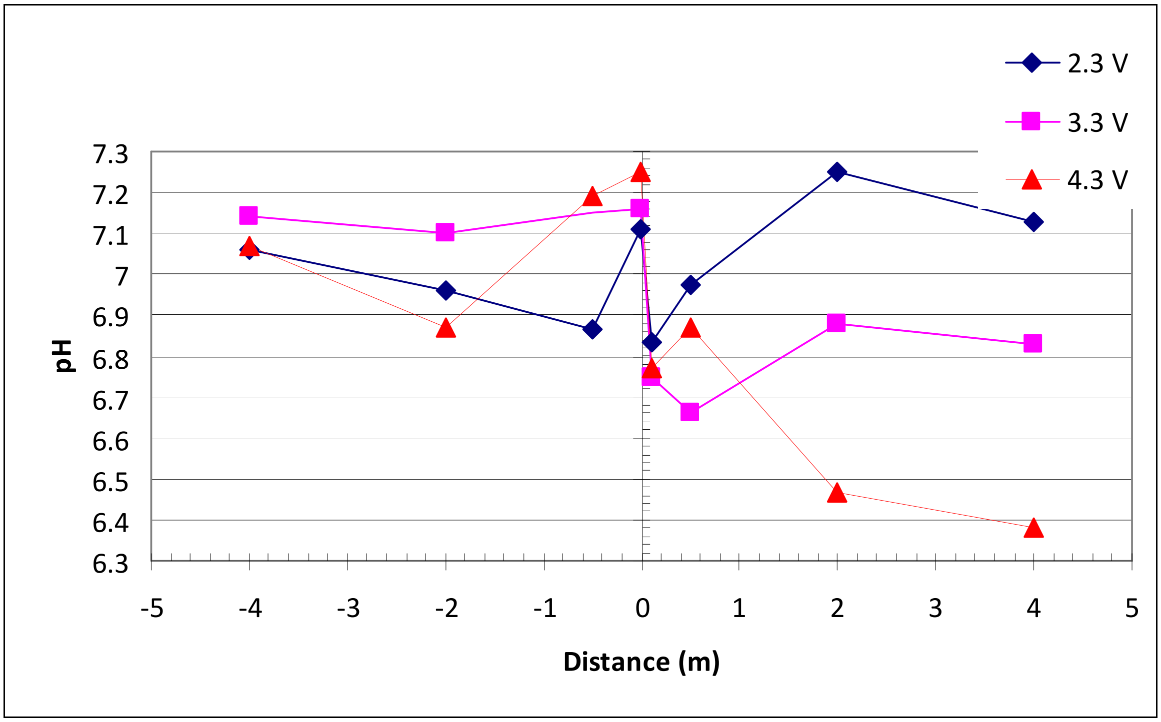


Figure 76 – pH measured at 2.3V (4/13/2006), 3.3V (8/29/2006), and 4.3V (10/10/2006).

Redox Couples – As a cross-check, concentrations of nitrate and ammonia were measured to resolve redox conditions. The results are presented in Table 14. Unfortunately, we have been unable to find corresponding electrode-based Eh values that could be used as a basis for verifying each method in Dr. Gilbert's notes. In general, the Eh values are similar to the background values from Table 3 and lower than the values in Figure 75. A possible explanation for the discrepancy with Figure 75 is that sample preservation failed to prevent equilibration of the redox couple with atmospheric conditions prior to analysis.

Table 15 - Eh calculation parameters and calculated Eh values

LOCATION	APPLIED VOLTAGE (2/28/2007)	NO_3^- CONC. (mg/L)	NO_3^- CONC. (mmol/L)	NH_4^+ CONC (mg/L)	NH_4^+ CONC (mmol/L)	pH	CALCULATED Eh (mV)
4m up	4.3V	0.39	0.006	7.33	0.41	7.07	343
2m up	4.3V	0.39	0.006	5.01	0.28	6.87	359
0.5m down	4.3V	2.4	0.039	2.96	0.16	6.87	367
2m down	4.3V	3.2	0.052	3.34	0.19	6.55	391

In more detail, Table 14 Eh values were calculated from measured concentrations of the NO_3^-/NH_4^+ redox couple. The half-cell redox reaction for the couple is:

$$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$$

From this, the Nernst equation can be used to calculate an Eh value:

$$E_h = E_h{}^0 - 59\,mV\left(\frac{1}{n}\log\frac{[red]}{[ox]} - \frac{m}{n}\,pH\right)$$

Where Eh^0 is the standard oxidation potential for the redox couple, *[red]* is the molar concentration of the reduced species, *[ox]* is the molar concentration of the oxidized species, and *m* and *n* are the stoichiometric coefficients for protons and electrons transferred, respectively, in the half cell reaction. For the NO_3^-/NH_4^+ redox couple, Eh^0 is assigned a value of 878 mV (Benjamin 2002), *m* is 10 and *n* is 8, per the half cell reaction given above. From this, Eh is calculated as follows:

$$E_h = 878\,mV - 59\,mV\left(\frac{1}{8}\log\frac{[NH_4{}^+]}{[NO_3{}^-]} - \frac{10}{8}\,pH\right)$$

5.2 LONG-TERM VIABILITY

The use of a permeable reactive barrier is typically a long-term strategy for managing plumes. As such, the ability to sustain treatment with minimal maintenance is critical. The following reviews the performance of key system components. The basis for most of this review is information collected using the Campbell Scientific Data Logger. Unfortunately, failure of the data logger led to the loss of data collected from November 2006 through March 2007. Also, due to the loss of Dave Gilbert, we have been unable to interpret some of the amperage data that was collected.

5.2.1 SOLAR POWER SUPPLY

Figure 77 presents the reference electrode potentials measured versus the upgradient cathode and the downgradient anode. This data provides a number of useful insights. In regards to the power supply, Figure 77 demonstrates that the e^-barrier was continuously powered for all but a three-week period at the end of 2006 through early 2007. This interruption was due to a malfunction in the DC-DC converter, and not to issues with the power supply. The solar power supply meets the needs of the demonstration. Another key observation from Figure 77 is that all systems worked sufficiently well along the main transect through the e^-barrier to impose a large shift in redox conditions in the aqueous phase for all but three weeks of the 120-week demonstration.

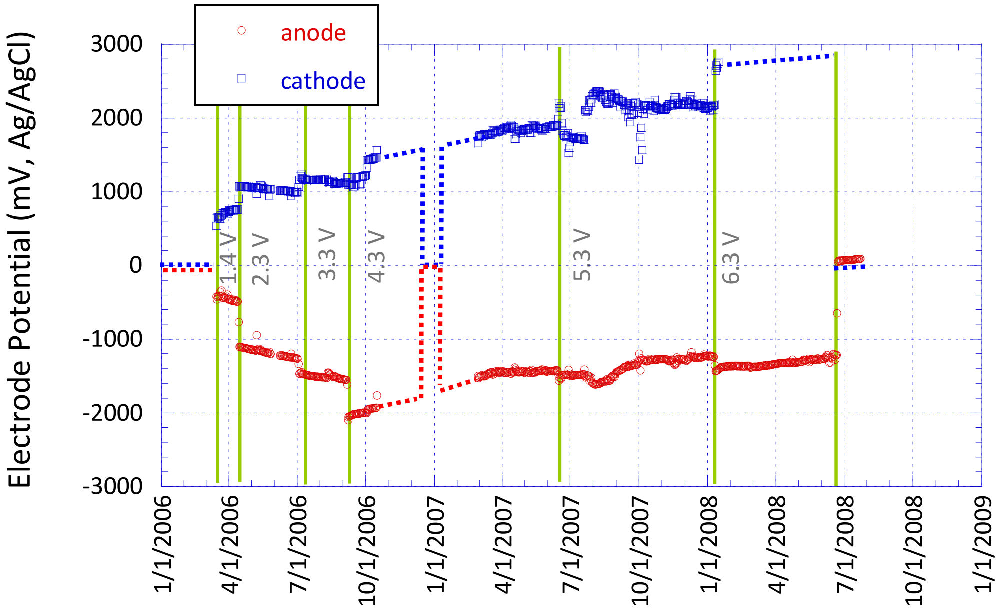


Figure 77 – Cathode (upgradient) and anode (downgradient) reference electrode potentials along the center of the e$^-$barrier (dashed lines are estimated conditions during the period when the data logger failed).

5.2.2 VOLTAGE REGULATION

The solar power supply was configured to provide 48V DC. This was stepped down to the applied voltages at the electrode using two systems. The first system used three separate voltage controllers for panels 1-5, 6-10 and 11-15. Following data presented in Figure 78, the first system applied uniform potential to the three sets of panels up to 4.3 V in early 2007. Subsequently, performance of the first system was impaired. During select periods, no power was applied to panels 1-5, and at 5.3V the applied potentials to panels 6-10 and 11-15 drifted. In January 2007, the three separate controllers were replaced with a single voltage controller for all panels. This system sustained constant applied voltages to all three panel sets until mid-June 2008 when this controller failed. The reason for this failure has not been resolved.

Overall, the voltage controllers were problematic. In large part, this can be attributed to the non-standard application of the equipment we were using. While advice from experts was solicited, it was at times flawed. Future applications of solar power for DC remediation will require refinement of the equipment applied herein. Sustaining applied voltage was not an issue in prior e$^-$barrier demonstrations conducted at F.E. Warren Air Force Base and Canadian Forces Base Borden, Ontario. These applications relied on line power and more conventional AC-DC rectifiers used in cathodic protection.

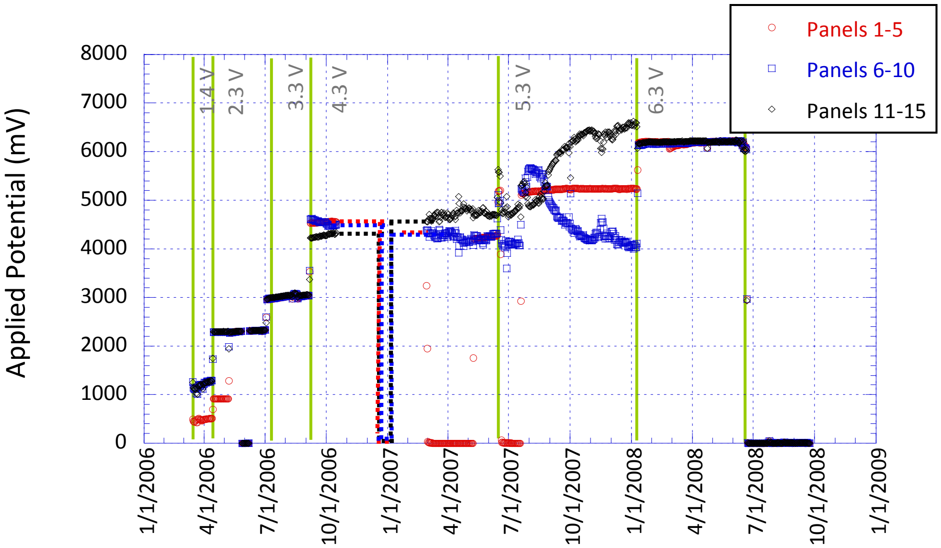


Figure 78 – Applied voltage by panel sets.

5.2.3 POLARITY REVERSAL

Throughout operations of the e$^-$barrier, the polarity of the electrodes was reversed for one hour daily. Controllers for this system worked well until the very end of the demonstration when an aluminum wire connection providing power to electrical relay switches failed. The failure was related to fatigue of the aluminum in a compression connection at a battery. Future systems should avoid using aluminum wiring in compression connections where it can fatigue and resulting in loss of electrical continuity.

5.2.4 ELECTRODES

A primary concern with e$^-$barriers is the longevity of the electrodes. Two causes of possible failure are encapsulation by inorganic precipitates (scale formation) and corrosion. Potential symptoms of electrode failure include:

- Loss of imposed redox conditions in the aqueous phase over time. Per Figure 78, there is no evidence of this.
- Increased head loss across the barrier (plugging). Per Figure 42, there is no evidence of increased head loss across the e$^-$barrier over time.
- Loss of treatment with time. The available performance data provides no indications that the e$^-$barrier's performance was failing over time.
- Loss of current density versus time. Unfortunately, we were unsuccessful in our efforts to collect current data through much of the experiment (see Figure 36). With this we are unable to draw conclusions regarding electrode stability from current data.

From the above, there seems to be no evidence that the electrodes were failing over the 120 weeks of operation. Further insights regarding electrode longevity are presented in the Addendum to the Cost and Performance Report for ER-0112. This suggests the potential for Ti-mmo electrodes can remain viable for extended periods of one of more decades.

5.3 IMPLEMENTABILITY

Throughout the installation and operations, no major implementability issues were encountered. The biggest constraints remain:

- Emplacing the e$^-$barrier panel at a depth greater than a few tens of feet
- Limited apparent depletion of target compounds in field applications
- Cost, as discussed in Section 6

5.4 SUMMARY OF PERFORMANCE RESULTS

Table 15 presents a summary of results relative to the performance objectives.

Table 16 - Performance objectives and results

PERFORMANCE OBJECTIVE	RESULT
Contaminant removal	Unfortunately, results from the demonstration failed to show large improvement in water quality downgradient of the e$^-$barrier. In general, site cleanup goals were not achieved. Decreasing upgradient contaminant concentrations during operations complicates analysis of the results.
Long-term viability	The solar power supply and electrodes were reliable. Problems were encountered with voltage regulators and data logging systems. Similar problem are likely to be avoidable in future systems. Desired shifts in redox potential through the e$^-$barrier were sustained for 120 out of 123 weeks. The three-week down period was associated with the failure of a voltage regulator.
Implementability	No major issues were encountered with implementability. The most significant limitation is that deep installations (> 30 feet) will likely be challenging.

Most critically, the results from the demonstration failed to show large improvement in water quality downgradient of the e$^-$barrier. The following explores possible explanations for this result.

Design, Construction, and Installation - Overall, the design, construction, and installation of the e$^-$barrier went well (see Section 6.2). This included a number of successful design innovations, including use of a four-electrode system, seals at the base of the wall to limit underflow, wing walls at the end of the e$^-$barrier to limit untreated flow around the barrier, vinyl sheet pile sections as a mounting platform for the electrode panel, and solar power supply. With this, we don't see any consequential problems with the design, construction, or installation of the e$^-$barrier.

Operations – Similarly, the operation of the e$^-$barrier went well. Glitches that did occur with voltage controllers and data collections systems seem likely to have had little effect on the performance of the e$^-$barrier along the primary monitoring transect.

Hydrology – The demonstration location involved a thin (2-5 foot) near-surface aquifer in an arid environment. During the demonstration, up to four significant rain events caused 0.5- to 1.5-foot increases in water levels and disruptions in groundwater flow patterns (Figure 42). Coinciding with these storms, contaminants in the unsaturated zone (Figure 51) were likely leached into the saturated zone. Both variable flow patterns and contaminant leaching from the overlying vadose zone are possible explanations for some of the ambiguous water quality data presented in Section 6.1.3.

Limited fraction of total contaminants in the treated phase – Considering groundwater concentration data (Section 6.1.3) and soil concentration (Section 5.7.4), only a small fraction of the total contaminants in the demonstration area is in the water phase in the transmissive sands. Much of the contaminant mass in the demonstration area occurs as sorbed or dissolved phases in low permeability zones. This is a critical limitation, since the e^-barrier only treats contaminants in the phase that is passing through the barriers via the transmissive zone. With this, it is possible that the effects of the e^-barrier on mobile dissolved phase constituents is being masked by the release of immobile sorbed contaminants and/or immobile aqueous phase contaminants in zones of lower permeability (e.g., interbeds of silt in the alluvium or the underlying Pierre Shale).

Table 16 illustrates the above challenge with site data. The first column presents the highest concentrations of contaminants of concern in groundwater-based data, based on information presented in Section 6.1.3. The second column presents the highest total concentrations of contaminants present in soils, based on data presented in Section 5.7.4. Using concentration data and assuming a porosity of 30%, the third column provides estimates of the fraction of total contaminant mass per unit volume of porous media that is present in the aqueous phase. Observed fractions of contaminants in the aqueous phase range from 0.02 to 0.004. Converting these values to percentages, as little as 2 to 0.4% of the contaminant mass present is in an aqueous phase that can be addressed directly by the e^-barrier.

Table 17 – Comparison of high concentrations of contaminants of concern in groundwater to total concentrations

	HIGH VALUE IN GROUNDWATER (µg/L)	HIGH VALUES IN SOILS (TOTAL CONCENTRATION) (µg/kg)	GROUNDWATER CONC. MASS PER UNIT VOLUME /TOTAL CONC. MASS PER UNIT VOLUME
RDX	2.4	100	0.004
1,3,5-TNT	1,200	5,000	0.04
HMX	13	100	0.02
2,4-DNT	50	2,000	0.004
1,3,5-TNB	3,000	30,000	0.02

5.5 QA/QC

The quality assurance project plan (QAPP) is presented in the project Demonstration Plan. QA/QC included duplicate samples, matrix spike samples, field blanks, and split samples. Results are as follows:

- The average RPD for the 12 duplicate samples was 34%. The reason for the high relative variance was likely the low absolute levels of RDX measured (e.g., less than 1 µg/L). For TNB, detected concentrations were much higher throughout the study (ranging from 500 to 4,000 µg/L). The RPD for TNB was 8.0%, with none of the values outside of the 20% tolerance.

- The average recovery for matrix spike samples was 103% for RDX. The range of recoveries was 72 to 133%. Spike amounts for other analytes could not be located in Dr. Gilberts notes; unfortunately, spike recoveries could therefore not be calculated.

- Three field blank samples were found in the output data analysis. All were non-detect for RDX, HMX, 2,4,6-TNT, TNB, and 2,4-DNT. If more field blanks were collected, results have not been located.

- Two split samples were collected for confirmatory analysis by an external laboratory (TestAmerica, Arvada, Colorado). RDX was not detected in the external laboratory-analyzed samples (reporting limits 10 µg/L). The relative percent difference values for TNB in these samples were 11 and 23%.

6.0 COST ASSESSMENT

Following the ESTCP Final Report Guidance (ESTCP, 2008) this section presents costs associated with e$^-$barrier implementation. This includes a cost model, cost drivers, and full-scale cost analysis.

6.1 COST MODEL

Table 17 presents installation costs for e$^-$barriers based on data collected from the demonstration. Building on the data, capital costs are estimated as:

$$\$Capital = \$33{,}000 + (\frac{\$675}{ft^2} * Plume\_x\sec tion\_area) \qquad \textbf{Equation 1}$$

Table 18 presents operations and maintenance costs. Building on this data, lifecycle operations and maintenance costs are estimated as:

- With full replacement every ten years

$$\$O \,\&\, M = \# \, years * \left(\frac{\$30{,}000}{year} + \frac{\$67 * Plume\_x\sec tion\_area}{ft^2 * year} \right) \qquad \textbf{Equation 2}$$

- Without full replacement every ten years

$$\$O \,\&\, M = \# \, years * \frac{\$30{,}000}{year} \qquad \textbf{Equation 3}$$

Text in the remainder of this section provides the basis for cost information in Table 17 and Table 18.

Table 18 - e^{-}barrier installation costs

COST ELEMENT	COST TYPE	DESCRIPTION	COST	UNIT COST[1]
Laboratory studies	Labor	Engineer/project lead	$6,000	Lump sum
		Student (graduate and undergraduate)	$2,000	Lump sum
	Materials	Reactors and disposables	$1,500	Lump sum
	Instrument use	GC/MS and HPLC	$800	Lump sum
	Subtotal		**$10,300**	**Lump Sum**
Baseline characterization	Labor	Engineer/project lead	$32,000	$133.33/ft^2
		Student (graduate and undergraduate)	$9,000	$37.50/ft^2
	Materials	Disposables	$1,000	$4.17/ft^2
	Instrument use	GC/MS and HPLC	$3,000	$12.50/ft^2
	Subtotal		**$45,000**	**$187.50/ft^2**
Materials and panel fabrication	Materials (e-barrier)	Titanium/MMO mesh electrode	$11,020	$45.91/ft^2
		Vinyl sheet pile	$3,208	$13.37/ft^2
		Geonet/geotextile	$246	$1.03/ft^2
		Reference electrodes	$605	$2.50/ft^2
	Materials (electrical system)	Solar array	$19,595	$81.65/ft^2
		Data logger/ and communication system	$2,910	$12.13/ft^2
		Miscellaneous hardware	$2,742	$11.43/ft^2
	Labor	Engineer/project lead	$11,000	$45.83/ft^2
		Student (graduate and undergraduate)	$9,000	$37.50/ft^2
	Subtotal		**$60,326**	**$251.35/ft^2**
Installation	Contractor	Mobilization	$22,335	**Lump Sum**
		Installation	$7,100	$29.58/ft^2
	Utilities	Solar Array Installation	$1,776	$7.40/ft^2
	Labor	Engineer/project lead	$17,000	$70.83/ft^2
		Student (graduate and undergraduate)	$6,000	$25.00/ft^2
	Waste disposal	Offsite disposal of excavated soils as a non-hazardous waste	$2,156	$8.98/ft^2
	Subtotal		**$54,421**	**$234.85/ft^2**
Total installation costs	**Lump sum costs**		**$32,635**	**$32,635**
	Per ft^2 costs		**$161,903**	**$675/ft^2**

1 – Unit cost presented based on dividing costs by the area of the intercepted plume's maximum water level (240 ft^2).

Table 19 - e^-barrier operations and maintenance costs

COST ELEMENT	COST TYPE	DESCRIPTION	COST	UNIT COST[1]
Operations costs	Labor and expenses	Monthly downloads of data via a wireless connection, review of monthly data, annual inspections, and annual water quality monitoring.	\$30,000/year	Lump Sum
Maintenance costs	Labor and expenses	Assuming a ten year life cycle, cost for all system components (1/10 of per ft^2 installation costs)	\$31,920/year	\$66.50/ft^2/year
Total operations and maintenance costs	**Lump sum costs**		**\$30,000/year**	**\$30,000/year**
	Per ft^2 costs (assuming full replacement every 10-years)		**\$31,920/year**	**\$66.50/ft^2/year**

1 – Unit cost presented based on dividing costs by the area of the intercepted plume's maximum waterlevel (240 ft^2).

Laboratory Studies - Prior to field activities, laboratory studies were conducted to validate e^-barrier effectiveness in treating contaminants of concern and to aid in resolving operational parameters. Laboratory studies included 1-D column studies and 2-D tank studies. Related costs include labor, materials, and analysis. Analyses were conducted in-house by CSU.

Baseline Characterization - Baseline characterization activities commenced June 2005 and continued through e^-barrier installation in January of 2006. Related activities included installation of 11 temporary wells, water quality sampling, aquifer testing, and conducting site topographical surveys. These activities provided a basis for final e^-barrier design. Relevant information includes groundwater flow direction, seepage velocity, concentrations of target contaminants, and dissolved organic and inorganic species that may affect e^-barrier performance.

Materials and Fabrication - Material and fabrication costs in Table 17 include e^-barrier components, electrical system components, and labor for fabrication. Components of the e^-barrier include:

- Titanium/MMO electrode material: the active component of the e^-barrier which drives sequential oxidation/reduction of contaminants in groundwater,
- Vinyl sheet piling: the "backbone" of the e^-barrier, or the frame to which electrode materials were attached
- Geonet/geotextile: provide spacing between electrodes
- Ag/AgCl reference electrodes: provide reference for measured applied potential at electrode surface

Electrical system components include:

- Solar array: solar panels, batteries, and related controllers
- Data logger and communications system: used to log applied potentials and run remote data acquisition
- Miscellaneous hardware: wiring, electrical relays, conduit, fittings, and monitoring systems.

e$^-$Barrier components were purchased independently and panels were then fabricated at CSU. Labor costs include cutting holes into vinyl sheet piling, mounting electrode panels, and installation of groundwater quality monitoring systems. Final fabrication tasks, including installation of groundwater monitoring ports, were completed at the site prior to installation.

Installation - Installation costs presented in Table 17 include contractor costs and CSU labor costs. A general contractor (Metrix) was retained for e$^-$barrier installation. The contractor cost presented includes mobilization, soil excavation, e$^-$barrier emplacement, backfilling, solar array installation, cleanup, disposal, and demobilization. CSU labor costs include support and oversight of installation as well as startup tasks completed after installation and before system startup. These tasks included wiring and testing of components.

Primary installation tasks were completed during the week of January 30, 2006. Primary installation tasks (soil excavation, e$^-$barrier emplacement, and backfilling) required approximately two days to complete. Subsequent tasks included wiring and testing the electrical components. Prior to startup, adequate time was allowed to re-establish groundwater flow through the e$^-$barrier. The system began operation on March 14, 2006.

Waste Disposal – Trench cuttings were loaded into roll-off boxes and subsequently transported to the Southside Landfill for disposal as nonhazardous waste.

Operation Costs - Operation presented in Table 18 reflects the labor and expense costs from the demonstration and the anticipated level of effort associated with monthly downloads of data via a wireless connection, review of monthly data, annual inspections, and annual water quality monitoring.

Maintenance Costs – Maintenance costs presented in Table 18 are based on the assumption that the e$^-$barrier and all of its components would need to be replaced every ten years.

6.2 COST DRIVERS

Building off of Table 17 and Table 18, Figure 79 presents the distribution of the lifecycle costs for a 10-year operation period for a system based on the demonstration barrier attributes. A primary assumption employed in this distribution is that operation would continue after ten years and that the entire system would need to be replaced every ten years. Interestingly, operations (monthly downloads of data via a wireless connection, review of monthly data, annual inspections, and annual water quality monitoring) at $30,000/year is the largest cost. This is followed by maintenance cost (based on full replacement every ten years) and capital cost (composed of characterization, materials, panel fabrication, and installation).

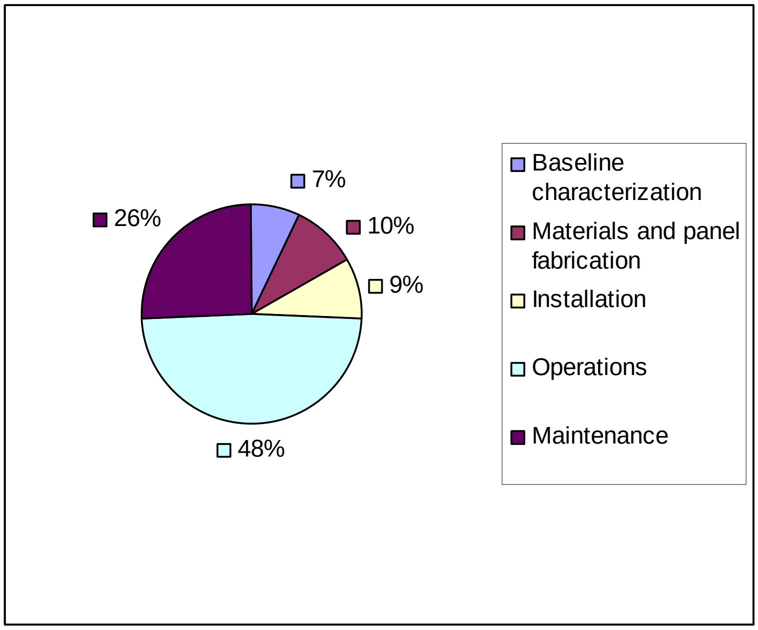


Figure 79 – Distribution of lifecycle cost for a ten-year period (operations and maintenance cost assumes complete replacement of all components every 10 years).

6.3 FULL-SCALE COST ESTIMATE

Following the Mulch Barrier Wall Demonstration Cost and Final Technical Report (GSI Environmental, 2008 – ER-0426), Table 19 presents a design basis for a full-scale system. Using Table 19 attributes and Equations 1-3, Table 20 presents estimates of cost based on common metrics for water treatment. Note that care should be used in applying this cost estimation processes to other site. In particular, sites with deeper installation depths may have higher installation costs. One factor not taken into account that could provide lower costs is economies of scale. It is anticipated that at most sites this could provide a 10-20% reduction in costs.

Table 20 – Basis for full-scale cost estimates

FEATURES	DESCRIPTION
Barrier Length	500 feet
Saturated thickness	5 feet
Groundwater flux (Darcy velocity)	32 feet/yr
Annual discharge (Area * Groundwater flux)	581,000 gal/year
Influent RDX concentration	3 μg/L
Effluent RDX concentration [1]	0.02 μg/L
Annual mass of RDX treated (ΔC * Annual Discharge)	0.0066 kg/yr

1) Based on observed downgradient RDX concentrations less than detection limits downgradient of the e^-barrier at 6.3V.

Table 21 – Estimate of 10-year lifecycle costs for a full-scale system using a common metric for water treatment systems

METRIC	TOTAL CAPITAL, OPERATIONS, AND MAINTENENACE COST ($) FOR 10 YEARS WITH FULL REPLACEMENT EVERY TEN YEARS	TOTAL CAPITAL, OPERATIONS, AND MAINTENENACE COST ($) FOR 10 YEARS WITHOUT FULL REPLACEMENT EVERY TEN YEARS
10-year lifecycle cost	$3,700,000	$2,200,000
Cost per ft^2 of intercepted plume	$1,500 /ft^2	$810 /ft^2
Cost per 1000 gallons treated	$640/ 1000 gallons	$350/ 1000 gallons
Cost per kg treated	$56,000,000 / kg	$31,000,000 / kg

6.4 COST COMPARISION TO COMPETING TECHNOLOGIES

In addition to this project, ESTCP has funded two other PRB demonstrations for energetic compounds:

- Remediation of 2,4,6-TNT and RDX in Groundwater Using Zero-Valent Iron Permeable Reactive Barriers (ER-0223), and

- Treatment of RDX and/or HMX Using Mulch Biowalls (ER-0426)

Using data from these projects, Table 21 compares the costs of e$^-$barrier to other promising barrier technologies for energetic compounds. The basis for the estimates is a 10-year lifecycle analysis and the design basis introduced in Table 20. Overall, bark mulch has the lowest cost. Both bark mulch and ZVI are less than one-third the cost of an e$^-$barrier. Also presented in Table 21 are e$^-$barrier costs generated from our earlier ESTCP e$^-$barrier demonstration conducted at F.E. Warren AFB (ER-0112). Cost for the Pueblo project are a third higher than the estimates of the e$^-$barrier cost developed from the F.E. Warren effort. Higher costs for the Pueblo project reflect use of a solar power supply, use of a four electrode system (versus three at F.E. Warren), the absence of a discount for economies of scale, and more current pricing for materials.

Table 22 – Comparison of PCD e$^-$barrier costs to cost for other reactive barrier technologies

METRIC	E$^-$BARRIER (THIS PROJECT ER-0519)	BARK MULCH (ER-0426)	ZERO VALENT IRON (ER-0223)	E$^-$BARRIER F.E. WARREN AFB (ER-0119)
10-year lifecycle cost w/o replacement	$2,200,000	$630,000	$680,000	1,300,000
Cost per ft^2 of intercepted plume	$810 /ft^2	$250/ft^2	$270/ft^2	$530/ft^2
Cost per 1000 gallons treated	$350/ 1000 gallons	$110/ 1000 gallons	$116/ 1000 gallons	$230/ 1000 gallons
Cost per kg treated	$31,000,000/ kg	$9,600,000/ kg	$10,000,000/ kg	20,000,000 /kg

Note that all technologies have annual monitoring costs of $30,000/year.

7.0 IMPLEMENTATION ISSUES

7.1 ENVIRONMENTAL CHECKLIST AND REGULATORY ISSUES

The following describes steps involved in obtaining permission to conduct the e^-barrier field demonstration.

1) Permission was obtained from Base Personnel, State Regulators, and USEPA regulators. This involved:
    a) Initial discussions
    b) Providing work plans for review and approval
2) Utility clearances were obtained for all subsurface investigations and excavations

As no chemicals are introduced, and no known adverse byproducts are produced, no special permits were required. The primary issues with the e^-barrier installation were standard worker safety concerns encountered at construction sites where potentially hazardous compounds are present in soil and water.

7.2 END-USER ISSUES

The vision behind developing the e^-barrier has been the potential of developing a new technology that has significant advantages in terms of cost and/or performance. Through this and two earlier field demonstrations, numerous technical challenges have been met and overcome. Key among these has been the identification of stable electrode materials, developing systems for installation, and automation of operations. While the technology has been proven to be implementable, it seems that it has failed in reaching the goal of having significant advantages in terms of cost and/or performance for energetic compounds. In particular, it appears that iron and bark mulch barrier are likely to be less expensive and more effective than the e^-barrier. In part, this observation is driven by the advancements with iron and bark mulch barriers that have occurred concurrently with the development of e^-barrier. Given the above observations, it seems that the future of e^-barrier for energetic compounds is limited. At best, its niche may be sites where iron or bark mulch are ineffective for the target contaminants and/or other constraining attributes (such inorganic constituent that drive adverse plugging) hinder other applications.

As a footnote, technology developed through advancement of the e^-barrier is currently being spun into other novel remediation technologies. These include:

- Above-ground water systems for point-of-use groundwater treatment - The vision is that point-of-use treatment of groundwater is an emerging solution for large and dilute plumes, and that electrolytic process can be a critical component of practical treatment systems.

- *In situ* systems for oxygen delivery - Components of the e^-barrier technology are currently being considered for delivery of oxygen into soils and groundwater at sites impacted by petroleum hydrocarbons.

8.0 REFERENCES

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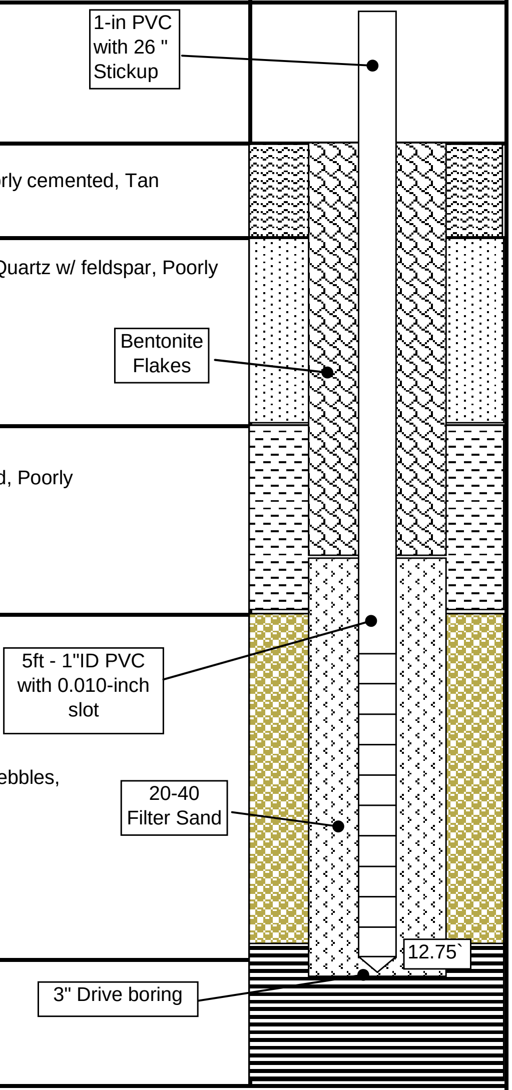
Appendix A. Soil Boring Logs

Soil Boring **Colorado State University - Center for Contaminant Hydrology**

Project Number 532463	**Boring No.** ESTCP #1		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** -TOC 4633.48 Grade 4631.31	
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.1	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	**Rec.**	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Moderately sorted, Silt w/ fine sand, Poorly cemented, Tan
2		Sand, Moderately sorted, Fine to medium, Quartz w/ feldspar, Poorly cemented, Light pink
3	3`	
4		
5		
6		Clay, Moderatley sorted, Clay with fine sand, Poorly cemented, Tan with iron stains
7		
8	3`	
9		
10		Sand, Poorly sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
11		
12		
13	5`	
14		Shale, Moderately Cemented, Black
15		Total Depth 15`

Startigraphy & Well Completion



Development, ~ 6L, Mud to clear, Good yield

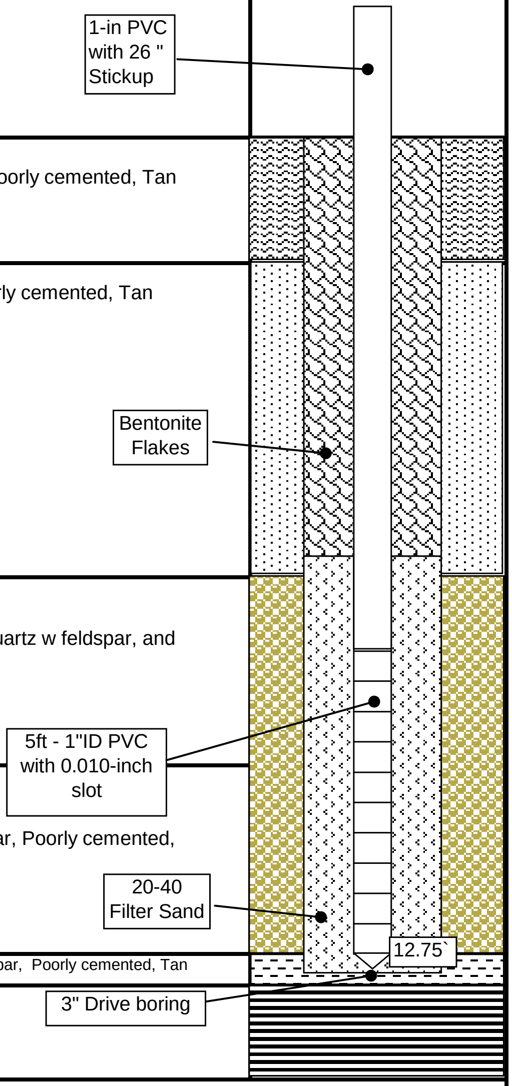
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP #2		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.44	Grade 4631.27
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.07	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Moderately sorted, Silt w/ fine sand, Poorly cemented, Tan
2		
3	4`	Sand, Moderately sorted, Fine with silt, Poorly cemented, Tan
4		
5		
6		
7		
8	3`	Sand, Moderately sorted, Fine to coarse, Quartz w feldspar, and microcline, Poorly cemented, Light pink
9		
10		
11		Sand, Well sorted, Coarse, Quartz w feldspar, Poorly cemented, Pink
12	3`	
13		Clay, Poorly sorted, Clay with coarse sand, Quartz w feldspar, Poorly cemented, Tan
14		Shale, Moderately Cemented, Black
15		

Startigraphy & Well Completion



Total Depth 15`

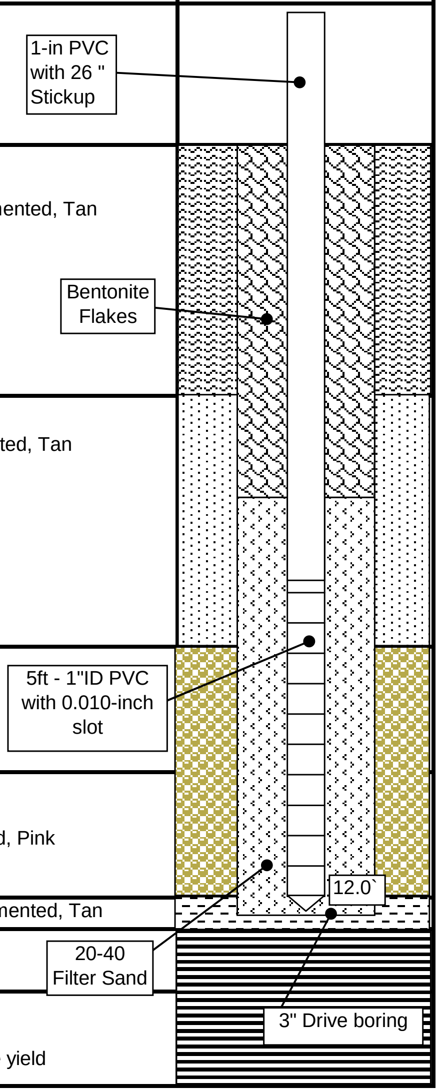
Development, ~ 6L, Mud to clear, Good yield

Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP #3		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.62 Grade 4631.45	
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4622.95	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	**Rec.**	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color	**Startigraphy & Well Completion**
-2			
-1			
0			
1		Silt, Moderately sorted, Silt w/ fine sand, Poorly cemented, Tan	
2			
3	3`		
4			
5		Sand, Moderately sorted, Fine w/silt, Poorly cemented, Tan	
6			
7			
8	3`		
9		Sand, Moderately sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light pink	
10			
11		Sand, Well sorted, Ccoarse, Quartz w/ feldspar and microcline, Poorly cemented, Pink	
12	3.5`	Clay, Poorly sorted, Clay with coarse sand, Poorly cemented, Tan	
13		Shale, Moderately Cemented, Black	
14		Total Depth 13.5`	
15		Development, ~ 3L, Mud to clear, Moderate yield	



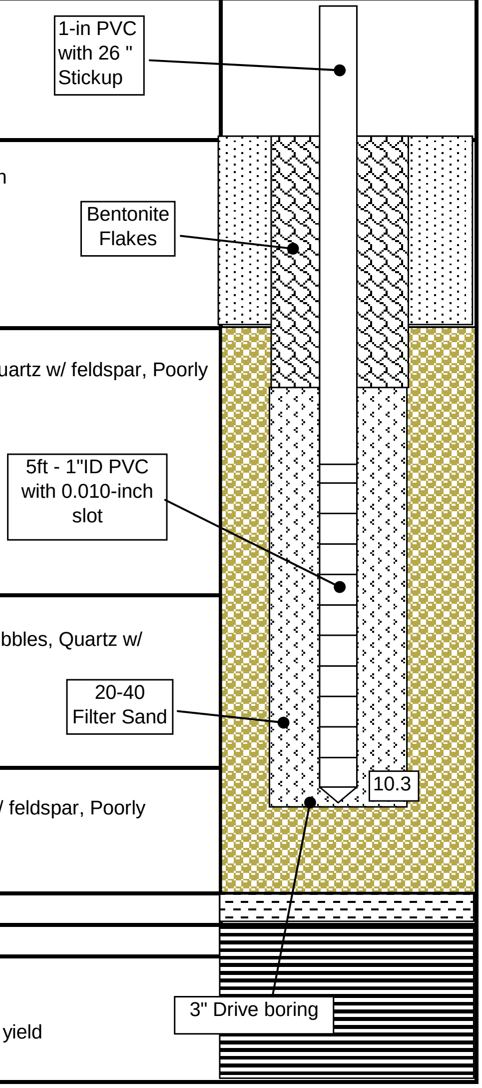
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP #4		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.25	Grade 4631.09
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.18	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Sand, Well sorted, Fine,Poorly cemented, Tan
2		
3	3`	
4		Sand, Moderately sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light pink
5		
6		
7		
8	2.5`	Sand, Moderately sorted, Medium to coarse w pebbles, Quartz w/ feldspar, Poorly cemented, Light pink
9		
10		
11		Sand, Well sorted, Coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
12	3`	Clay, Well sorted, Clay, Poorly cemented, Tan
13		Shale, Moderately Cemented, Black
14		Total Depth 13` Development, ~ 2L, Mud to clear, Low yield
15		

Startigraphy & Well Completion



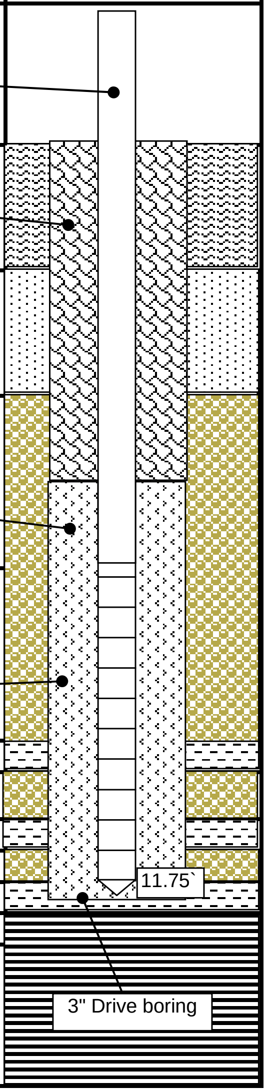
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP #5		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.70	Grade 4631.54
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.03	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2 -1 0		
1 2		Silt, Well sorted, Silt, Poorly cemented, Tan
3 4		Sand, Well sorted, Fine, Poorly cemented, Tan
5 6		Sand, Moderately sorted, Medium to coarse, Quartz, Poorly cemented, White
7 8 9		Sand, Moderately sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light Pink
10		Clay, Poorly sorted, Clay with coarse sand, Poorly cemented, Tan with iron stains
		Sand, Moderately sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light Pink
11		Clay, Poorly sorted, Clay with coarse sand, Poorly cemented, Tan with iron stains
		Sand, Moderately sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light Pink
12		Clay, Poorly sorted, Clay with coarse sand, Poorly cemented, Tan with iron stains
		Shale, Moderately Cemented, Black
13 14 15		Total Depth 13` Development, ~ 1.5L, Turbid to clear, Poor yield

Startigraphy & Well Completion



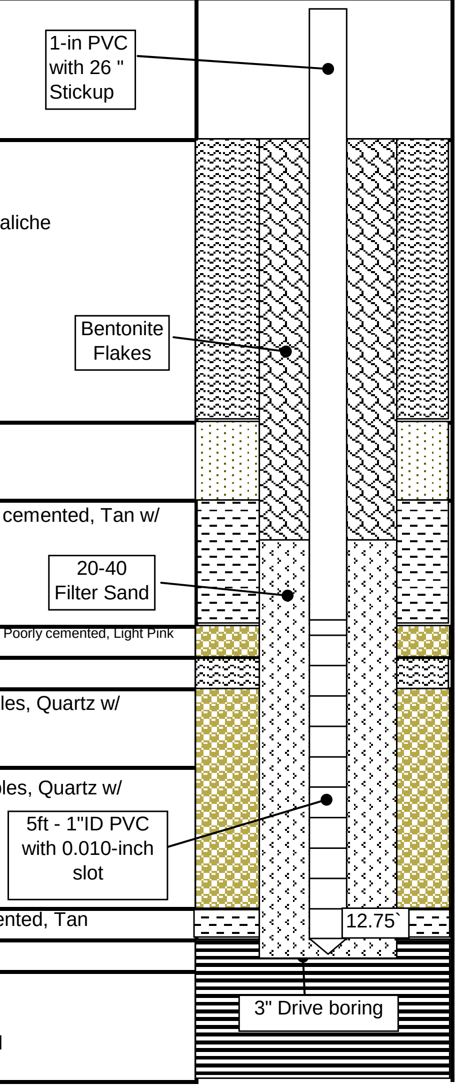
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 6		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4634.68	Grade 4632.51
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.16	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Well sorted, Silt , Poorly cemented, Tan, Minor caliche
2		
3	3`	
4		
5		Sand, Well sorted, Fine , Poorly cemented, Tan
6		Clay, Moderatley sorted, Clay with fine sand, Poorly cemented, Tan w/ iron stains
7	3`	
8		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Light Pink Silt, Well sorted, Silt , Poorly cemented, Tan
9		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Light Pink
10		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar and microcline, Poorly cemented, Pink
11		
12	3.5`	Clay, Well sorted, Clay with fine sand, Poorly cemented, Tan
13		Shale, Moderately Cemented, Black
14		Total Depth 13.5` Development, ~ 4L, Clear, Moderate yield
15		

Startigraphy & Well Completion



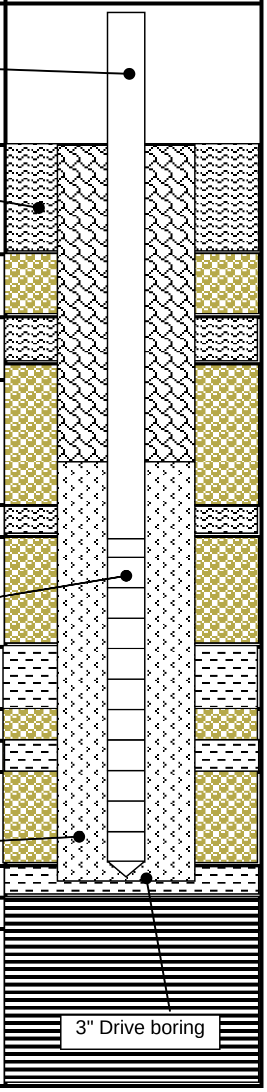
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 7		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4634.29	Grade 4632.13
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4622.86	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	**Rec.**	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Well sorted, Silt, Poorly cemented, Tan
2		Sand, Poorly sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
3		Silt, Well sorted, Silt, Poorly cemented, Brown
4		
5		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
6		Silt, Well sorted, Silt, Poorly cemented, Brown
7		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
8		Clay, Poorly sorted, Clay with fine to coarse sand, Poorly cemented, Tan
9		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink
10		Clay, Poorly sorted, Clay with fine to coarse sand, Poorly cemented, Tan
11		Sand, Well sorted, Coarse, Quartz w/ feldspar, Poorly cemented, Pink
12		Clay, Well sorted, Clay, Poorly cemented, Gray Shale, Moderately Cemented, Black
13		Total Depth 13.5`
14		Development, ~ 5L, Clear with some gravel pack, nerar steady flow, Good yield
15		

Startigraphy & Well Completion



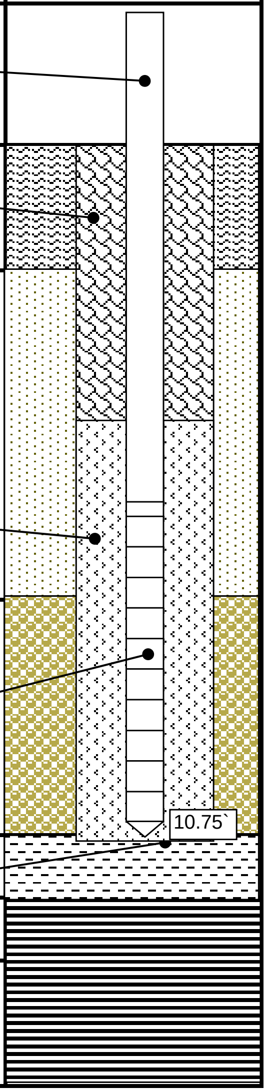
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 8		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.32	Grade 4631.16
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.00	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

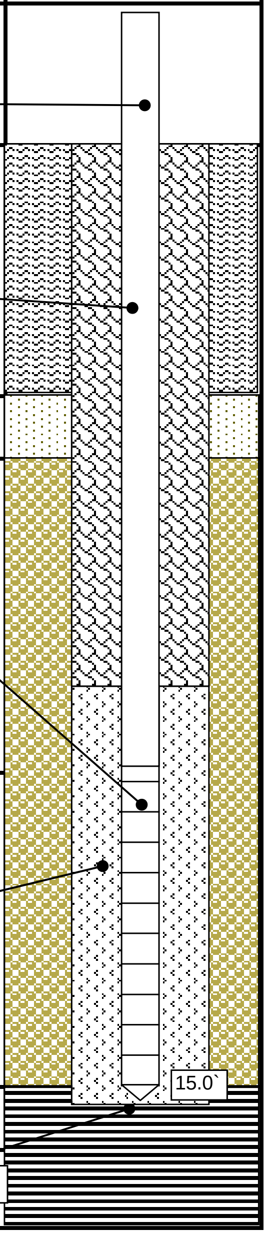
Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Well sorted, Silt , Poorly cemented, Tan
2		
3		Sand, Moderately sorted, Fine to medium, Quartz, Poorly cemented, Light brown
4		
5		
6		
7		
8		Sand, Well sorted, Medium to coarse, Quartz w/ feldspar, Poorly cemented, Light pink
9		
10		
11		Clay, Well sorted, Clay, Poorly cemented, Tan
12		Shale, Moderately Cemented, Black
13		Total Depth 13`
14		Development, ~ 3L, Clear, Low yield
15		

Startigraphy & Well Completion



Soil Boring   Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 9		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4635.47	Grade 4633.30
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.24	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color	**Startigraphy & Well Completion**
-2 -1 0			
1 2 3 4	3`	Silt, Moderately sorted, Silt w/ fine sand, Poorly cemented, Tan	
5		Sand, Well sorted, Fine, Poorly cemented, Tan	
6 7 8 9 10	3`	Sand, Poorly sorted, Fine to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Pink	
11 12 13 14 15	3`	Sand, Moderately sorted, Coarse with pebbles, Quartz w/ feldspar, Poorly cemented, Pink	
16	1`	Shale, Moderately Cemented, Black	

Total Depth 16`

Development, ~ 10L, Mud to clear, Good yield

Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 10		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC	Grade
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color	**Startigraphy & Well Completion**
-2 -1 0			**No Well Installed**
1 2		Silt, Well sorted, Silt , Poorly cemented, Tan	▨
3 4		Sand, Moderately sorted, Fine to medium, Poorly cemented, Tan	░
5 6 7 8 9		Sand, Poorly sorted, fine to coarse, Quartz, Poorly cemented, White	▩
10		Shale, Moderately Cemented, Black	☰
11 12		Total Depth 10.0` No Well Installed	☰

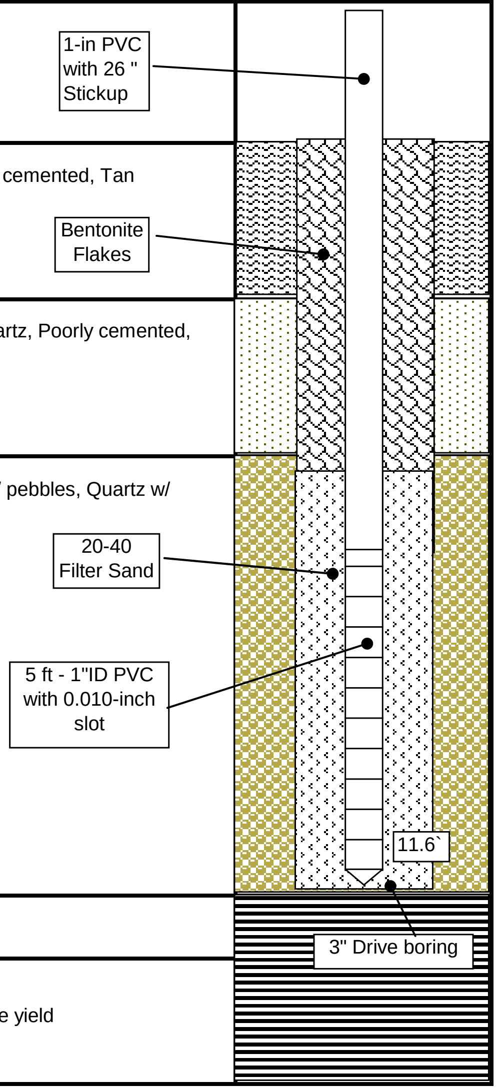
Soil Boring

Colorado State University - Center for Contaminant Hydrology

Project Number 532463	**Boring No.** ESTCP # 11		Sheet 1 of 1
Project ESTCP-PCD e-barrier	**Location** Between Ponds	**Elevation** - TOC 4633.63	Grade 4631.47
PSA	**Drilling Equipment** GeoProbe Direct Push		
Water Level 4623.16	**Start** 6/21/05	**Finish** 6/21/05	**Logger** Tom Sale

Interval	Rec.	**Soil Description** - Soil, Grain size distrib, Mineralogy, Cementation, Color
-2		
-1		
0		
1		Silt, Moderately sorted, Silt w/fine sand, Poorly cemented, Tan
2		
3	3`	Sand, Moderately sorted, Fine to medium, Quartz, Poorly cemented, White
4		
5		
6		Sand, Moderately sorted, Medium to coarse w/ pebbles, Quartz w/ feldspar, Poorly cemented, Light pink
7		
8	2`	
9		
10		
11		
12	3`	
13		Shale, Moderately Cemented, Black
14		Total Depth 13` Development, ~ 4L, Clear, Moderate yield
15		

Startigraphy & Well Completion



Appendix B. Points of Contact

POINT OF CONTACT NAME	ORGANIZATION NAME AND ADDRESS	PHONE/FAX/EMAIL	ROLE(S) ON PROJECT
Tom Sale, Associate Professor, CSU, Civil and Environmental Engineering	Colorado State University, Engineering Research Center, Fort Collins, Colorado 80523	970-491-8413 (CSU) 970-491-8224 (Fax) tsale@engr.colostate.edu	Principal Investigator
Mitch Olson, Research Associate, Civil and Environmental Engineering	Colorado State University, Engineering Research Center, Fort Collins, Colorado 80523	970-491-8720 (CSU) 970-491-8224 (Fax) Mitchell.olson@colostate.edu	Project Researcher
Matt Petersen, Former Graduate Student, currently with GE Global Research	GE Global Research Center 1 Research Circle Niskayuna, NY 12309	T: +1 518 387 7054 F: +1 518 387 6972 matthew.petersen@ research.ge.com	Graduate Research Assistant
Dominic Leffler, CSU, Research Associate Environmental Health Services	Colorado State University, Environmental Health Services, 149E General Services Building, Fort Collins, Colorado, 80523	970-491-4830 (w) 970-491-4808 (f) dleffler@lamar.colostate.edu	Health and Safety and Hazardous Materials
Christopher Pulskamp, Chief Environmental Management, PCD	Pueblo Chemical Depot 104 W.B. St. Pueblo, CO 81003	719-549-4220	Site Contact Coordination of On-Site Activities
Andrea Leeson	ESTCP Program Office 901 North Stuart Street, Suite 303, Arlington , Virginia 22203	703-696-2118 (w) 703-696-2114 (f)	ESTCP Program Manager
Erica Becvar	HQ AFCEE/ERT 3207 Sidney Brooks Road Brooks AFB TX 78235-5344	210-536-4314 (w) 210-536-4330 (f)	ESTCP Project Liaison