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Agency

In-Situ DUOX™ Chemical Oxidation Technology to Treat Chlorinated Organics at the Roosevelt Mills Site, Vernon, CT

Site Characterization and Treatability Study Report

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

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Sally Gutierrez, Director
National Risk Management Research Laboratory

Abstract

A study was performed investigating the feasibility of applying the DUOX™ chemical oxidation technology to chlorinated solvent contaminated media at the Roosevelt Mills site in Vernon, Connecticut. The Roosevelt Mills site is a former woolen mill that included dry cleaning operations. The plant also housed metal plating operations. The primary contaminants of concern are chlorinated organic solvents: tetrachloroethene (PCE); trichloroethene, (TCE); cis-1,2-dichloroethene (DCE); and vinyl chloride (VC). The DUOX™ technology, developed by researchers at the Environmental Research Institute (ERI) at the University of Connecticut claims to provide a cost-effective, *in-situ* oxidation process to neutralize chlorinated organic chemicals. The DUOX™ technology utilizes a combination of two types of oxidants to destroy unsaturated chlorinated solvents. The oxidants belong to the persulfate and permanganate families of inorganic compounds. Sodium persulfate is used to satisfy the soil oxidant demand (SOD) and minimize the quantity of potassium permanganate needed to mineralize target compounds. This facilitates the transport of permanganate through the aquifer, allowing for more uniform distribution of permanganate and the use of a much smaller quantity. In turn, this alleviates problems caused by excess permanganate (precipitated manganese dioxide that can result in reduced aquifer permeability).

The study was performed under the auspices of the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program. The SITE study consisted of: (1) a site characterization within and outside the Roosevelt Mills building to identify chlorinated source material and characterize the extent of the dissolved phase plume, and (2) a laboratory treatability study to evaluate the effectiveness of the DUOX™ technology on the impacted media at the site.

Results from the study are summarized below:

- A chlorinated solvent source area was located underneath the Roosevelt Mills building in a portion of the foundation fill material (upper 1-3 ft). It appears that pure-phase PCE exists as distinct globules within the coarse-grained fluidized zone.
- Groundwater results, both from inside and outside the building, indicate the presence of a dissolved chlorinated solvent plume emanating from the vicinity of the source area identified in the building.
- The near-surface fill material (source area matrix for the PCE) exhibits a very low soil oxidant demand.
- Permanganate alone and in combination with persulfate is effective in reducing the levels of chlorinated solvents in the site groundwater as well as in spiked soil samples simulating a free-phase globular distribution.
- Persulfate alone, as tested, was ineffective in reducing the levels of chlorinated solvents in any of the experiments. However, due to low SOD, there is no need to use persulfate for the chlorinated solvent source area.

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Abbreviations and Acronyms

ARA	Applied Research Associates
BTSA	Brownfields Targeted Site Assessment
CPT	Cone penetrometer
DCE	Dichloroethene
DNAPL	Dense non-aqueous phase liquid
EPA	U.S. Environmental Protection Agency
ERI	Environmental Research Institute
mg/Kg	Milligrams per kilogram
mg/L	Milligrams per liter
mL	Milliliter
MMFC	Mark Metal Finishing Corporation
NA	Not analyzed
ND	Non-detectable, or not detected at or above the method detection limit
ORD	Office of Research and Development (EPA)
ORP	Oxidation reduction potential
OSWER	Office of Solid Waste and Emergency Response (EPA)
PAHs	Polyaromatic hydrocarbons
PCE	Tetrachloroethene
PSD	Particle size distribution
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act
SAIC	Science Applications International Corporation
SOD	Soil oxidant demand
SITE	Superfund Innovative Technology Evaluation
SVOCs	Semivolatile organic compounds
S.U.	Standard units
TCE	Trichloroethene
TOC	Total organic carbon
ug/Kg	Micrograms per kilogram
ug/L	Micrograms per liter
um	Micron
USTs	Underground storage tanks
TPH	Total petroleum hydrocarbons
VOA	Volatile organic analysis
VOCs	Volatile organic compounds
VC	Vinyl chloride

Acknowledgments

This report was prepared under the direction of Mr. Paul Randall, the EPA Technical Project Manager for this SITE demonstration.

The demonstration required the combined services of several individuals from Science Applications International Corporation (SAIC), Applied Research Associates (ARA), the Environmental Research Institute (ERI), and the Town of Vernon Connecticut. Dr. Scott Beckman of SAIC served as the SITE work assignment manager for the implementation of site characterization and treatability study activities as well as the completion of this report. Dr. Joel Hayworth served as the project manager for ARA. Dr. Amine Dahmani of the Environmental Research Institute of the University of Connecticut provided assistance in the collection of samples and execution of the treatability study. Mr. Larry Shaffer of the Town of Vernon provided access assistance to the Roosevelt Mills site. The treatability study was performed at ARA's facility in Panama City, Florida. The cooperation and efforts of these organizations and individuals are gratefully acknowledged.

This report was prepared by Dr. Scott Beckman and Ms. Rita Stasik of SAIC. Ms. Stasik also served as the SAIC Quality Assurance (QA) Coordinator for data review and validation.

Section 1.0
Introduction

1.1 Background

A study was performed investigating the feasibility of applying the DUOX™ chemical oxidation technology to chlorinated solvent contaminated media at the Roosevelt Mills site in Vernon, Connecticut. The DUOX™ technology, developed by researchers at the Environmental Research Institute (ERI) at the University of Connecticut (referred to as the developer), claims to provide a cost-effective, *in-situ* oxidation process to neutralize chlorinated organic chemicals. The study was performed under the auspices of the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program. The SITE Program is a formal program established by the EPA's Office of Solid Waste and Emergency Response (OSWER) and Office of Research and Development (ORD) in response to the Superfund Amendments and Reauthorization Act of 1986 (SARA). The SITE Program promotes the development, demonstration, and use of new or innovative technologies to clean up Superfund sites across the country.

The purpose of the study was to: (1) perform a site characterization of the Roosevelt Mills site to gain an understanding of the extent of groundwater chlorinated solvent contamination and the location of a potential chlorinated solvent source area. The site characterization would be used to assist in determining site-specific parameters associated with the application of the DUOX™ technology, and (2) perform treatability studies on contaminated soil and groundwater from the site that represent potential matrices and conditions that may be considered for subsequent pilot-scale testing at Roosevelt Mills.

This report will present background information on the Roosevelt Mills site and the DUOX™ technology, discuss the results from the site characterization and rationale for selecting media for study, and present the results and conclusions from the treatability study.

1.2 Roosevelt Mills Site

The Roosevelt Mills site is a former woolen mill that included dry cleaning operations. The plant also housed metal plating operations. The primary contaminants of concern are chlorinated organic solvents: tetrachloroethene (PCE); trichloroethene, (TCE); *cis*-1,2-dichloroethene (DCE); and vinyl chloride (VC).

Roosevelt Mills, now owned by the Roosevelt Acquisition Corporation, operated as a woolen mill from the mid-1800s to the late 1980s. The 7-acre site contains four main buildings (see **Figure 1-1**): a three-story Granite Mill Building, constructed in 1836; a one-story addition to the Granite Mill Building, constructed in 1937; a five-story Factory Building, constructed in 1907; and a Boiler House, also constructed in 1906. The Hockanum River has been channeled into two pathways (canal outlet and wasteway) that flow beneath the Granite Mill Building and the Factory Building. A pump-house is adjacent to the Factory Building at the east bank of the Hockanum River. Shenipsit Lake and a water treatment plant that is operated by the Connecticut Water Company border the northern portion of Roosevelt Mills. Groundwater beneath the site and within a 0.5-mile radius of the site is classified as GA (water suitable for drinking without treatment). Shenipsit Lake is utilized as a public water supply reservoir.

Operations conducted at Roosevelt Mills included wool carding, picking, dyeing, knitting, button manufacturing, and dry cleaning. Wool dyeing was conducted in the dye house north of the Granite Mill Building until 1937, then in the "1937 addition" until 1972, when the addition was leased to the Mark Metal Finishing Corporation (MMFC). Aluminum anodizing and electroplating were the two main activities of the MMFC conducted in the "1937 addition" from 1972 to 1996. Dyeing continued in the west basement area of the Factory Building after 1972. Past waste disposal practices by Roosevelt Mills are not known; however, it is probable that the mill discharged waste products to the Hockanum River. Potential sources of site contamination (**Figure 1-1**) include: floor pits; dyeing area; dry-cleaning area; floor trench that discharged to the river; chemical storage area; electroplating area; former pond and waste house, contaminated soil with boiler slag and ash; fuel oil underground storage tanks (USTs); and a former drum storage area. Roosevelt Mills ceased operations in the mid-1980s, and the site is currently abandoned.

According to a December 1998 Roy F. Weston Inc. report entitled “Roosevelt Mills Site, Brownfields Targeted Site Assessment”, EPA-Region I conducted in 1988 an emergency removal of containerized waste and raw materials left in the basement of the factory building when site operations ceased in the mid-1980s. It was noted that PCE was used as a dry-cleaning solvent in the basement dry-cleaning area of the factory building and that raw materials were stored in the basement dyeing and dry-cleaning area of the factory building. Drummed wastes removed during the removal action included several hundred 5 to 55-gallon drums of chemicals associated with dyeing and wool treatment. The drums contained petroleum naphtha, sodium chlorite, sodium acetate, sodium hypochlorite, sodium bisulfate, copper sulfate, sodium sulfate, tetrasodium pyrophosphate, acetic acid, formic acid, sodium hydroxide, hydrochloric acid, botylcarnityl (a pesticide), organic dyes, and pigments.

Other than the 1988 emergency removal, the only remediation measure implemented to date was the removal and replacement of the leaking USTs in the early 1980s. Approximately 1000 cubic yards of petroleum-contaminated soil was excavated, stockpiled on-site, and subsequently removed from the site. Another 10,000-gallon UST discovered leaking in 1985 was replaced with another 10,000 gallon UST.

Historical site characterization and assessment activities at the Roosevelt Mills site include limited soil sampling in the factory and boiler house (1988), installation of groundwater monitoring wells (1990), Phase I and II site assessments (1995), and a Brownfield Targeted Site Assessment (BTSA, 1997). Of theses activities, the BTSA conducted in 1997 provided the most complete picture of the site to date, and provides a starting point for developing a strategy for additional field sampling.

The Roosevelt Mills Brownfields Targeted Site Assessment (BTSA) was conducted by Roy F. Weston, Inc. in two Phases. Phase I sampling was performed in August, 1997; Phase II sampling was performed in April, 1998. During Phase I work, 21 soil samples, 6 sediment samples, and 8 groundwater samples were collected. During Phase II work, 22 soil samples and 7 groundwater samples were collected. Phase I and II samples were analyzed for potential contaminants of concern, including VOCs, SVOCs, TPH, RCRA Metals, PAHs, and Cyanide.

Results of groundwater samples collected during the BTSA reveal the presence of tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC) at the site. These compounds are found within the near-surface aquifer primarily underlying the mill and main factory buildings. The presence of DCE and VC in the groundwater is evidence that PCE and TCE are being anaerobically biodegraded at the site. Further, the lateral distribution of these compounds follows the direction of groundwater flow and is consistent with migration away from a source region of active biodegradation .

1.3 DUOX™ Technology Description

The DUOX™ technology utilizes a combination of two types of oxidants to destroy unsaturated chlorinated solvents. The oxidants belong to the persulfate and permanganate families of inorganic compounds. The most economical oxidants from each class of oxidants are sodium persulfate ($Na_2S_2O_8$) and potassium permanganate ($KMnO_4$). This *in-situ* chemical oxidation process involves injecting a solution of one or more oxidants in series or simultaneously into the subsurface to mineralize the target contaminants.

In a typical process application, sodium persulfate is first injected into the subsurface and consumed by the combined effect of mineralizing target contaminants and satisfying soil oxidant demand (SOD) (due to reduced conditions and/or high background levels of natural organic matter). The primary purpose of sodium persulfate is to satisfy the SOD and minimize the quantity of potassium permanganate needed to mineralize target compounds. This facilitates the transport of permanganate through the aquifer, allowing for more uniform distribution of permanganate and the use of a much smaller quantity of permanganate. In turn, this alleviates problems caused by excess permanganate (precipitated manganese dioxide that can result in reduced aquifer permeability). This sequential dual treatment protocol can be repeated as many times as necessary to reduce contaminant concentrations to site target levels.

For the proper application and success of this technology, injection well location and oxidant injection rates must be based on a thorough evaluation of the site hydrogeologic conditions and the nature of the organic matter present at the site. An understanding of the extent of contamination at the site is, therefore, an integral part of this technology. Thus, a careful evaluation of the site-specific parameters, and the extent of contamination, is needed for the proper application and success of this remedial technology.

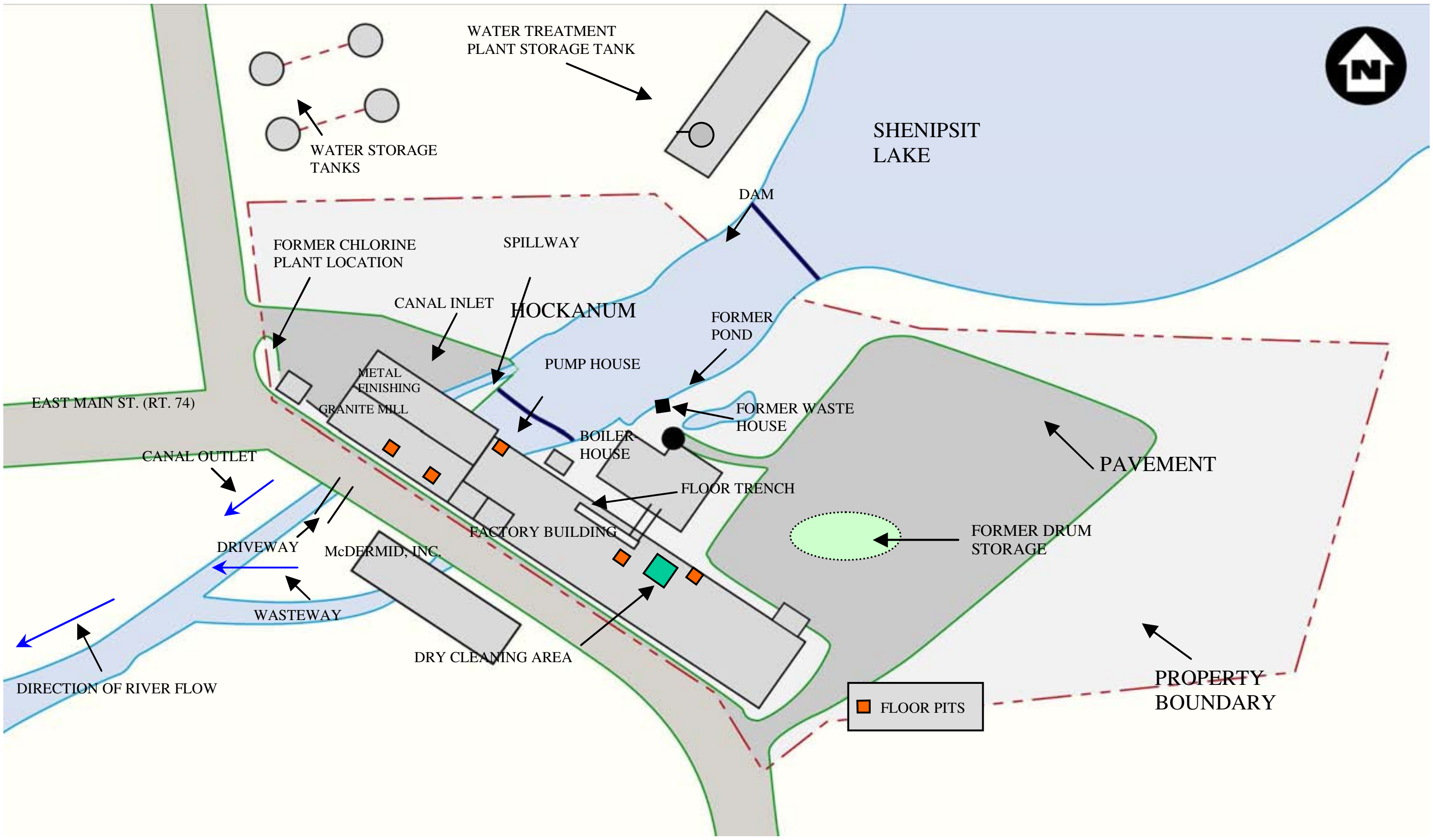


Figure 1-1. Roosevelt Mills site map.

Section 2.0
Site Characterization

2.1 Site Characterization Objectives

The site characterization objectives, as well as sampling and analysis methodologies, is described in the document: "*Quality Assurance Project Plan for the SITE Demonstration of In-Situ DUOX™ Chemical Oxidation Technology to Treat Chlorinated Organics at the Roosevelt Mills Site, Vernon, CT (October 2001*)" The two main goals of the site characterization were to: (1) Retrieve soil and groundwater samples to perform the treatability tests from both the contaminant source area (soil) and the dissolved groundwater plume that meet the following criteria: Soil PCE concentrations of 500-10,000 mg/Kg; Groundwater PCE concentrations of >50 mg/L, and (2) Characterize in sufficient detail to implement, if deemed feasible from the treatability study, a field demonstration of the DUOX™ technology. Characterization goals consist of locating and delineating PCE source areas believed to be beneath the building, defining the extent and concentration of the VOC contaminant plume, and determining the hydrogeologic properties that would be necessary to apply the DUOX™ technology at the Roosevelt Mills site.

Additional goals for the site characterization included: (1) determining the location and delineation of a potential TCE source area if one exists, (2) assessing background levels of metals in the groundwater and soil, and (3) determining the extent and distributions of non-critical VOCs (e.g., acetone) that may be present in the groundwater and/or soil.

2.2 Site Characterization Execution

Site characterization activities were initiated on January 14, 2002 and ended on January 28, 2002. The field activities focused on the collection of groundwater and soil samples both within the structure of the mill and outside the building. In addition to the collection of groundwater and soil samples, the field investigation focused on the collection of field parameters for groundwater (dissolved oxygen, ORP, pH), as well as the collection of subsurface geophysical and visual information via CPT sensors (piezocone and videocone).

Site characterization employed the use of a cone penetrometer (CPT) outfitted with several subsurface sensors and sample acquisition tools. CPT sensors and tools utilized were: (1) a standard piezocone for evaluating the site hydrogeological properties, (2) a Video-CPT for visually identifying the presence of pure-phase chlorinated solvents, (3) a Conesipper tool to collect groundwater samples, and (4) a VERTEK soil sampler to collect discrete soil samples as well as cores for use during the treatability study. Hydrogeological properties at all sample locations were assessed by the use of a standard piezocone. The piezocone determines soil stratigraphy, relative density, strength and hydrogeologic information. At selected depth intervals, pore water pressure was monitored over time to determine relative hydraulic conductivity and hydrostatic head. The video-CPT tool was used to discern the presence of pure-phase solvent by providing a visual assessment of free product which shows up as visually discernable globules.

Initial site characterization activities were focused on determining the location and extent of free product within the building. Based on a conceptual model of the contaminant distribution developed prior to the field investigation, candidate site locations within the building were probed using the Video-CPT tool for the source area. **Figure 2-1** depicts the probable source areas for the chlorinated solvents, and served as the starting locations for exploratory drilling. Locating the source area was the critical first step in defining the remainder of the investigation, and for collecting groundwater and soil samples for the treatability study. Once the source area was located, attention turned to the collection of groundwater samples both inside the building and outside the mill. **Figure 2-2** depicts the locations of the proposed sampling points outside of the mill building. These samples were used to assess the magnitude and extent of the dissolved plume emanating from the source area. It is important to note that samples from several of the outside locations were difficult to obtain due to

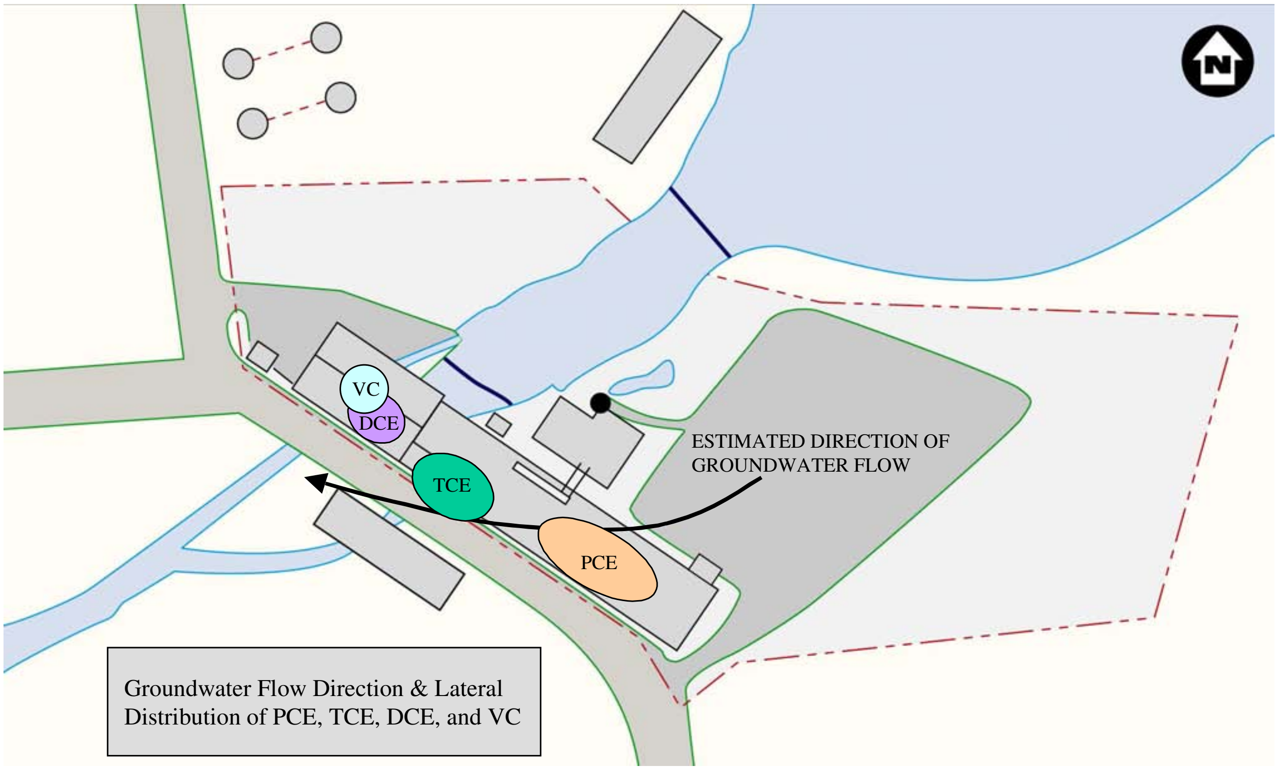


Figure 2-1. Conceptual model of suspected chlorinated solvent source areas.

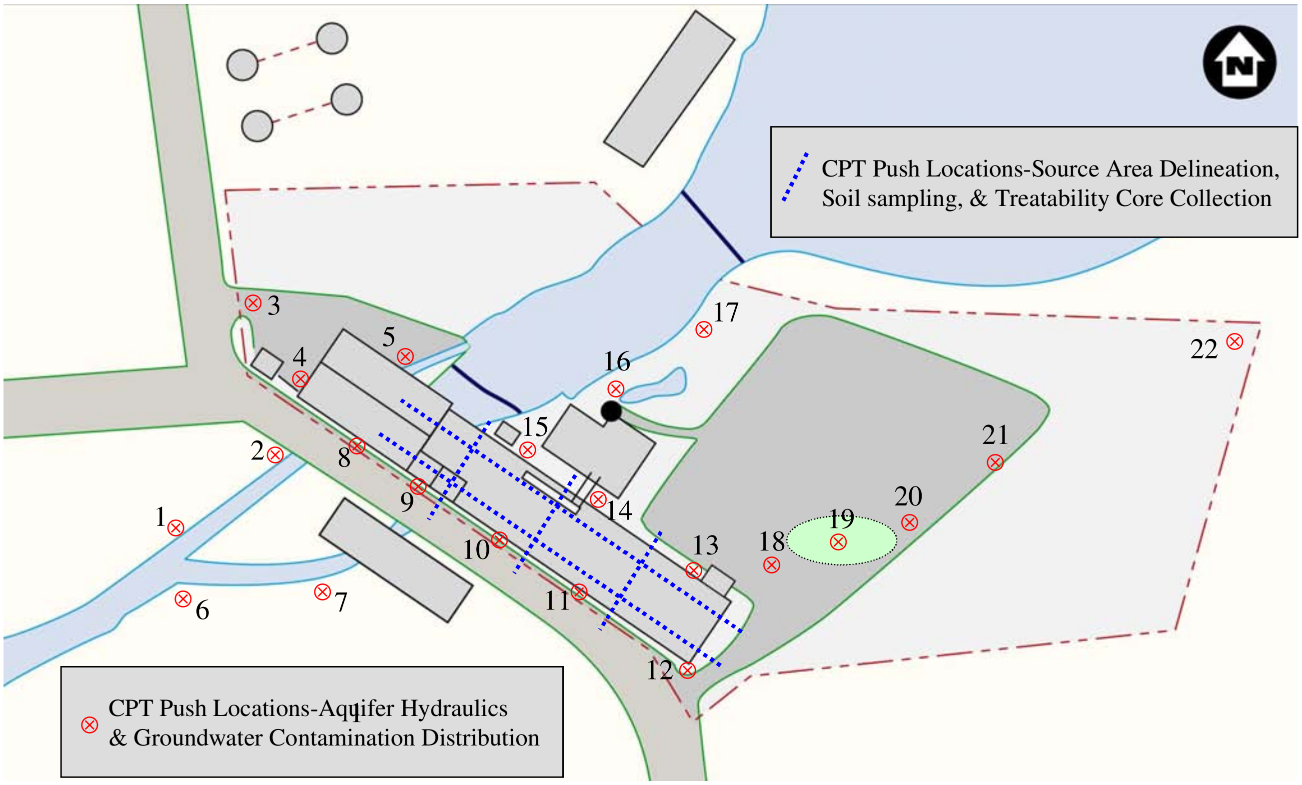


Figure 2-2. Proposed outside sampling locations.

accessibility issues. Subsequent to the January 2001 field effort, ERI performed a site characterization to obtain some of the samples that were not recovered in January. In addition to the collection of samples for analysis, soil cores and contaminated groundwater was recovered for the subsequent treatability study.

Site characterization activities were impacted by the physical conditions associated with sampling and working within the building and subsurface conditions related to the sub-basement. Noteworthy conditions consisted of: (1) a lack of reliable sub-floor plans which required very careful consideration of probe-hole placement and resulted in numerous zones of refusal (2) several areas within the work space that contained asbestos including construction debris and large mill equipment that required re-evaluation of the sampling layout and rig movement, and (3) cold conditions in the building causing ice hazards. In spite of these challenging sample conditions, the source area was delineated and samples were acquired and analyzed to meet the project objectives.

2.3 Site Characterization Results

As previously discussed, the site characterization focused on identification of the source area within the building, and the assessment of the magnitude and extent of soil and groundwater contamination. The following sections will present the results from these two efforts.

2.3.1 Source Area Delineation

Initial efforts focused on the detection and delineation of probable source areas within the building. To accomplish this task, the Video-CPT tool, along with the piezocone tool, were utilized. **Figure 2-3** depicts the push locations inside the building. These locations have the prefix “I” in the text to denote samples taken inside the building. The process consisted of advancing these CPT tools, and visually assessing in real-time, the presence of free phase material. Once detected, a core could be recovered and analyzed for Dense Non-Aqueous Phase Liquid (DNAPL) VOCs from the zones of interest. It was anticipated that the DNAPL source area would be encountered in the deeper strata underlying the building floor. This was based on the tendency for denser-than-water chlorinated solvents to accumulate within the basal sections of aquifers. Contrary to this supposition, no DNAPL was found at depth at the push locations investigated.

The chlorinated solvent source area was located within the basal portion of foundation fill material (upper 1-3 ft) near sample locations I8 and I10. It appears that pure-phase PCE exists as distinct globules within this fluidized zone rather than as a residual phase trapped by pore tension. This is supported by the video cone results and material cores. **Figure 2-4** is a screen capture of the Video-CPT and illustrates the globular nature of the PCE distributed within the coarse grained fill matrix. There is no evidence that the source area exists to the east at or past I7, and to the south past I11. The source area exists within a poorly sorted, fluidized zone which begins under the building foundation and extends to approximately 3 ft below the ground surface. Below the upper fill zone is a more consistent aquifer composed primarily of distinct sand layers interbedded with silty sand and gravel-sand layers (native material). The upper and underlying systems are hydraulically connected and so the groundwater within each is contaminated. However, PCE within the upper zone cannot overcome the pore pressures within the lower system and thus do not appear contaminated as free product. This is supported by video cone results, several core samples, and groundwater samples.

The globular nature of the PCE in the fill material results in a very heterogeneous distribution. Soil samples taken from this zone support the heterogeneous distribution of the source area. A soil sample from I10 in the 1-3’ fill material exhibited a tetrachloroethene (PCE) concentration of 1,720 ug/Kg, while a soil sample from the same interval from adjacent I11 exhibited no detectable VOCs. Furthermore, analysis of this fill material is difficult due to the coarse nature and the globular distribution of the PCE within the pore space. In order to assess the level of contamination in this zone, a large volume of material should be extracted and analyzed.

Although there is no evidence of free product in the underlying native material, there are significant levels of dissolved chlorinated volatile organic compounds in the groundwater. These compounds represent both dissolved PCE as well as PCE degradation products derived from reductive dechlorination. It is postulated that PCE has diffused, in a dissolved state, from the overlying fill material into the native material and is being transported in the groundwater system. Reductive dechlorination is occurring in portions of the underlying groundwater system.

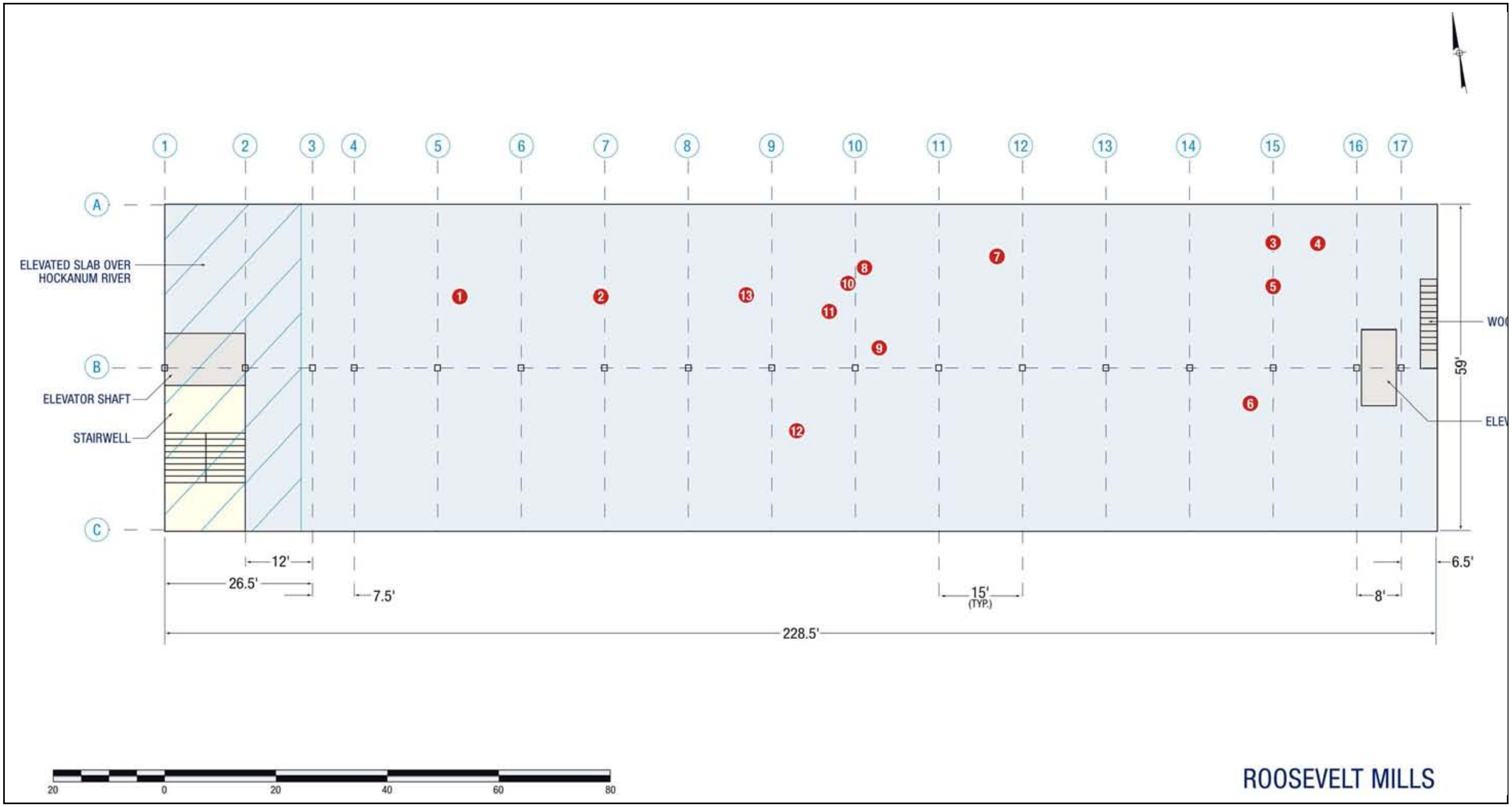


Figure 2-3. **CPT push locations inside the building.**

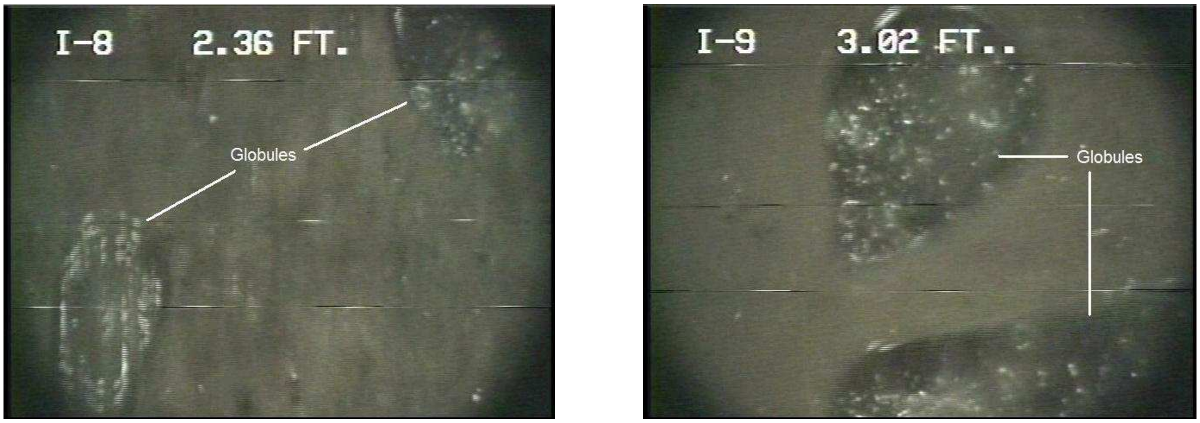


Figure 2-4. Globules of PCE in the near-surface fill material (from Video-CPT).

2.3.2 Soil and Groundwater Characterization Results

Tables 2-1 and **2-2** presents the results of the volatile organic compounds in groundwater and soil from both inside and outside of the building. **Table 2-3** presents the results of metals and other analytes from the soil and groundwater. **Figure 2-5** depicts the distribution of soil and groundwater contamination within the building.

The results from the VOC data, both from inside and outside the building, indicate the presence of a dissolved chlorinated solvent plume emanating from the vicinity of the source area identified in the building. There are several noteworthy characteristics of the solvent plume: (1) concentrations of PCE and chlorinated solvent daughter products are highest directly beneath the source area with concentrations of several hundred ppb, (2) there is evidence that reductive dechlorination is occurring due to the presence of PCE daughter products, and (3) the plume is migrating to the southwest and is consistent with the general groundwater flow. **Figure 2-6** depicts the predicted movement of PCE based on a groundwater model using data from this study as well as regional groundwater flow data.

Groundwater and soil samples acquired from outside of the building to the northeast do not contain significant levels of volatile organic compounds. This area was a potential area of concern due to the reported storage of drums containing hazardous materials. No significant chlorinated solvents were detected, and minor hits of petroleum-based hydrocarbons were encountered.

2.4 Results from ERI's Field Investigation

The Environmental Research Institute of the University of Connecticut, performed a field investigation subsequent to SAIC's field deployment in January. The purpose of ERI's investigation was to further delineate the concentration and extent of chlorinated solvent contamination inside and outside of the building. The results from ERI's characterization confirm and are consistent with the information gathered in January 2002.

ERI's data is presented in **Table 2-4**. **Figure 2-7** depicts sample locations. Note: ERI's data has not been evaluated by the EPA and is presented here for data comparisons.

Table 2-1. Volatile Organic Compounds in Groundwater.

SAMPLE ID	Matrix	Units	Acetone	Benzene	Bromomethane	Carbon disulfide	Chloromethane	1,1-Dichhloroethane	cis-1,2-Dichloroethene	t-1,2-Dichlorethene	MeCl2	PCE	Ethylbenzene	Toluene	TCE	VC	Xylenes	Styrene
I1-(7-9)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.2 J	1 U	1 U	1 U	2 U	1 U	1 U	1 U	1 U	2 U	3 U	1 U
I2-(1-4)-GW	GW	ug/L	101	1 U	1 U	1 U	1 U	1 U	1 U	1 U	2 U	14	15	2.7	1	2 U	47	1 U
I5-(2.5-4)-GW	GW	ug/L	4 U	1 U	2 U	1 U	1 U	U	1 U	1 U	2 U	0.9 J	1 U	0.2 J	1 U	2 U	3 U	1 U
I7-(7-10)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.3 J	1 U	1 U	1 U	2 U	1 U	1 U	0.2 J	1 U	2 U	3 U	1 U
I8-(4-6.5)-GW	GW	ug/L	4 U	0.1 J	2 U	1.6	1 U	1.5	32	1.1	2 U	231	1 U	0.5 J	50	4.1	0.3 J	1 U
I9-(3-5.5)-GW	GW	ug/L	4 U	1 U	2 U	1 U	1 U	1 U	1 U	1 U	2 U	60	1 U	1 U	3.1	2 U	3 U	1 U
I10-(6-9)-GW	GW	ug/L	4 U	1 U	1 U	1 U	0.3 J	1 U	1 U	1 U	2 U	20	1 U	1 U	0.4 J	2 U	3 U	1 U
I11-(4-7)-GW	GW	ug/L	4 U	1 U	1 U	1 U	0.2 J	1 U	0.2 J	1 U	2 U	323	1 U	0.2 J	1.4	2 U	3 U	1 U
I11-(4-7)-Gwdup	GW	ug/L	4 U	1 U	2 U	1 U	0.2 J	1 U	1 U	1 U	2 U	127	1 U	1 U	1.6	2 U	3 U	1 U
I12-(7-9)-GW	GW	ug/L	55	1 U	2 U	1 U	1 U	1 U	2.9	1 U	2 U	172	2.2	0.4 J	4.3	2 U	8.7	1 U
I13-(3-6)-GW	GW	ug/L	149	1 U	2 U	1 U	1 U	1 U	36	1.1	2 U	69	1 U	1 U	115	0.7 U	3 U	1 U
O18-(10-13)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.5 J	1 U	1 U	1 U	2 U	1 U	1 U	0.3 J	1 U	2 U	3 U	1 U
O22-(6-9)	GW	ug/L	4 U	1 U	2 U	1 U	1 U	1 U	1 U	1 U	2 U	1 U	1 U	1 U	1 U	2 U	3 U	1 U
O24-(4-7)-GW	GW	ug/L	4 U	1 U	2 U	1 U	1 U	1 U	1 U	1 U	2 U	1 U	1 U	1.9	1 U	2 U	3 U	1 U
O26-(6-9)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.3 J	1 U	1 U	1 U	2 U	0.3 J	1 U	1 U	0.3 J	2 U	3 U	1 U
O27-(12.5-15.5)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.3 J	1 U	1 U	1 U	2 U	1 U	1 U	1 U	1 U	2 U	3 U	1 U
O28-(12-15)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.2 J	1 U	1 U	1 U	2 U	0.2 J	1 U	1 U	1 U	2 U	3 U	1 U
O29-(10-13)-GW	GW	ug/L	4 U	1 U	2 U	1 U	1 U	1 U	1 U	1 U	2 U	1 U	1 U	0.2 J	1 U	2 U	3 U	1 U
O29-(10-13)-GW-dup	GW	ug/L	4 U	1 U	2 U	1 U	1 U	1 U	1 U	1 U	2 U	1 U	1 U	1 U	1 U	2 U	3 U	1 U
O30-(17-20)-GW	GW	ug/L	4 U	1 U	2 U	1 U	0.4 J	1 U	1 U	1 U	2 U	1 U	1 U	1 U	1 U	2 U	3 U	1 U

U = Not Detected at the concentration indicated (e.g. 4U means not detected at a 4 ug/L detection limit)

J = Estimated Value

Table 2-2. Volatile Organic Compounds in Soil.

SAMPLE ID	Matrix	Units	Acetone	Benzene	Bromomethane	Carbon disulfide	Chloromethane	1,1-Dichhloroethane	cis-1,2-Dichloroethene	t-1,2-Dichlorethene	MeCl2	PCE	Ethylbenzene	Toluene	TCE	VC	Xylenes	Styrene
I1-(8-10)-S	Soil	ug/Kg	320 U	81 U	160 U	81 U	39 J	81 U	81 U	81 U	160 U	34 J	81 U	81 U	81 U	160 U	240 U	81 U
I7-(6-8)-S	Soil	ug/Kg	220 U	56 U	110 U	56 U	56 U	56 U	56 U	56 U	110 U	56 U	56 U	56 U	56 U	110 U	170 U	56 U
I8-(4.5-6.5)-S	Soil	ug/Kg	220 U	54 U	110 U	54 U	20 J	54 U	54 U	54 U	110 U	54 U	54 U	54 U	54 U	110 U	160 U	54 U
I10-(7-9)-S	Soil	ug/Kg	220 U	56 U	110 U	56 U	56 U	56 U	56 U	56 U	110 U	22 J	56 U	56 U	56 U	110 U	170 U	56 U
I10-(7-9)-Sdup	Soil	ug/Kg	17 U	56 U	28 J	56 U	56 U	56 U	56 U	56 U	8.7 J	56 U	56 U	56 U	56 U	110 U	170 U	56 U
I11-(5-7)-S	Soil	ug/Kg	240 U	58 U	120 U	58 U	58 U	58 U	58 U	58 U	120 U	58 U	58 U	58 U	58 U	120 U	170 U	58 U
I12-(7-9)-S	Soil	ug/Kg	220 U	56 U	110 U	56 U	58 U	58 U	58 U	58 U	110 U	58 U	58 U	58 U	58 U	110 U	170 U	58 U
I13-(2-4)-S	Soil	ug/Kg	240 U	62 U	120 U	62 U	30 J	62 U	62 U	62 U	120 U	300	62 U	62 U	37 J	120 U	190 U	62 U
I2-(1-3)-S	Soil	ug/Kg	220 U	55 U	110 U	55 U	55 U	55 U	55 U	55 U	110 U	270	63	12 J	16 J	110 U	160 U	55 U
O24-(6-7.7)-S	Soil	ug/Kg	34 U	56 U	110 U	56 U	56 U	56 U	56 U	56 U	17 J	56 U	8 J	27 J	49 J	110 U	27 J	3.7 J
O27-(5-7)-S	Soil	ug/Kg	14 U	59 U	120 U	59 U	59 U	59 U	59 U	59 U	7.1 J	59 U	59 U	59 U	44 J	120 U	180 U	3.9 J
O28-(13-15)-S	Soil	ug/Kg	14 U	57 U	110 U	57 U	57 U	57 U	57 U	57 U	7.1 J	57 U	57 U	57 U	38 J	110 U	170 U	57 U
O29-(9-10.5)-S	Soil	ug/Kg	19 U	57 U	110 U	57 U	57 U	57 U	57 U	57 U	9.6 J	57 U	57 U	57 U	36 J	110 U	170 U	57 U
O30-(15-17)-S	Soil	ug/Kg	17 U	55 U	110 U	55 U	55 U	55 U	55 U	55 U	8.5 J	55 U	55 U	55 U	36 J	110 U	160 U	3.3 J
O18-(12-14)-S	Soil	ug/Kg	260 U	66 U	37 J	66 U	66 U	66 U	66 U	66 U	130 U	66 U	66 U	66 U	66 U	130 U	200 U	66 U
O19-(10-12)-S	Soil	ug/Kg	260 U	64 U	130 U	64 U	64 U	64 U	64 U	64 U	130 U	64 U	64 U	64 U	64 U	130 U	190 U	64 U
O20-(5-7)-S	Soil	ug/Kg	240 U	62 U	120 U	62 U	62 U	62 U	62 U	62 U	120 U	62 U	62 U	62 U	62 U	120 U	190 U	62 U
O21-(6-8)-S	Soil	ug/Kg	280 U	69 U	140 U	69 U	69 U	69 U	69 U	69 U	140 U	69 U	69 U	69 U	69 U	140 U	210 U	69 U
O23-(2-4)-S	Soil	ug/Kg	240 U	60 U	120 U	60 U	60 U	60 U	60 U	60 U	120 U	60 U	60 U	60 U	60 U	120 U	240 U	60 U
O25-(8-10)-S	Soil	ug/Kg	260 U	64 U	130 U	64 U	64 U	64 U	64 U	64 U	130 U	64 U	64 U	64 U	64 U	130 U	190 U	64 U
O25-(8-10)-Sdup	Soil	ug/Kg	260 U	64 U	130 U	64 U	64 U	64 U	64 U	64 U	130 U	64 U	64 U	64 U	64 U	130 U	190 U	64 U
O26-(3-5)-S	Soil	ug/Kg	240 U	7 J	120 U	61 U	61 U	61 U	61 U	61 U	120 U	61 U	16 J	48 J	61 U	120 U	80 J	61 U

U = Not Detected at the concentration indicated (e.g. 220U means not detected at a 200 ug/Kg detection limit)

J = Estimated Value

Table 2-3. Metals and Additional Analytes in Groundwater and Soil.

SAMPLE ID	Matrix	Units	As	Cr	Fe	Pb	Mn	Se	K	Na	Sulfide	TOC	pH	Total Solids
I1-(7-9)-GW	GW	mg/L	0.014	0.12	90	0.049	1.4	0.01U	4.5	11				
I5-(2.5-4)-GW	GW	mg/L	0.14	0.45	740	0.53	28	0.01U	210	56				
I7-(7-10)-GW	GW	mg/L	0.034	0.23	590	0.26	19	0.01U	230	18				
I8-(4-6.5)-GW	GW	mg/L	0.14	0.93	660	1.3	43	0.01U	160	36				
I9-(3.0-5.5)-GW	GW	mg/L	0.098	0.47	670	0.43	29	0.01U	120	17				
I1-(8-10)-S	Soil	mg/Kg	3.1U	39		3.1		3.1U			30U	27200	6.76	61.7
I10-(7-9)-S	Soil	mg/Kg	2.1U	11	28000	1.1U		3.2			30U	320U		89.7
I11-(5-7)-S	Soil	mg/Kg	2.2U	8.7	28000	1.1U		3.2			30U	340U		86.2
I12-(7-9)-S	Soil	mg/Kg	2.1U	9.7	29000	1.1U		2.1U			30U	370U		89.3
I13-(2-4)-S	Soil	mg/Kg	2.4U	11	30000	2.4		4.7			30U	1480		80.2
I2-(1-3)-S	Soil	mg/Kg	2.1U	6.4	31000	4.2		3.2						91.1
I7-(6-8)-S	Soil	mg/Kg	2.2U	5.6		1.1U		2.2U			30U	290U	6.11	89.4
I8(4.5-6.5)-S	Soil	mg/Kg	2.1U	12		1.0U		4.1			30U	290U	8.47	91.8
O18-(12-14)-S	Soil	mg/Kg	2.4U	13	11000	3.6		2.4U			30U	280U		75.3
O19-(10-12)-S	Soil	mg/Kg	2.4U	22	20000	5.9		2.4U			30U	290U		78.4
O20-(5-7)-S	Soil	mg/Kg	1.9U	19	16000	4.7		1.9U			30U	400U		80.7
O21-(6-8)-S	Soil	mg/Kg	2.3U	15	13000	3.4		2.3U			30U	280U		72.9
O23-(2-4)-S	Soil	mg/Kg	2.3U	13	19000	1.1		2.3U			30U	430U		83
O24-(6-7.7)-S	Soil	mg/Kg	3.9	7.9	24000	3		3			60U	4500		90
O25-(8-10)-S	Soil	mg/Kg	2.4U	8.5	80	1.2		2.4U				3600		78.4
O25-(8-10)-S (dup)	Soil	mg/Kg	2.4U	12	14000	3.7		2.4U						
O26-(3-5)-S	Soil	mg/Kg	13	27	23000	26		3.7			30U	85000		82
O27-(5-7)-S	Soil	mg/Kg	2.4U	9.3	20000	2.4		2.4U			30U	4500		84.2
O28-(13-15)-S	Soil	mg/Kg	2.1U	17	25000	3.1		2.1			30U	260U		87
O29-(9-10.5)-S	Soil	mg/Kg	2.2U	11	11000	3.3		2.2U			30U	330U		87.2
O30-(15-17)-S	Soil	mg/Kg	2.2U	19	24000	2.2		3.3			30U	410U		91.6
I12-(7-9)-S	SPLP	mg/Kg	0.02U	0.01U	3.5	0.01U		0.02U						
O28-(13-15)-S	SPLP	mg/Kg	0.02U	0.01U	0.02U	0.01U		0.02U						

U = Not Detected at the concentration indicated (e.g. 3.1U means not detected at a 3.1 mg/Kg detection limit)

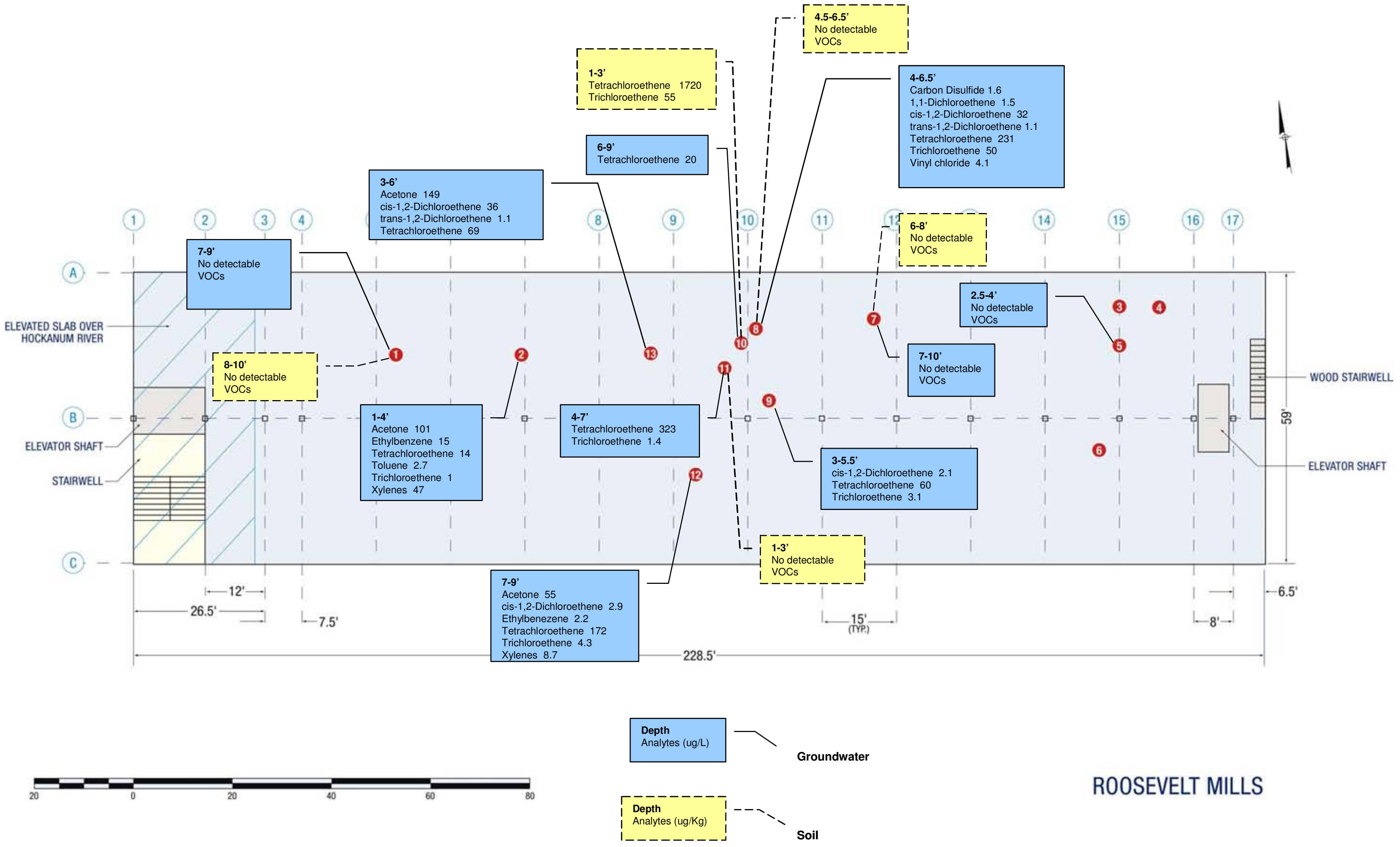
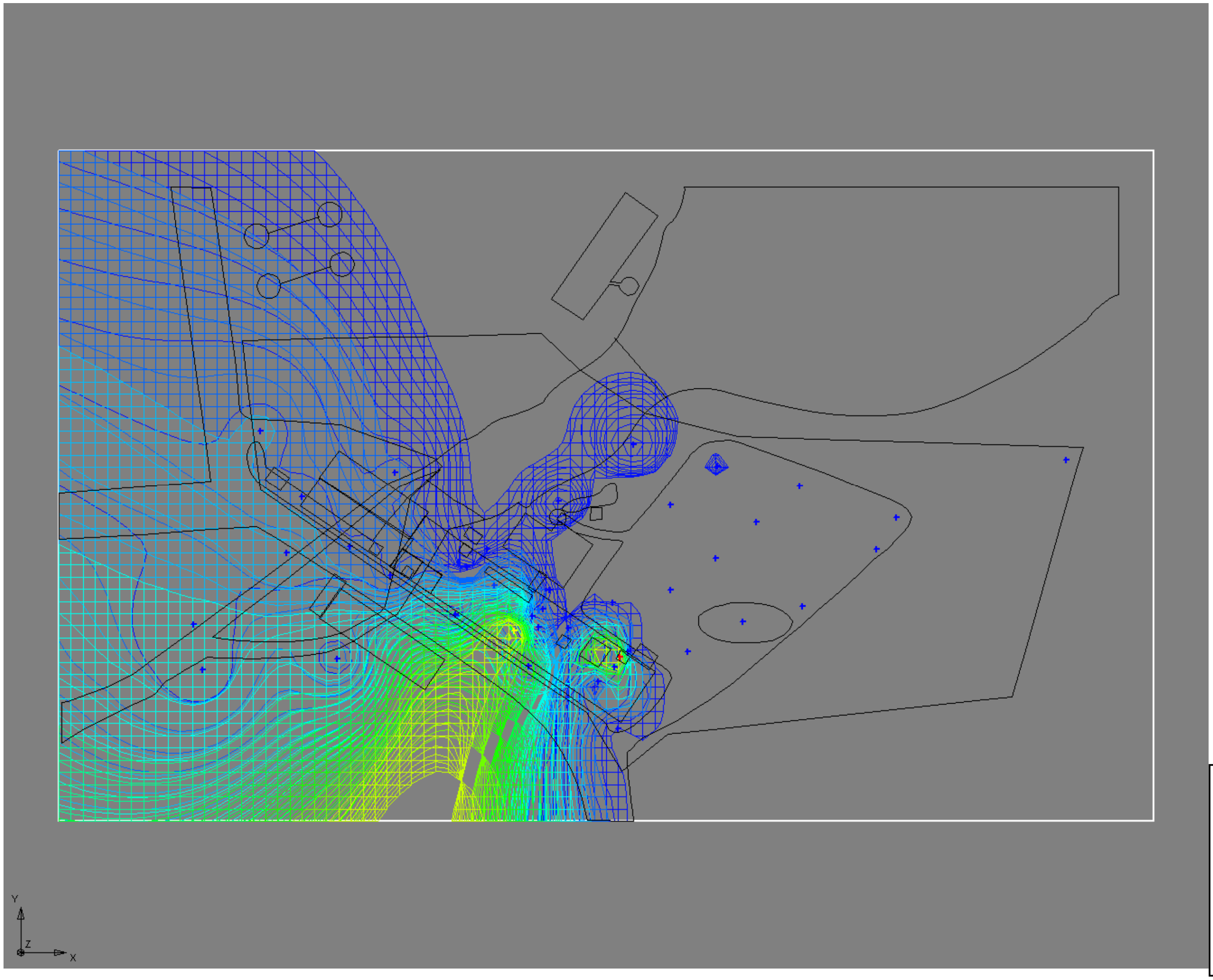


Figure 2-5. Soil and groundwater results from inside the building.



Note: Yellow and orange areas indicate probable higher concentrations, while green and blue areas indicate probable lower concentrations.

Figure 2-6. **Predicted PCE groundwater plume.**

Table 2-4. ERI VOC Data.

Sample#	RM4-9-7.5*	RM8-8	RM9-12	RM9-15	RM10-12	RM10-14	RM11-1-23-22	RM11-1-26-25	RMB28-14-13
Sampling date	2/19/02	2/11/02	2/12/02	2/12/02	2/13/02	2/13/02	2/14/02	2/14/02	5/8/02
Compound									
Trichloroethene	8.6	36.1	5	18.4					10.7
Tetrachloroethene	44.9	30.7	2.1	31.6	1.1***	1.2***			27.2
(Cis)-1,2-Dichloroethene		17.1	1.9	3					13.6
Chloroethene (Vinyl Chloride)		1.2							
4-iso-Propyltoluene		10.8							
Naphthalene		3.6							
(trans)-1,2-Dichloroethene			1.3						0.8
MTBE							2.5	4	
Sample#	RMB24-13-10**	RMB20-7-4	RMB20-10-7	RMB14-8-5					
Sampling date	5/30/02	5/31/02	5/31/2002	6/10/02					
Compound									
Trichloroethene	7.4			3.4					
Tetrachloroethene	24	6.5	9.8	9.5					
(Cis)-1,2-Dichloroethene	12.6			2.3					
Chloroethene (Vinyl Chloride)				1.4					
Sample#	RMB13-8-5	RMB13-15-12	RMB12-8-5	RMB12-15-12	RMB11-8-5-G	RMB11-13-10-G	RMB10-8-5	RMB9-6-4	
Sampling date	6/10/02	6/10/02	6/11/02	6/11/02	6/11/02	6/11/02	6/12/02	6/12/02	
Compound									
Trichloroethene							2.4	3.4	
Tetrachloroethene	679	4	164	3.3	776	235	14.4	6.9	
(Cis)-1,2-Dichloroethene								2.7	

Table 2.4 (cont'd)

Sample#	RMB6-7-4	RMB15-10-7	RMB15-6-3	RMB15-7-6	RMB17-6-4	RMB18-5-3	RMB18-14-10		
Sampling date	6/13/02	6/3/02	6/3/02	6/3/02	6/4/02	6/4/02	6/4/02		
Compound									
Trichloroethene	211		15.5	5.4	4.3	346			
Tetrachloroethene	321	2.4	19.4	7.5	7.4	287	4.6		
(Cis)-1,2-Dichloroethene	154		3.1	1.4		41.1			
(trans)-1,2-Dichloroethene						1.1			
1,1-Dichloroethene	1.3								

Sample#	RMB23-8-5	RMB23-11-8	RMB22-8-5	RMB22-11-8	RMB27-12-9	RMB21-11-8	RMB21-8-5	RMB26-12-9	RMB26-9-6
Sampling date	6/5/02	6/5/02	6/5/02	6/5/02	5/29/02	5/30/02	5/30/02	5/29/02	5/29/02
Compound									
Trichloroethene	3.7	3.6	5.9	3.7	2.2	1.3	2.7		1.4
Tetrachloroethene	32.5	39.8	70.8	51.4		13	33		9.4
(Cis)-1,2-Dichloroethene	1.1		1.2		4.8			4.2	

Sample#	020603-TB	020604-TB	LAB BLK	020614-FB	020614-TB	020613-FB	020605-TB	020611-TB	LAB BLK	020529-TB
Sampling date	6/3/02	6/4/02	6/6/02	6/14/02	6/14/02	6/13/02	6/5/02	6/11/02	6/18/02	5/29/02
Compound										
Chloroethene (Vinyl Chloride)							3			
Acetone	5	6		4	4	6		4		4
Dichloromethane		1	2		1			2	2	
Naphthalene	3	3								
Methyl Ethyl Ketone (MEK)								2		1

Table 2.4 (cont'd)

Sample#	020612-TB	020612-FB	020613-TB	020530-TB	020531-TB	020610-TB	020211-FB	020213-TB	020213-FB	020212-FB
Sampling date	6/12/02	6/12/02	6/13/02	5/30/02	5/31/02	6/10/02	2/11/02	2/13/02	2/13/02	2/12/02
Compound										
Tetrachloroethene							0.6		1.1	
Acetone	4	4	4		4	4		3	5	6
Dichloromethane				3	3	1				
Methyl Ethyl Ketone (MEK)						2				

* RM4-9-7.5 means RM at SAIC location 4 from 9 to 7.5 ft BGS

**RMB24-13-10 means RMB at ERI location 24 from 10 to 13 BGS

*** FB has 1.1 ppb of PCE

TB is trip blank

FB is field blank

List of Non-Detect Samples

Field samples

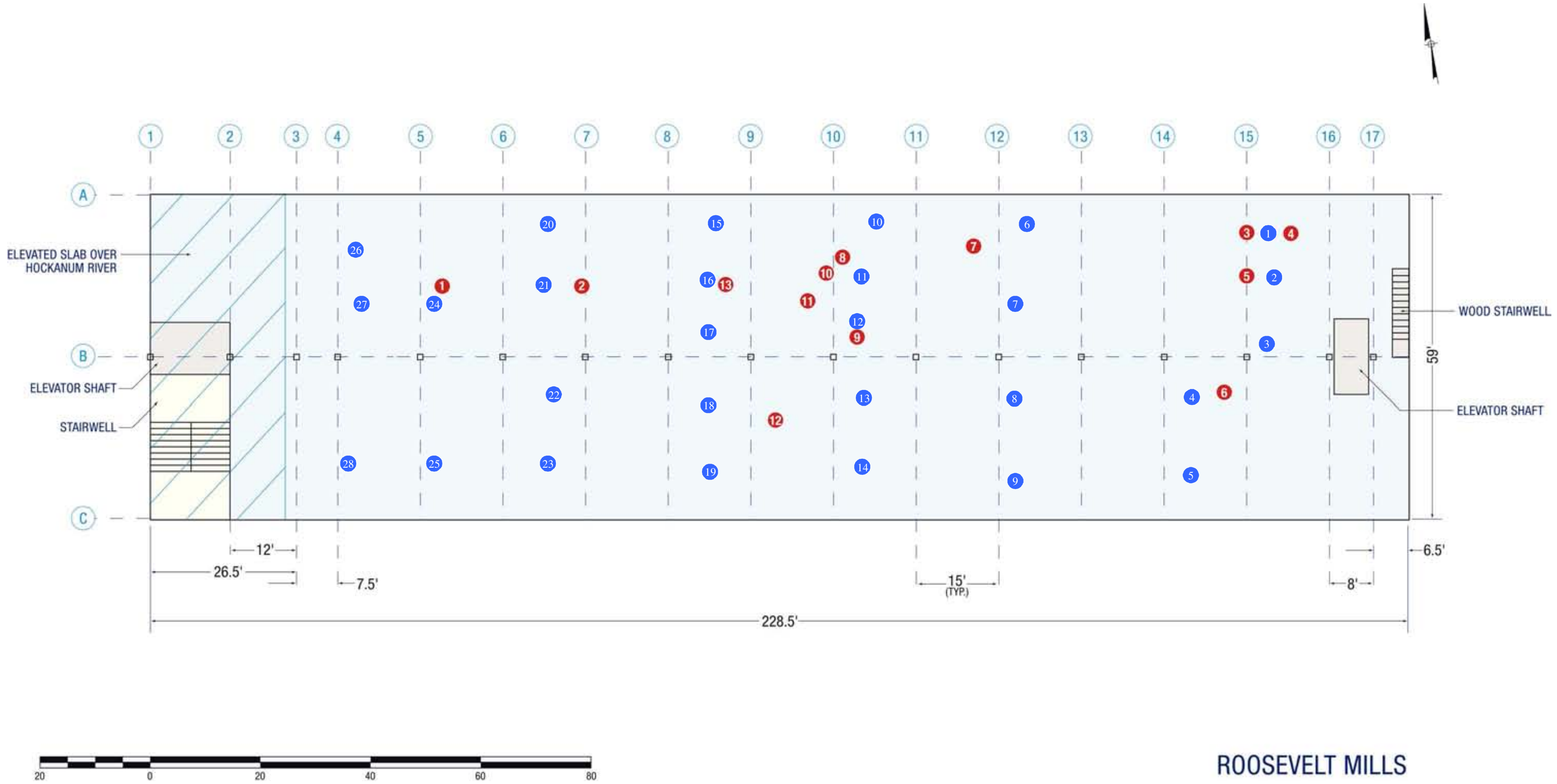
RMB24-9-6
RMB14-12-9
RMB10-9-7
RMB7-11-7
RMB5-7-3
RMB4-4-2
RMB3-5-4
RMB16-18-14
RMB13-25-21
RMB13-25-21-B
RMB16-8
RMB16-11
RM12-31-30-A (unfiltered)
RM12-31-30-A (filtered)
RMB17-7-6

Blanks

020531-FB
020530-FB
020529-FB
Lab Blank 6/3/02
020610-FB
020611-FB
020211-TB
Lab Blank 2/11/02
Lab Blank 2/15/02
020212-TB
020214-TB
020214-FB
Lab Blank 2/15/02
Lab Blank 2/22/02
020215-TB
020215-FB
020219-FB
020219-TB
020218-FB
020218-TB
020605-FB
020610-FB

Shallow refusal locations

RMB1	refusal at 1.5'
RMB2	refusal at 1'
RMB8	refusal at 2'
RMB19	refusal at 3'
RMB25	refusal at 3'



ERI locations are in blue

Figure 2-7. ERI's sampling locations

Section 3.0
Treatability Study

3.1 Purpose of the Treatability Study

The usability and benefits of the DUOX™ technology are dependent on the types and concentrations of the contaminants of concern, as well as characteristics of the associated matrix (soil and groundwater). Therefore, laboratory-based treatability studies are necessary prior to field implementation of the technology. Several treatability tests can be performed. Dosing experiments are needed to determine adequate oxidant types and concentrations in order to assure complete oxidation of the chlorinated organics (in soil and groundwater) without overdosing. Overdosing is undesirable from a cost perspective as well as potentially interfering with beneficial downgradient naturally-occurring reductive dechlorination processes. Dosing experiments addressing soil oxidant demand (SOD) are also beneficial for determining the expenditure of oxidants due to soil characteristics (oxidizable minerals and organic carbon compounds). SOD expenditure is a key feature of the DUOX™ technology, since low-cost oxidants are used to expend SOD. Finally, optimized oxidant candidates are tested on retrieved materials from the site to simulate treatment and determine reduction rates and efficiencies. For the Roosevelt Mills study, it was necessary to develop and test a spiked soil-fill matrix based on the results from the site characterization study. The findings from the site characterization study indicated that the source of the PCE was associated with a near-surface, coarse-grained fill material containing heterogeneously distributed globules of PCE. It was impossible to set-up identical replicates for the treatability study due to the inherent heterogeneity of the contaminated fill material. Therefore, uncontaminated fill material was retrieved from the site, screened, and spiked with appropriate levels of PCE to simulate globular-phase contamination.

The following sections discuss the treatability study objectives, experimental design, and results and conclusions.

3.2 Treatability Study Objectives

The objectives of the treatability study focused on evaluating the ability of the DUOX™ technology to treat both dissolved chlorinated organics in the groundwater as well as the globular free-phase PCE in the shallow fill material. Therefore, two primary objectives were established for the treatability study, and are summarized below:

1. Groundwater treatment - Concentrations of each of the target VOCs (PCE, TCE, DCE, VC), present in the groundwater, will reach 5 ug/l or less at the end of a 120 hr batch test using an optimized oxidant mixture (determined during optimization experiments) employing both oxidant solutions in series or combination.

2. Soil/Groundwater treatments - Achieve a 90 % reduction in the mass of PCE (based on the comparison of the post-treatment soil/water matrix) from the final experiments (performed in triplicate) employing both oxidant solutions in combination, with the calculated spiked concentrations based on the amount of PCE or chlorinated VOCs added to the soil/water system.

Secondary objectives for the treatability study included the evaluation of the behavior of heavy metals in the contaminated matrix when treated by the DUOX^{TM} technology and the monitoring of pH, ORP, anions (chloride and sulfate), particle size distribution (PSD), oxidant concentrations and TOC.

3.3 Treatability Study Experimental Design

The project objectives were evaluated by a series of tasks and experiments. These tasks were sequentially performed in order to: (1) characterize groundwater and fill material from the site for use in the evaluation experiments (Task 1), (2) determine the soil oxidant demand (SOD) of candidate oxidants alone and in combination as a means of determining the optimal oxidant solution for the subsequent evaluation (Task 2) , and (3) using the information from Tasks 1 and 2, perform the evaluation for the project objectives (Task 3). The three tasks are discussed in the following sections:

3.3.1 Task 1 - Preparation and Characterization of Soil and Groundwater

In order to generate a suitable and reproducible soil matrix for the evaluation experiment in Task 3, it was necessary to determine the grain size distribution of the fill material. Since the fill material is poorly-sorted and heterogeneous, containing excessively large cobbles, using this material without screening would require very large sample sizes to ensure a representative, reproducible sample for testing. Approximately 75 Kg of uncontaminated fill material was collected from the Roosevelt Mills site, characterized, and split into replicates for testing under Tasks 2 and 3.

Roosevelt Mills site groundwater was used in the treatability study. Both clean and contaminated groundwater were collected in a manner minimizing the soil particle content. Contaminated groundwater was collected just prior to the start of the groundwater treatability tests, and stored in 1-L VOCs-compatible Tedlar bags from the hot/treatment zones of the site while the clean groundwater was collected in 1-gallon amber glass bottles from areas absent of VOCs. Prior to use, triplicate groundwater samples (for both clean and contaminated groundwater) were characterized for parameters including VOCs, TOC, pH, metal content [including Na, K, Ca, Mg, Fe, Al, Mn, Cr, As, Se and Pb], alkalinity and anions (chloride and sulfate).

3.3.2 Task 2 - Determination of Soil Oxidant Demand

The results from this task provided data on the soil oxidant demand for individual oxidants and combinations. Potential cost reduction by applying the dual oxidants in combination or in sequence was evaluated based on the data obtained from this set of experiments. The source soil prepared in Task 1 was used to determine the soil oxidant demand under various testing conditions (e.g., different oxidant/soil ratios). Tests were performed in duplicate using a set of amber jar reactors on a rotator system used to enhance the contact between soil particles and the oxidant during the test.

Soil oxidant demand (SOD) was determined by oxidizing a certain amount (e.g., 50 g) of soil with the appropriate volume (e.g., 250 mL) of oxidant solutions in a desired oxidant/soil ratio (i.e., 0.5, 1, 3, 5, and 10 g/Kg). Two oxidants (i.e., $KMnO_4$ and $Na_2S_2O_8$) were applied separately, in sequence and in combination.

The oxidant concentrations in the reactors were periodically monitored during a test period of 10 days. The tests were run in duplicate to ascertain the reproducibility and reliability of the experimental data. The oxidant solutions used in the tests include 0.1, 0.2, 0.6, 1.0 and 2.0 g/L, corresponding to the oxidant/soil ratio of 0.5, 1, 3, 5 and 10 g/Kg, respectively (**Table 3-1**). In addition, duplicate control experiments (i.e., oxidant solutions in the absence of the soil as shown in Tests 1F, 2F, 3F and 4F in **Table 3-1**) were run to estimate the amount of oxidant consumption due to auto-decomposition during the test. Variation in the oxidant concentration with time was established by monitoring a data point every 2 days during the test. The SOD was determined using the following equation.

$$SOD = V(C_0-C_s)/m_{soil}$$

where V = the total volume of oxidant solution in the reactor; C_0 = initial oxidant concentration; C_s = the oxidant concentration at the time of sample collection; m_{soil} = the mass of dry soil used in the reaction. Because both the studied oxidants are light sensitive, experiments were conducted in a manner minimizing light exposure (e.g., wrapping the reactors with aluminum foil or using amber reaction jars) to limit any photo-catalyzed decomposition.

An additional control experiment (i.e., Test 1G) was used to establish the baseline of metal ions (i.e., Cr, As, Pb and Fe), in order to understand the impact of chemical injection on the Roosevelt Mills site soil matrix (by comparing the levels of targeted metal ions between the soil-DI water mixture and the soil-oxidant mixture). The impacts of chemical oxidation with $KMnO_4$ and $Na_2S_2O_8$ on the leaching of selected metals (e.g., As, Cr, Pb and Fe,) from the soil were examined. This was accomplished by determining the increase in dissolved metal ions (collected by filtering samples with 0.45 µm filters) in the samples at the end of the selected oxidation tests. The amount of the increase in dissolved metal ions was determined by comparing the metal ion concentrations of control samples (i.e., Task 2-1G) with those of the oxidant-containing samples (i.e., Tasks 2-1D, 2-2D and 2-3D). The pH and oxidation-reduction potential of all samples were measured so that a correlation between metal leaching with pH, oxidation reduction potential (ORP) and oxidant concentration can be established.

Table 3-1. Test Conditions of Batch Experiments for Soil Oxidant Demand (Task 2)

Test	Total Oxidant Solution Vol., ml	Initial $KMnO_4$ Conc., g/L	$KMnO_4$/Soil ratio g/kg-dry soil	Water/Dry-soil Ratio
2-1A	250	0.1	0.5	5:1
2-1B	250	0.2	1	5:1
2-1C	250	0.6	3	5:1
2-1D	250	1.0	5	5:1
2-1E	250	2.0	10	5:1
2-1F	250	1.0	No soil	NA
2-1G	250	DI water (no oxidant)	No $KMnO_4$	5:1
Test	**Total Oxidant Solution Vol., ml**	**Initial $Na_2S_2O_8$ Conc. g/L**	**$Na_2S_2O_8$/Soil ratio g/kg-dry soil**	**Water/Dry-soil ratio**
2-2A	250	0.1	0.5	5:1
2-2B	250	0.2	1	5:1
2-2C	250	0.6	3	5:1
2-2D	250	1.0	5	5:1
2-2E	250	2.0	10	5:1
2-2F	250	1.0	No soil	NA
Test	**Total Oxidant Solution Vol., ml**	**Initial $KMnO_4$ Conc. g/L (with 1 g/L $Na_2S_2O_8$)**	**$KMnO_4$/Soil ratio g/kg-dry soil**	**Water/Dry-soil ratio**
2-3A	250	0.1	0.5	5:1
2-3B	250	0.2	1	5:1
2-3C	250	0.6	3	5:1
2-3D	250	1.0	5	5:1
2-3E	250	2.0	10	5:1
2-3F	250	1.0	No soil	NA
Test	**Total Oxidant Solution Vol., ml**	**Initial $KMnO_4$ Conc. g/L (with pretreatment by 1 g/L $Na_2S_2O_8$ for 72 h)**	**$KMnO_4$/Soil ratio g/kg-dry soil**	**Water/Dry-soil ratio**
2-4A	250	0.1	0.5	5:1
2-4B	250	0.2	1	5:1
2-4C	250	0.6	3	5:1
2-4D	250	1.0	5	5:1
2-4E	250	2.0	10	5:1
2-4F	250	1.0	No soil	NA

Notes: 1. All experiments were conducted in duplicate

3.3.3 Task 3 - Degradation of VOCs in Groundwater and Soil by $KMnO_4$, $Na_2S_2O_8$ and the Dual Oxidants

In Task 3, the ability of $KMnO_4$ and $Na_2S_2O_8$ to degrade the targeted VOCs in the Roosevelt Mills site groundwater and prepared soil matrix was investigated. Three sets of batch experiments (Tasks 3-1, 3-2 and 3-3) were used to evaluate the effectiveness of degrading VOCs (in aqueous phase and in pure phase) with chemical oxidation under various media: (1) contaminated groundwater (2) soil with "contaminated" groundwater mixture (i.e., soil + clean groundwater spiked with targeted VOCs at 10 mg/L), and (3) soil with "free product" mixture (i.e., soil spiked with pure PCE). The oxidant dose was determined from the Task 2 results.

Experiments were conducted under headspace free and relatively constant temperature conditions using appropriate reactors (e.g., 40-mL volatile organic analysis (VOA) vials and a vial rotator system for mixing). A list showing experimental conditions and monitored parameters for Task 3 is presented in Table 3-2. The experiments were operated for a reaction period of 120 hours. The experimental procedures are described below.

In Task 3-1, the site VOC contaminated groundwater was used to determine the effectiveness of the DUOX™ technology in treated soluble chlorinated solvents in groundwater. The following experimental design was used:

- 6 vials used to determine initial (3 vials) and final (3 vials) VOCs levels as a control (Test 3-1D),
- vials (1 test in triplicate) used to determine VOC degradation by $KMnO_4$ oxidation (3-1A),
- vials (1 test in triplicate) used to determine VOC degradation by $Na_2S_2O_8$ oxidation (3-1B),
- vials (1 test in triplicate) for determining VOC degradation by $KMnO_4/Na_2S_2O_8$ oxidation (3-1C),
- vials used to determine the initial pH, ORP, chloride and oxidant levels (for 3-1D)
- another 6 vials (two for each oxidant) used to determine final pH, ORP, chloride production and oxidant concentrations at the end of the tests (3-1A, 3-1B, 3-1C).

These vials were injected with appropriate amounts of oxidant solutions to initiate the reactions. After the addition of the desired amount of oxidant, vials were placed in a rotator/shaker placed in an incubator set at 20 °C for 120 hours.

In Tasks 3-2 and 3-3 (see Table 3-2), procedures similar to the Task 3-1 experiments were followed with the following differences. For Task 3-2, a selected amount of soil and appropriate amounts of clean groundwater spiked with VOCs at the desired concentration (mixed to distribute the VOCs), was placed in each of the 23 vials or appropriate reactors, and an appropriate amount of the oxidant was added. For Task 3-3, a selected amount of soil was placed into each of the 23 vials or reactors, then pure-phase PCE was added to the soil. Distilled water was added to maintain a 5:1 water:soil ratio. Oxidants were added as above. This last task (3-3) was meant to simulate "pockets" of free product found in the soil void spaces, as observed during the site characterization efforts. The amount of pure product spiked during the third test of the treatability study is the estimated amount expected to produce free-product globules of a similar size and proportion (water-filled pore space versus PCE-filled pore space) as those observed during the site characterization. Spiking 10 ul of pure PCE into a treatability test sample of 8 grams for a concentration of approximately 2000 mg/Kg, met this requirement.

Table 3-2: Test Conditions for Evaluating the Degradation of VOCs in Groundwater and Soil

Task	Reaction media	Oxidant(s) 0.6 g/L concentration	No. of Reaction Vials	Aq/soil ratio
3-1A	Contaminated groundwater	$KMnO_4$	5	No soil
3-1B		$Na_2S_2O_8$	5	No soil
3-1C		$KMnO_4/ Na_2S_2O_8$	5	No soil
3-1D		None (Control experiment)	8	No soil
3-2A	Soil/groundwater spiked with 10 mg/L targeted VOCs (PCE, TCE and cis-DCE)	$KMnO_4$	5	5:1
3-2B		$Na_2S_2O_8$	5	5:1
3-2C		$KMnO_4/ Na_2S_2O_8$	5	5:1
3-2D		None (Control experiment)	8	5:1
3-3A	Soil spiked with pure PCE; distilled water	$KMnO_4$	5	5:1
3-3B		$Na_2S_2O_8$	5	5:1
3-3C		$KMnO_4/ Na_2S_2O_8$	5	5:1
3-3D		None (Control experiment)	8	5:1

NOTE: Reaction time (120 hrs) and temperature (20 degrees C) constant for all tests

3.4 Treatability Study Results and Conclusions

The following sections present the results from the three experimental tasks and discuss these results in relation to the usability of the DUOX™ technology at the Roosevelt Mills site.

3.4.1 Task 1 Results and Conclusions

3.4.1.1 Particle Size Distribution

The results from the particle size distribution (Task 1-A) are presented in **Table 3-3**. Approximately 100 grams of material was sampled from the near-surface shallow material and sieved through four sieves (10, 40, 100 and 200). The sieving operation was replicated four times, and reproducibility between replicates was good. Based on these results, it was decided that sieving through a No. 8 sieve (2.36 mm) would remove the oversize material and provide a suitable matrix for the testing in terms of reproducibility, and would be representative of the fill material.

3.4.1.2 Characterization of Fill Material

The clean fill material was characterized for metals, TOC, pH, total chloride, percent moisture and select chlorinated VOCs to: (1) determine the levels of metals and organic components that may expend oxidants, and (2) confirm that the material is clean relative to the chlorinated volatile organics. Results from the characterization are presented in **Table 3-4**. Three samples were analyzed for the analytes discussed above. Overall, reproducibility between the samples was good. The analysis for metals and TOC did not indicate the presence of compounds that would significantly expend the oxidant solutions. The analysis for VOCs did not indicate the presence of significant chlorinated materials that would influence the spiking experiment under Task 3.

3.4.1.3 Groundwater Characterization

Clean and contaminated groundwater from the Roosevelt Mills site was collected and analyzed for the purpose of determining inorganic and organic characteristics for Task 3 experiments. Results are presented in **Table 3-5** for the background area and in **Table 3-6** for the contaminated area. Three replicates were analyzed from both areas. The replicate data indicate good reproducibility. The results indicate that the groundwater sampled from the background area did not contain detectable levels of chlorinated solvents. The groundwater collected from the contaminated area at the site contained approximately 200 ug/L of PCE and was deemed appropriate for testing under Task 3.

3.4.2 Task 2 Results and Conclusions

Soil oxidant demand was evaluated on non-contaminated near-surface fill material to determine the levels and types of oxidants that would be most applicable for testing under Task 3. Under Task 2, two oxidants (potassium permanganate and sodium persulfate) were evaluated alone and in combination at five different concentration levels (0.1 g/L, 0.2 g/L, 0.6 g/L, 1.0 g/L, and 2.0 g/L) over a ten-day period. The oxidant concentrations were periodically measured over the ten-day period. The amount of oxidant consumed over the ten days is an indication of the soil oxidant demand (excluding auto-decomposition). **Figures 3-1** through **3-4** depict the results of the soil oxidant demand experiments for: (1) potassium permanganate (at the five concentrations), (2) sodium persulfate (at the five concentrations), (3) potassium permanganate (at the five concentrations) with 1 g/L of sodium persulfate, and (4) potassium permanganate (at the five concentrations) with a 72 hour pretreatment with 1 g/L sodium persulfate.

The experiments indicate that the near-surface fill material exhibits minimal soil oxidant demand, as demonstrated by the small decrease in oxidant concentration over the ten-day period for all oxidants and oxidant combinations. This is consistent with the findings from the characterization analyses under Task 1 which demonstrated that the fill material has low total organic carbon and low concentrations of metals that would expend the oxidants.

Based on the results from these experiments, it was decided that oxidant concentrations at 0.6 g/L would be used for the Task 3 studies. This determination was based on: (1) the levels of chlorinated solvents in the contaminated media, and (2) the fact that approximately 90% of the oxidants remained after the ten-day study at the 0.6 g/L concentration.

Table 3-3. Sieving Results for the Fill Material

Test # 1A-1					
Soil Weight	100.4	grams			
Time	40	minutes			
Sieve NO	Tare (g)	Sieved Weight (g)	Soil Retained (g)	% Retained	Particle Size Range (mm)
10	488.6	507.6	19.0	18.9	2 to 5
40	389.0	441.5	52.5	52.3	0.475 to 2
100	347.5	373.5	26.0	25.9	0.125 to 0.475
200	329.4	331.3	1.9	1.9	0.075 to 0.125
Bottom	503.8	504.5	0.7	0.7	< 0.075
		Total:	100.1		
Test # 1A-2					
Soil Weight	101.0	grams			
Time	40	minutes			
Sieve NO	Tare (g)	Sieved Weight (g)	Soil Retained (g)	% Retained	Particle Size Range (mm)
10	488.5	508.4	19.9	19.3	2 to 5
40	389.0	439.6	50.6	49.2	0.475 to 2
100	347.2	374.5	27.3	26.5	0.125 to 0.475
200	329.4	331.4	2.0	1.9	0.075 to 0.125
Bottom	503.7	504.5	0.8	0.8	< 0.075
		Total:	100.6		
Test # 1A-3					
Soil Weight	102.9	grams			
Time	40	minutes			
Sieve NO	Tare (g)	Sieved Weight (g)	Soil Retained (g)	% Retained	Particle Size Range (mm)
10	488.5	508.7	20.2	19.6	2 to 5
40	388.9	446.4	57.5	55.9	0.475 to 2
100	347.3	369.8	22.5	21.9	0.125 to 0.475
200	329.4	331.0	1.6	1.6	0.075 to 0.125
Bottom	503.7	504.4	0.7	0.7	< 0.075
		Total:	102.5		
Test # 1A-4					
Soil Weight	100.7	grams			
Time	40	minutes			
Sieve NO	Tare (g)	Sieved Weight (g)	Soil Retained (g)	% Retained	Particle Size Range (mm)
10	488.4	510.2	21.8	21.2	2 to 5
40	388.9	439.6	50.7	49.3	0.475 to 2
100	347.3	373.2	25.9	25.2	0.125 to 0.475
200	329.3	330.9	1.6	1.6	0.075 to 0.125
Bottom	503.7	504.3	0.6	0.6	< 0.075
		Total:	100.6		

Table 3-4. Fill Characterization Results

	Sample 1	**Sample 2**	**Sample 3**
Metals *(mg/kg dw)*			
Aluminum	40000	26000	28000
Arsenic	8.5	7.1	9.4
Chromium	100	74	80
Iron	97000	62000	68000
Lead	49	44	44
Manganese	2300	2300	1500
Selenium	<7.1	<7.1	<7.1
TOC *(mg/kg, dw)*	<510	<510	<510
Total Chloride *(mg/kg)*	70	70	70
pH	9.75	9.67	9.67
Moisture *(%)*	0.67	0.64	0.66

VOCs *(ug/kg dw)*					
	VC	t-DCE	c-DCE	TCE	PCE
Sample 1	<200	<200	<200	<200	<200
Sample 2	<200	<200	<200	<200	<200
Sample 3	<200	<200	<200	<200	<200

Table 3-5. Background Groundwater Characteristics

	Replicate 1	Replicate 2	Replicate 3
Metals *(mg/L)*			
Aluminum	<0.20	<0.20	<0.20
Arsenic	<0.010	<0.010	<0.010
Calcium	12	12	12
Chromium	<0.010	<0.010	<0.010
Iron	2.3	2.5	2.4
Lead	<0.0050	<0.0050	<0.0050
Manganese	0.28	0.29	0.29
Magnesium	3.4	3.6	3.6
Sodium	8.7	9.1	8.9
Potassium	5.9	6.1	6
Selenium	<0.010	<0.010	<0.010
TOC *(mg/L)*	1.6	1.6	1.5
Chloride *(mg/L)*	3.6	3.6	3.4
Sulphate *(mg/L)*	19.5	19.6	19.5
pH	8.45	8.22	8.1
ORP*(mv)*	862	817	800
Alkalinity *(mg/L)*	55	54	53

VOCs *(ug/L)*					
	VC	t-DCE	c-DCE	TCE	PCE
Replicate 1	<4	<4	<4	<4	<4
Replicate 2	<4	<4	<4	<4	<4
Replicate 3	<4	<4	<4	<4	<4

Table 3-6. Contaminated Groundwater Characteristics.

	Replicate 1	Replicate 2	Replicate 3
***Metals** (mg/L)*			
Aluminum	<0.20	<0.20	<0.20
Arsenic	<0.010	<0.010	<0.010
Calcium	15	14	14
Chromium	<0.010	<0.010	<0.010
Iron	<0.050	<0.050	<0.050
Lead	<0.0050	<0.0050	<0.0050
Manganese	0.021	0.021	0.021
Magnesium	2.6	2.5	2.6
Sodium	5.9	5.8	5.9
Potassium	3.9	3.9	3.9
Selenium	<0.010	<0.010	<0.010
***TOC** (mg/L)*	<1.0	<1.0	<1.0
***Chloride** (mg/L)*	4.2	4.2	4.2
***Sulphate** (mg/L)*	18.7	18.7	18.6
pH	7.68	7.66	7.67
***ORP**(mv)*	810	827	832
***Alkalinity** (mg/L)*	40	41	41

***VOCs** (ug/L)*					
	VC	t-DCE	c-DCE	TCE	PCE
Replicate 1	<8	<8	<8	<8	212
Replicate 2	<8	<8	<8	<8	201
Replicate 3	<4	<4	<4	<4	223

In order to determine the potential effect of the oxidants on metal solubilization, select experiments were sampled for metals on initial oxidant addition and at the end of the ten-day experiment. In addition, a DI water control (no oxidant) was sampled initially and at the end of ten days. The samples were filtered through a 0.45um filter and analyzed to determine dissolved metals. Results from the study are presented in **Table 3-7**. The study demonstrated that there were minor increases in some soluble metals in some of the experiments. Chromium increased (relative to the control) in the experiments that used potassium permanganate. Manganese also increased (relative to the control) in the experiments that used potassium permanganate.

3.4.3 Task 3 Results and Conclusions

Task 3 activities investigated the performance of the DUOX™ technology for the treatment of chlorinated solvents in groundwater and a soil/groundwater matrix. Under this task, three sets of experiments were performed. Task 3-1 investigated the ability of the oxidants (alone and in combination) to treat PCE contaminated groundwater from the Roosevelt Mills site. Task 3-2 investigated the ability of the oxidants (alone and in combination) to treat a spiked groundwater that was added to the near-surface fill material. Task 3-3 evaluated the ability of the oxidants (alone and in combination) to treat PCE as a free-phase globular component in the near-surface fill material. Results from these experiments are presented and discussed in the following sections.

3.4.3.1 <u>Task 3-1 – Treatment of Contaminated Groundwater with Oxidants</u>

Under this task, groundwater from the Roosevelt Mills site, contaminated with approximately 130 ug/L of PCE, was treated with potassium permanganate and sodium persulfate, alone and in combination, for 120 hours to determine the ability of the oxidants to degrade the PCE

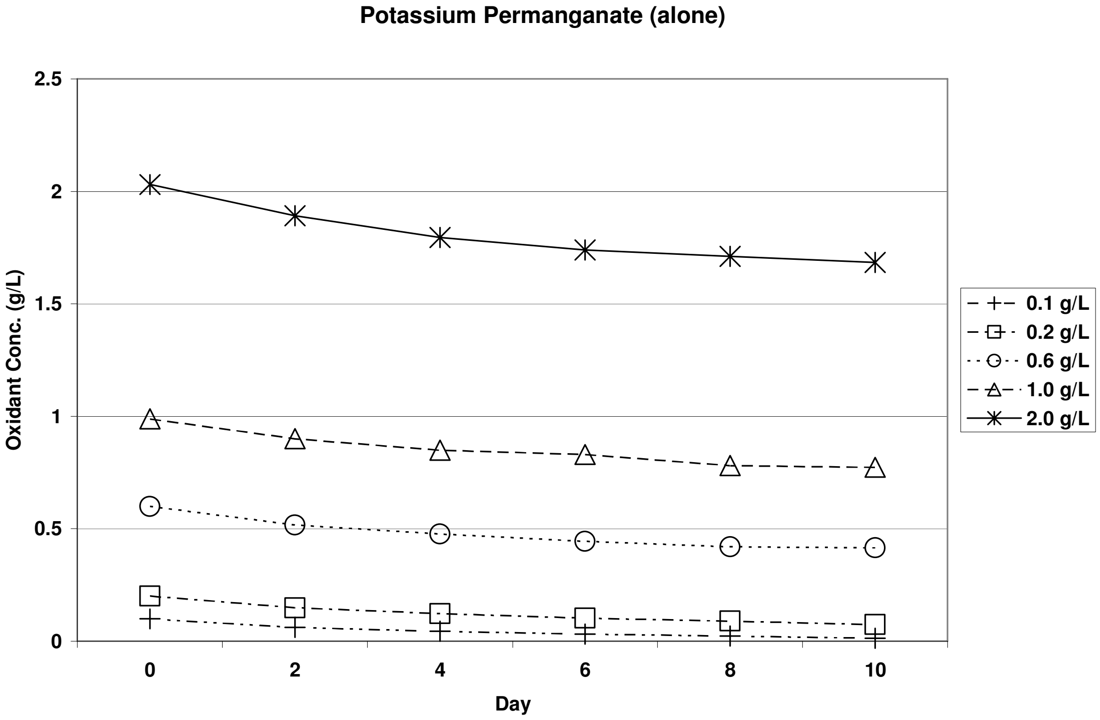


Figure 3-1. Oxidant consumption over time – Potassium Permanganate (alone).

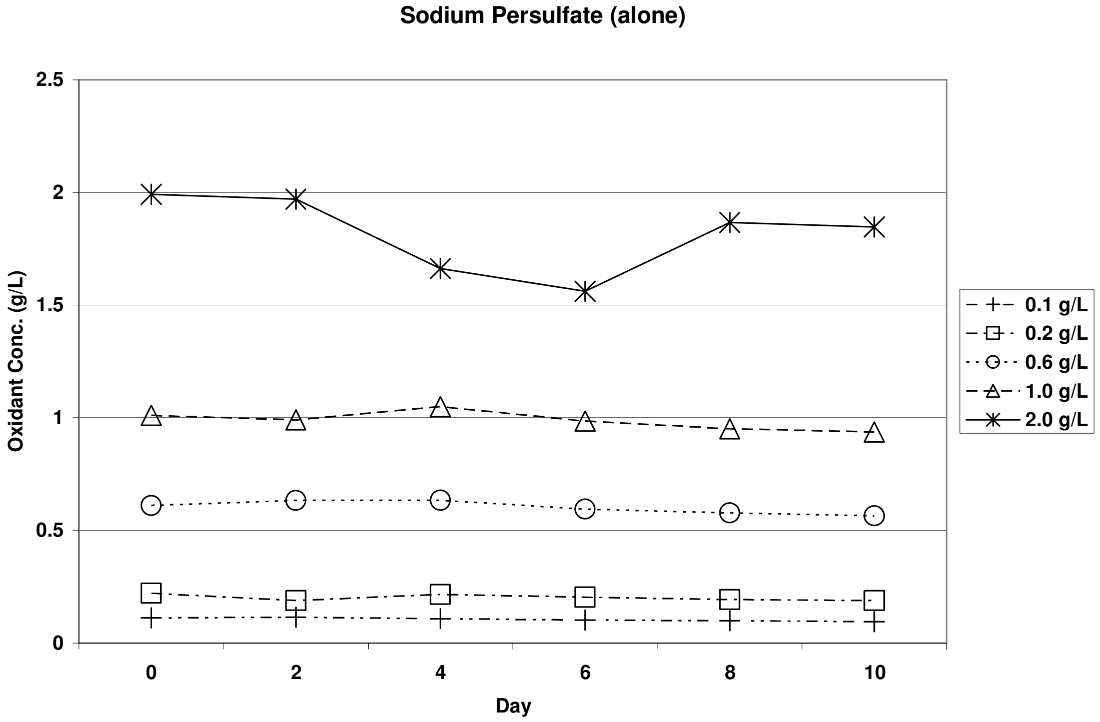


Figure 3-2. Oxidant consumption over time – Sodium Persulfate (alone).

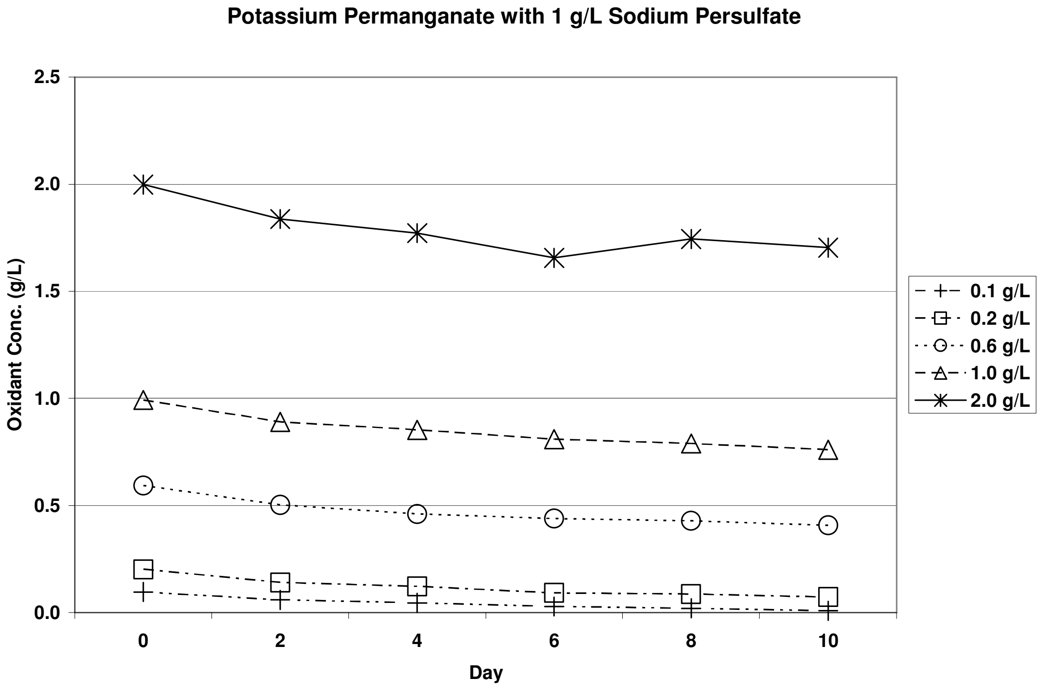


Figure 3-3. Oxidant consumption over time –Potassium Permanganate with 1 g/L Sodium Persulfate.

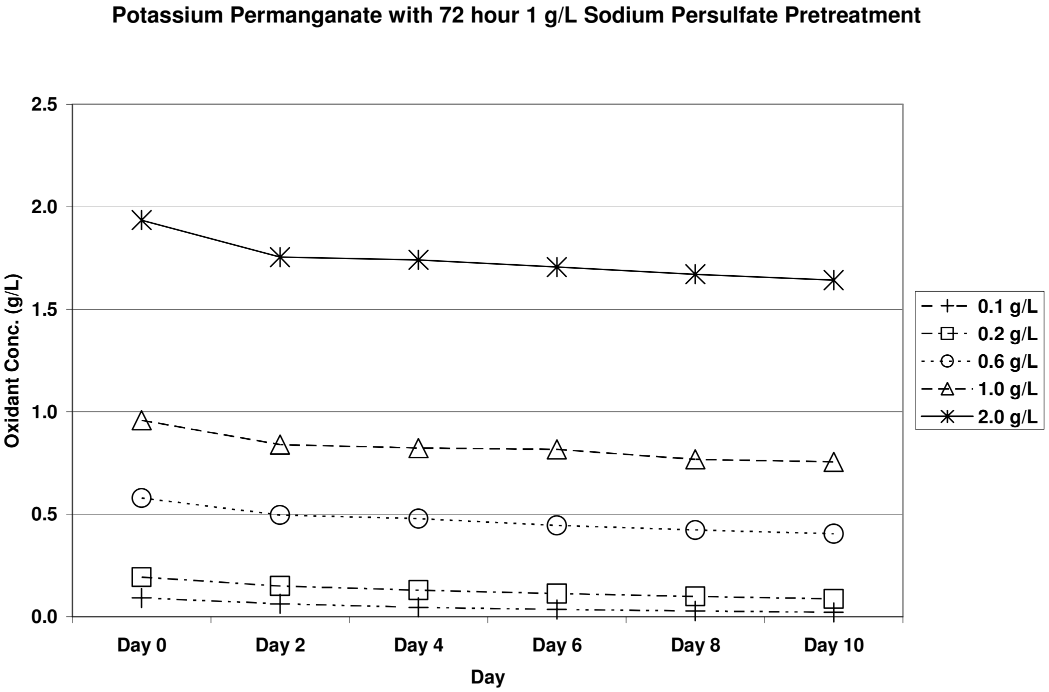


Figure 3-4. Oxidant consumption over time –Potassium Permanganate with 72 hour 1 g/L Sodium Persulfate pretreatment.

Table 3-7. Soluble Metals Before and After Ten Days of Oxidant Treatments

Sample	Stage	Al mg/L	As mg/L	Cr mg/L	Fe mg/L	Pb mg/L	Mn mg/L	Se mg/L
Control (no oxidant)	Initial	0.34	<0.010	<0.010	0.062	<0.0050	1.4	<0.010
Control (no oxidant)	Final	1	<0.010	<0.010	<0.050	<0.0050	<0.010	<0.010
Permanganate (1.0 g/L)	Initial	0.46	<0.010	<0.010	<0.050	<0.0050	38	0.018
Permanganate (1.0 g/L)	Final	0.37	<0.010	0.042	<0.050	<0.0050	3.9	<0.010
Persulfate (1.0 g/L)	Initial	0.43	<0.010	<0.010	0.066	<0.0050	0.59	<0.010
Persulfate (1.0 g/L)	Final	0.83	<0.010	<0.010	<0.050	<0.0050	<0.010	<0.010
Permanganate (1.0 g/L) and Persulfate (1.0 g/L)	Initial	<0.2	<0.010	<0.010	<0.050	<0.0050	49	0.018
Permanganate (1.0 g/L) and Persulfate (1.0 g/L)	Final	0.27	<0.010	0.04	<0.050	<0.0050	44	0.018
Permanganate (1.0 g/L) and 72 hr pretreat with persulfate (1.0 g/L)	Initial	<0.2	<0.010	<0.010	<0.050	<0.0050	2.7	<0.010
Permanganate (1.0 g/L) and 72 hr pretreat with persulfate (1.0 g/L)	Final	0.31	<0.010	0.021	<0.050	<0.0050	22	0.012

to less than 5 ug/L.. Results from this task are presented in **Table 3.8**.

Oxidants were added to the reaction vessels at a concentration of 0.6 g/L and reacted at 20°C for 120 hours. Five reaction vessels were used for each oxidant treatment and combination as well as a control (no oxidants). Two of the vials were used to measure the following parameters: pH, ORP, oxidant concentration, chloride, and sulfate. Three vials were used to analyze for chlorinated solvents. The vials were analyzed for these parameters at the start of the reaction (0 hour) and at the end of the reaction (120 hours), except for chlorinated solvents which were only measured at the end of the reaction. In addition, a control sample (no oxidants) was analyzed at time 0 and at 120 hours.

Results from the control samples reveal that the contaminated groundwater started at an average PCE concentration of 131 ppb, and after 120 hours averaged 126 ppb, indicating that there was no significant loss in volatiles over the course of the experiment. It is important to note that the groundwater contained only PCE as the chlorinated solvent, and the other VOCs (VC, DCE, and TCE) were below the detectable levels of 5 ug/L. Results from the other analytes indicate minimal changes over time. As a baseline, pH was approximately 8.6, ORP around 900, chloride 3.5 mg/L, and sulfate approximately 17 mg/L.

The potassium permanganate treatment successfully reduced the PCE to less than 5 ug/L after 120 hours, thereby meeting the project claim. In addition, there was an increase in pH, as well as an increase in both chloride and sulfate. In addition, there was no discernable expenditure of oxidant over the 120 hours. The sodium persulfate treatment did not reduce the concentration of PCE to less than 5 ug/L, and therefore the project objective was not met for this oxidant. The concentration of PCE was reduced to approximately 40 ug/L after 120 hours. It is important to note that the lack of a reduction to less than 5 ug/L is not totally unexpected, since the main purpose of this oxidant is to minimize or eliminate soil oxidant demand, as opposed to being an oxidizing agent for the chlorinated solvents. The combined oxidants (potassium permanganate and sodium persulfate) successfully reduced the PCE to less than 5 ug/L after 120 hours and met the project claim. As with the potassium permanganate treatment, pH, chloride, and sulfate increased. Again, there was no discernable expenditure of oxidants over the 120 hours.

Table 3-8. Results from Contaminated Groundwater Treatment

Initial Oxidant Conc (g/L)	Time	pH	ORP (mV)	Oxidant Conc (g/L)	Chloride (mg/L)	Sulfate (mg/L)	PCE (ug/L)	Average PCE (ug/L)	Met Claim
$KMnO_4$ (0.6)	120hr						**<5**	**<5**	**YES**
$KMnO_4$ (0.6)	120hr						**<5**		
$KMnO_4$ (0.6)	120hr						**<5**		
$KMnO_4$ (0.6)	120hr	9.5	946	0.557	4.5	21.8			
$KMnO_4$ (0.6)	120hr	9.2	955	0.584	5.8	20.1			
$KMnO_4$ (0.6)	0hr	8.9	923	0.560	4.7	21.6			
$KMnO_4$ (0.6)	0hr	8.8	938	0.563	4.3	21.0			
$Na_2S_2O_8$ (0.6)	120hr						**48**	**40**	**NO**
$Na_2S_2O_8$ (0.6)	120hr						**38**		
$Na_2S_2O_8$ (0.6)	120hr						**34**		
$Na_2S_2O_8$ (0.6)	120hr	8.8	879	0.648	3.9	24.9			
$Na_2S_2O_8$ (0.6)	120hr	8.6	870	0.595	3.9	25.6			
$Na_2S_2O_8$ (0.6)	0hr	8.4	825	0.638	3.7	21.2			
$Na_2S_2O_8$ (0.6)	0hr	8.4	829	0.634	3.7	21.3			
Both (0.6)	120hr						**<5**	**<5**	**YES**
Both (0.6)	120hr						**<5**		
Both (0.6)	120hr						**<5**		
Both (0.6)	120hr	9.3	968	0.559	4.7	22.1			
Both (0.6)	120hr	9.2	972	0.569	4.6	21.5			
Both (0.6)	0hr	8.7	942	0.573	4.0	24.4			
Both (0.6)	0hr	9.0	928	0.573	4.9	24.0			
None (Control)	120hr						**137**	**126**	
None (Control)	120hr						**132**		
None (Control)	120hr						**108**		
None (Control)	0hr						**149**	**131**	
None (Control)	0hr						**133**		
None (Control)	0hr						**112**		
None (Control)	120hr	8.3	775		3.5	17.3			
None (Control)	120hr	8.2	815		3.7	17.2			
None (Control)	0hr	8.7	908		3.6	17.6			
None (Control)	0hr	8.5	900		3.4	16.7			

In summary, potassium permanganate, alone and in combination with sodium persulfate, successfully reduced the PCE contaminated groundwater from a starting concentration of approximately 130 ug/L to less than 5 ug/L over the 120 hour test. Sodium persulfate alone did not reduce the PCE to less than 5 ug/L.

3.4.3.2 Task 3-2 – Treatment of Contaminated Groundwater in a Soil Matrix With Oxidants

Task 3-2 evaluated the oxidants, alone and in combination, to treat a spiked groundwater in a soil (near-surface fill) matrix. For these experiments, 10 mg/L each of PCE, TCE, and DCE were added to 40 ml of uncontaminated groundwater from the site. Eight grams of the screened near-surface fill material (soil) was added to the spiked groundwater. The groundwater/soil matrix was reacted with the oxidants, alone and in combination, for 120 hours. A control sample with no oxidants was also run. The initial and final samples (0 and 120 hours) were analyzed for pH, ORP, chloride, and sulfate. The final samples were analyzed for each of the chlorinated VOCs in both the aqueous and solid phases and converted to mass in order to calculate percent reduction. The control sample was analyzed for chlorinated VOCs both at 0 hours and at 120 hours.

Table 3-9 presents the results of the chlorinated VOC reductions (as percent) after 120 hours of treatment. **Table 3-10** presents the results of the other measurements and analytes.

The permanganate (alone) treatment achieved average mass reductions of 99.5% for PCE, 99.5% for TCE, and 99.4% for DCE. Based on these mass reductions, the permanganate treatment successfully met the project objective of a 90% mass reduction for all three analytes. There was also a reduction in the concentration of the oxidant during the course of the experiment (average of 0.57 g/L at time 0 hour to 0.45 g/L at 120 hours). There was also an increase in pH, chloride, and sulfate.

The persulfate (alone) treatment achieved average mass reductions of 15% for PCE, 6% for TCE, and 14.3% for DCE. Based on these mass reductions, the persulfate treatment did not meet the project objective of a 90% reduction in mass for any of the three analytes. Furthermore, there was no discernable reduction in the concentration of the oxidant over the course of the experiment. There was also an increase in chloride and sulfate from 0 hours to 120 hours.

The combined permanganate and persulfate treatment achieved average mass reductions of 99.5% for PCE, 99.5% for TCE, and 99.4% for DCE. Based on these mass reductions, the combined treatment successfully met the project objective of a 90% mass reduction for all three analytes. As with the permanganate (alone) treatment, the combined treatment exhibited a reduction in the concentration of oxidants over the course of the experiment, indicating that the oxidants (predominately permanganate) were expended during the oxidation of the chlorinated VOCs. There was also an increase in pH, chloride, and sulfate over the course of the experiment.

It is important to note that the reductions shown in **Table 3-9** for tests performed on the spiked groundwater/soil matrix were determined based on a comparison of the total final mass to the initial mass of the contaminant of interest. The initial mass was determined by averaging the results of the control test samples for the spiked compounds PCE, TCE and DCE (three T=0 hours analyses and three T120 analyses). The control measurements were reproducible with average RSD values for each analyte of approximately 10%. Final mass was determined using the aqueous and soil concentrations with the associated volumes and weights for samples analyzed after 120 hours of treatment. For samples with analyte concentrations that were reported as non-detected, the detection limit value (0.005 mg/L for the aqueous phase and 0.200 mg/Kg for the soil phase) was used as the sample concentration for calculating mass.

3.4.3.3 Task 3-3 – Treatment of Free-Phase (Globular) PCE Contaminated Soil/Groundwater Matrix with Oxidants

The site characterization study at Roosevelt Mills identified a chlorinated solvent source area in the near-surface, coarse-grained fill material. This fill material was impacted by PCE primarily distributed as a globular free-phase product within the large pore-spaces. Therefore, a remedial action should consider treatment of this material. Based on this need, the treatability study investigated the applicability of the DUOX™ process for the treatment of this free-phase, globular material within the saturated near-surface fill material. Due to the heterogeneous distribution of this material at the site, it was necessary to develop a soil/groundwater matrix, spiked with PCE to simulate free-phase distribution of the PCE.

The simulated soil/groundwater matrix was prepared by spiking 10 ul of PCE into 8 grams of the screened fill

Table 3-9. Chlorinated VOC Results from Spiked Groundwater/Soil.

		Initial Mass: 0.485 mg				Initial Mass: 0.415 mg				Initial Mass: 0.375 mg			
Initial Oxidant Conc (g/L)	**Time**	**Final Mass, mg**	**PCE Mass Red.**	**Average PCE Red.**	**Met Claim**	**Final Mass, mg**	**TCE Mass Red.**	**Average TCE Red.**	**Met Claim**	**Final Mass, mg**	**DCE Mass Red.**	**Average DCE Red.**	**Met Claim**
$KMnO_4$ (0.6)	120hr	0.002	99.5	99.5	YES	0.002	99.5	99.5	YES	0.002	99.4	99.4	YES
$KMnO_4$ (0.6)	120hr	0.002	99.5			0.002	99.5			0.002	99.4		
$KMnO_4$ (0.6)	120hr	0.002	99.6			0.002	99.6			0.002	99.5		
$Na_2S_2O_8$ (0.6)	120hr	0.440	9.4	15	NO	0.415	0	6	NO	0.337	10	14.3	NO
$Na_2S_2O_8$ (0.6)	120hr	0.400	17.6			0.377	9.1			0.314	16.3		
$Na_2S_2O_8$ (0.6)	120hr	0.401	17.3			0.378	8.8			0.313	16.5		
Both (0.6)	120hr	0.002	99.6	99.5	YES	0.002	99.5	99.5	YES	0.002	99.4	99.4	YES
Both (0.6)	120hr	0.002	99.5			0.002	99.5			0.002	99.4		
Both (0.6)	120hr	0.002	99.5			0.002	99.5			0.002	99.4		
None	120hr	0.525				0.449				0.399			
None	120hr	0.473				0.408				0.359			
None	120hr	0.384				0.338				0.312			
None	0hr	0.506				0.426				0.395			
None	0hr	0.553				0.464				0.415			
None	0hr	0.472				0.402				0.369			

Note: Initial mass determined as the average of the no treatment tests at T=0 and T=120 hours (6 samples)
Note: Detection limit values were used as the sample concentration to calculate final mass for samples with the analytes reported as ND

Table 3-10. Other Analytes Results from Spiked Groundwater/Soil.

Initial Oxidant Concentration (g/L)	Time	pH	ORP (mV)	Oxidant Conc (g/L)	Cl (mg/L)	SO4 (mg/L)
$KMnO_4$ (0.6)	120hr					
$KMnO_4$ (0.6)	120hr					
$KMnO_4$ (0.6)	120hr					
$KMnO_4$ (0.6)	120hr	8.7	819	0.445	47.3	57.1
$KMnO_4$ (0.6)	120hr	9.1	825	0.447	45.3	50.6
$KMnO_4$ (0.6)	0hr	7.9	866	0.615	40.1	32.3
$KMnO_4$ (0.6)	0hr	8	879	0.523	40.1	30.1
$Na_2S_2O_8$ (0.6)	120hr					
$Na_2S_2O_8$ (0.6)	120hr					
$Na_2S_2O_8$ (0.6)	120hr					
$Na_2S_2O_8$ (0.6)	120hr	9.1	808	0.638	20.5	70.0
$Na_2S_2O_8$ (0.6)	120hr	8.8	801	0.642	22.0	66.7
$Na_2S_2O_8$ (0.6)	0hr	8.9	746	0.622	12.9	31.0
$Na_2S_2O_8$ (0.6)	0hr	8.6	742	0.623	12.2	29.9
Both (0.6)	120hr					
Both (0.6)	120hr					
Both (0.6)	120hr					
Both (0.6)	120hr	8.8	845	0.404	42.1	55.6
Both (0.6)	120hr	9	839	0.407	42.5	60.7
Both (0.6)	0hr	8.4	880	0.557	38.8	32.9
Both (0.6)	0hr	8.4	868	0.513	35.9	30.2
None	120hr					
None	120hr					
None	120hr					
None	0hr					
None	0hr					
None	0hr					
None	120hr	9.3	814		18.9	53.2
None	120hr	9.1	807		18.8	49.6
None	0hr	9	779		11.3	23.7
None	0hr	8.9	751		11.0	23.6

material, resulting in a concentration of approximately 2,000 mg/kg. Distilled water was then added to achieve a 5:1 (w/w) ratio of aqueous to soil. As in Task 3-2, oxidants alone and in combination, as well as a no oxidant control, were evaluated to determine the mass reduction in the PCE over a 120 hour period. This test was considered the most challenging due to the concentration and distribution of the free-phase PCE within the soil matrix.

Table 3-11 presents the results of the PCE reductions (as percent) after 120 hours of treatment, as well as the initial and final analysis of oxidant concentration, pH, ORP, chloride, and sulfate.

The permanganate (alone) treatment was able to successfully degrade an average of 94.1% of the PCE and met the project objective of a 90% or greater mass reduction. It is important to note that the oxidant consumption was high (0.55 g/L to 0.15 g/L), presumably due to the relatively high concentration of PCE in the experiment. Furthermore, the chloride content increased from approximately 11 mg/L at the beginning of the experiment to 212 mg/L at the end, and may indicate the generation of chloride from the degradation of the chlorinated PCE. In contrast to tests run under Tasks 3-1 and 3-2, pH dropped from an average of 9.6 to 7.6.

As seen in the previous tasks, the persulfate (alone) treatment was not successful in meeting the project objective. The average reduction in mass for the persulfate was 0.8%, thereby not meeting the project objective of a 90% reduction in the mass of PCE. Furthermore, there was virtually no change in oxidant consumption over the course of the experiment.

The combined permanganate and persulfate treatment achieved an average mass PCE reduction of 91.4%, and met the project objective for a 90% mass reduction. As with the permanganate (alone) treatment, there was a large expenditure of the oxidants, as well as a large increase in the chloride concentration. The pH also was lowered over the course of the demonstration. Based on the previous experiments, it is probable that the permanganate is the operative oxidant responsible for the observed decomposition.

It is important to note that **Table 3-11** presents conservative estimates of the efficacy of the oxidant treatment on free-phase PCE in the near-surface fill material, based on several of the conditions placed on the determinations. As noted for Task 3-2, initial mass was determined by averaging the results of the control test samples for the spiked compound PCE, which had an RSD of <15% for all six values (three T0 and three T120 hour results). The QAPP specified that the initial mass used in the determination of percent reduction would be calculated based on the known spiked amount (16.2 mg). However, using the observed initial mass as measured from the controls (9.1 mg) provides a more conservative estimate of efficiency. Furthermore, calculations for the percent reduction in the treatment systems using potassium permanganate alone and both oxidants together were performed using an estimated concentration for the aqueous phase that overestimated the contribution of this phase to the total final mass. The analysis of the aqueous samples for each of these tests (three test vials for the permanganate and three vials for the tests with both oxidants) resulted in PCE concentrations that exceeded the upper range of the analytical calibration curve. Since the entire sample was consumed during the analysis, reanalyzing a diluted sample was not possible. Results for other samples that exceeded the calibration curve and were reanalyzed at a higher dilution (e.g., the control samples which were expected to be high and therefore analyzed initially at a dilution and reanalyzed at a higher dilution as necessary), indicated that concentration results were 50-70% higher when the sample was reanalyzed at an appropriate dilution. For the aqueous samples that exceeded the calibration range for PCE, an estimated concentration of five times the observed concentration was used in determining the final mass of PCE for these tests (e.g., sample 3-3A-2 had an observed PCE concentration of 1.973 mg/L and a value of 9.865 mg/L was used in the calculation of final mass).

Table 3-11. Results from Free-Phase (Globular) PCE Contaminated Soil/Groundwater

Initial Oxidant Conc (g/L)	Time	pH	ORP (mV)	Oxidant Conc (g/L)	Cl (mg/L)	SO4 (mg/L)	Final PCE Mass, mg	PCE Mass Red.	Average PCE Red.	Met Claim
$KMnO_4$ (0.6)	120hr						0.338*	94.3	94.1	YES
$KMnO_4$ (0.6)	120hr						0.355*	94		
$KMnO_4$ (0.6)	120hr						0.389*	93.9		
$KMnO_4$ (0.6)	120hr	7.4	878	0.123	278.3	49.3				
$KMnO_4$ (0.6)	120hr	7.8	933	0.178	146.1	35.8				
$KMnO_4$ (0.6)	0hr	9.7	832	0.537	10.0	8.2				
$KMnO_4$ (0.6)	0hr	9.5	922	0.567	11.6	7.0				
$Na_2S_2O_8$ (0.6)	120hr						10.8	-18.5	0.8	NO
$Na_2S_2O_8$ (0.6)	120hr						7.91	13		
$Na_2S_2O_8$ (0.6)	120hr						8.41	7.6		
$Na_2S_2O_8$ (0.6)	120hr	9.8	946	0.645	22.6	46.9				
$Na_2S_2O_8$ (0.6)	120hr	9.6	818	0.702	23.6	43.2				
$Na_2S_2O_8$ (0.6)	0hr	9.6	890	0.695	9.4	10.9				
$Na_2S_2O_8$ (0.6)	0hr	9.6	945	0.574	8.9	10.0				
Both (0.6)	120hr						0.358*	92.2	91.4	YES
Both (0.6)	120hr						0.401*	90.5		
Both (0.6)	120hr						0.175*	91.6		
Both (0.6)	120hr	7.3	852	0.142	243.4	46.8				
Both (0.6)	120hr	6.5	947	0.095	279.7	41.5				
Both (0.6)	0hr	9.7	776	0.614	9.3	9.6				
Both (0.6)	0hr	9.8	762	0.605	2.9	5.6				
None	120hr						10.4			
None	120hr						8			
None	120hr						10.4			
None	0hr						7.23			
None	0hr						8.04			
None	0hr						10.4			
None	120hr	9.86	823		15.8	35.9				
None	120hr	9.91	814		15.1	29.6				
None	0hr	10.1	766		8.6	6.4				
None	0hr	10.1	785		9.4	7.2				

Note: Initial mass determined as the average of the no treatment tests at T=0 and T=120 hours (6 samples)
Note: Detection limit values were used as the sample concentration to calculate final mass for samples
With the analytes reported as ND
*Note: For tests with aqueous sample concentrations that exceeded calibration range, an estimate of 5 times the observed concentration was used (see text discussion) to calculate final mass.

3.5 Treatability Study General Conclusions and Discussion

The following general conclusions can be drawn from this treatability study:

1. The near-surface fill material (source area matrix for the PCE) exhibits a very low soil oxidant demand.
2. Permanganate alone and in combination with persulfate is effective in reducing the levels of chlorinated solvents in the site groundwater as well as in spiked soil samples simulating a free-phase globular distribution.
3. Persulfate alone was ineffective in reducing the levels of chlorinated solvents in any of the experiments.

There were minor increases in some soluble metals in some of the experiments.

Based on these conclusions, the chlorinated solvent contamination in both the soil and groundwater can be effectively treated by using permanganate as an oxidant. However, due to the low soil oxidant demand of the soil (near-surface fill), the rationale for using a dual oxidant approach (DUOX™) is unnecessary. Persulfate would only be necessary if there was a need to expend the soil oxidant demand before using a more costly oxidant such as permanganate.

The study also demonstrated the appropriate dosing required to treat the more difficult free-phase distributed PCE in the fill matrix. A remedial solution for this site could include a source removal or treatment strategy. The use of the permanganate could potentially be used as a source treatment for the near-surface contaminated fill material, as well as the groundwater, assuming that an appropriate means of introducing the oxidant into the subsurface can be implemented.

This study at Roosevelt Mills was not able to fully demonstrate the potential of the DUOX™ technology for the treatment of chlorinated solvents in soil and groundwater. The major benefit of the DUOX™ process, as compared to single phase oxidation technologies, is in the treatment of impacted media with significant soil oxidant demand. Since the media evaluated during this study did not exhibit significant soil oxidant demand, the full utility of the process was not demonstrated. The technology may have merit at other sites where significant soil oxidant demand would benefit from a DUOX™ approach.