

03-57-002801 and  
02-57-001682  
Reedsburg Cleaners

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ASSOCIATES



## REMEDIAL ACTION OPTIONS REPORT

Reedsburg Cleaners  
349 E. Main Street  
Reedsburg, Wisconsin

WDNR BRRTS# 03-57-002801  
WDNR BRRTS# 02-57-001682  
PECFA CLAIM# 53959-1941-49

- ▼ ENGINEERING
- ▼ ARCHITECTURE
- ▼ ENVIRONMENTAL
- ▼ SURVEYING/GIS
- ▼ COMMUNITY DEVELOPMENT

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**Reedsburg Cleaners**  
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**Prepared for:**  
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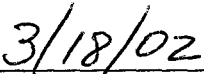
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I, Joel L. Janssen, hereby certify that I am a hydrogeologist as that term is defined in s. NR 712.03(1), Wis. Adm. Code, and that, to the best of my knowledge, all of the information contained in this document is correct and the document was prepared in compliance with all applicable requirements in chs. NR 700 to 726, Wis. Adm. Code.

  
\_\_\_\_\_  
Joel L. Janssen  
Hydrogeologist

  
\_\_\_\_\_  
Date

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## EXECUTIVE SUMMARY

Reedsburg Cleaners currently operates a dry cleaning business at 349 E. Main Street in Reedsburg, Wisconsin. A gas station previously operated at the site until the mid-1970s. Three 1,000-gallon leaded gasoline USTs (closed in-place) remain on-site. In 1994, tetrachloroethene (PCE) was spilled from an AST located on-site.

Drilling observations indicate that silty sand is present down to 10 feet. Weathered sandstone was encountered at 10 feet. Firm sandstone is present down to at least 41 feet.

Groundwater was encountered approximately 17 feet deep, within the sandstone. Groundwater flow is towards the southwest. There is an upward flow gradient within the sandstone aquifer. The hydraulic conductivity within the groundwater was calculated to be  $1.02 \times 10^{-2}$  cm/sec (MW-6). The calculated groundwater velocity is 0.8 ft/day.

Petroleum contamination in the soil covers only a small area near the USTs. PCE soil contamination covers approximately 3,000 square feet on the eastern portion of the site and extends down to 17 feet.

Natural attenuation groundwater monitoring indicates that the plume is under reducing conditions. Several daughter products of PCE degradation have been detected in different monitoring wells. These results indicate that anaerobic biodegradation (reductive dechlorination) is occurring within the plume.

We do not recommend actively remediating the petroleum soil and groundwater plume. We feel natural attenuation shall be sufficient to remediate the petroleum groundwater plume. Additional, remediation, PECFA costs shall be limited to monitoring the groundwater plume.

The following combined treatment options have been deemed the most cost-effective and feasible to remediate PCE in the soil and groundwater: enhanced in-situ anaerobic bioremediation, limited soil excavation, and soil vapor extraction (SVE).

The groundwater remediation will involve the installation of approximately 43 injection points across the site, pumping 80 lbs of Hydrogen Release Compound (HRC®) into each injection point. The groundwater remediation also includes the installation of an additional monitoring well and conducting a baseline groundwater sampling event. The estimated cost of groundwater remediation is \$46,300. The estimated operation & maintenance cost to monitor the groundwater for 3 ½ years is \$48,500.

Approximately 55 cubic yards of the most impacted chlorinated solvent soil will be removed and hauled off-site to be treated by chemical oxidation and then landfilled. The estimated cost to remove and treat this soil is \$27,600. A horizontal piping system

will be installed within the soil excavation, UST excavation, and into the surrounding soil. The estimated cost to install a SVE system is \$27,100. The estimated SVE O&M costs, for 2 years, are \$13,600.

The estimated cost to remediate & monitor the PCE soil contamination is \$68,300. The estimated cost to remediate & monitor the PCE groundwater contamination is \$94,800.

This report includes a description of different remediation alternatives, estimated capital costs, and O&M costs for each alternative. This information is intended to obtain approval of this Remedial Action Options Report from the Wisconsin Department of Natural Resources.

## 1.0 PROJECT BACKGROUND

### 1.1 PROJECT LOCATION AND DESCRIPTION

This report presents the findings of a subsurface remedial investigation, conducted in reference to a petroleum release and dry cleaner solvent release at Reedsburg Cleaners, 349 E. Main Street, Reedsburg, Wisconsin. The subject property is located within the SW ¼ of the NE ¼ of Section 10, T12N, R4E, Sauk County, Wisconsin. The geographic coordinates of the site are: N 43° 31' 56.7" W 90° 0' 17.5". The site's WTM91 coordinates are 519571, 339969. A site location map is provided as Figure 1.

Since contamination at this site has resulted from underground tank systems, where petroleum was stored for commercial purposes, this project is eligible for reimbursement under the Wisconsin Petroleum Environmental Cleanup Fund Act (PECFA). This project is also eligible for reimbursement under the Dry Cleaner Environmental Response Fund.

### 1.2 SITE BACKGROUND

On December 12, 1994, PCE was detected in a monitoring well located adjacent to Reedsburg Cleaners during a petroleum site investigation conducted at Spellman Monument (403 East Main Street). The DNR, in a letter dated November 15, 1995, requested that Reedsburg Cleaners investigate an apparent release of PCE from an on-site above-ground storage tank (AST) located on the subject site.

Petroleum contamination was detected at the Reedsburg Cleaners site during a site investigation on May 10, 1996, conducted by Advent Environmental. The DNR was notified of this contamination on July 11, 1996. In a letter dated July 31, 1996, the DNR set forth Reedsburg Cleaners' responsibility to investigate the degree and extent of the contamination.

### 1.3 NEARBY CONTAMINATED SITES

There are three active or closed LUST sites near the Reedsburg Cleaners.

<u>Site Name</u>	<u>Address</u>	<u>Status</u>	<u>Consultant</u>
Spellman Monument	403 E. Main Street	active	MSA
Cenex (CCP)	306 E. Main Street	active	REA
Gade Kleeber (City)	305 E. Main Street	closed	Vierbicher

The Spellman Monument site is located upgradient from Reedsburg Cleaners and recently installed a soil vapor extraction system. Free product has been identified within two wells, MW-2 & MW-4, at Spellman Monument (see Figure 3). The Cenex site is located downgradient from Reedsburg Cleaners and intends to utilize natural attenuation for site closure. The Gade Kleeber site is located downgradient from Reedsburg Cleaners and was closed in February 2000 utilizing natural attenuation.



## 1.4 CONTACT INFORMATION

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## 1.5 SITE CHARACTERIZATION

### 1.5.1 Site Geology

Field observations, during drilling operations, indicate that the upper 10 feet of soil is characterized by silty sand with trace gravel (SM/SW). Weathered sandstone was encountered at approximately 10 feet. The weathered sandstone averaged 5 feet thick and could be drilled through with the hollow-stem augers. Firm sandstone was encountered in SB-1 at 3 feet deep. Firm sandstone was encountered in P-1 at 9 feet and continued down to 41 feet.

### 1.5.2 Site Hydrogeology

The water table is located approximately 17 feet deep, within the sandstone. Groundwater at the site flows towards the southwest (see Figure 4). The horizontal hydraulic gradient, parallel to the direction of groundwater flow, averaged approximately 0.008 ft/ft. The groundwater velocity was calculated to be 0.8 ft/day. The vertical component of groundwater flow, between the monitoring wells and piezometers, is upward. The sandstone aquifer is at least 500 feet thick in the Reedsburg area.

## 1.6 EXTENT OF SOIL CONTAMINATION

A geologic cross-section and vertical profile of contaminants in the soil is graphically depicted in Figure 5. The approximate lateral distribution of PCE concentrations in the soil are graphically depicted in Figure 6.

Interpretation of the analytical and field data shows a PCE plume that encompasses an area of approximately 3,000 square feet and extends vertically from 0.5 feet to a maximum depth of 17 feet. The general distribution of PCE in the soil appears to be 9.5

feet thick, producing approximately 1,050 cubic yards of PCE contaminated soil. The PCE soil contaminant plume exists within the unsaturated soil zone, above the sandstone.

Petroleum impacted soil encompasses only a small area at the site. The area is concentrated by MW-1 and presumably near the USTs. The areal extent of petroleum contamination in the soil may only include 400 square feet. Only GRO and DRO were detected above NR 720 levels. BTEX compounds were not detected in any of the soil borings.

## 1.7 EXTENT OF GROUNDWATER CONTAMINATION

### 1.7.1 Petroleum Contaminant Distribution

A total BTEX isoconcentration map, Figure 7, shows that there are two sources of petroleum contamination that make up the groundwater plume at the site. The Spellman Monument site is located upgradient of the site (east). Petroleum contamination from the Spellman Monument site has migrated onto the Reedsburg Cleaners site. The two plumes of petroleum contamination can not be reasonably separated.

The horizontal extent of the combined BTEX plume is defined by the following monitoring wells: MW-5 & MW-9 (MSA), MW-4 & MW-9 (Gade), and MW-1 (Cenex). The vertical extent of petroleum contamination was defined by piezometers P-1 and P-2. There has been no downward migration of petroleum contamination into the sandstone aquifer.

### 1.7.2 Chlorinated Solvent Contaminant Distribution

A PCE isoconcentration map, Figure 8, shows that the source of chlorinated solvents emanates from the northeast corner of the site. The groundwater plume migrated off-site, towards the southwest and beneath Main Street. This pathway coincides with the direction of groundwater flow.

In December 1994, PCE contamination was first detected in MW-7 (MSA) at a level of 5,000 ug/l. During the August 2001 sampling event, the PCE level in MW-7 (MSA) was 14,000 ug/l.

The horizontal extent of the PCE plume is defined by the following monitoring wells: MW-5, MW-8, & MW-9 (MSA), MW-4 & MW-9 (Gade), and MW-1 (Cenex). The vertical extent of solvent contamination was defined by piezometers P-1 and P-2. There has been no downward migration of solvent contamination into the sandstone aquifer.

### 1.7.3 Natural Attenuation Assessment

Based on field and laboratory natural attenuation testing, the groundwater plume has the following characteristics:

- Oxygen levels are depleted
- Negative ORP values are present
- Nitrogen levels are 10 times lower than outside the plume
- Sulfate levels are similar to outside the plume
- Chloride levels are elevated
- Methane levels are elevated

Three daughter products of PCE degradation were detected within various wells: trichloroethene, 1,2-dichloroethane, and cis-1,2-dichloroethene. The above sampling results along with the presence of daughter products indicates that anaerobic biodegradation (reductive dechlorination) is occurring within the groundwater plume. The presence of BTEX compounds within the plume appears to help drive the dechlorination process.

## 2.0 REMEDIATION SYSTEM DESIGN

### 2.1 FEASIBILITY ASSESSMENT

The objectives of this feasibility assessment and evaluation of remedial action alternatives for this site are to mitigate the chlorinated solvent groundwater plume and remove the source (soil contamination) of further groundwater contamination in the sandstone aquifer. We do not recommend actively remediating the petroleum groundwater plume. We feel natural attenuation shall be sufficient to remediate the petroleum groundwater plume. Groundwater monitoring shall be conducted for several years to document the occurrence of natural attenuation within the petroleum plume. See Sections 2.3.4 and 2.3.8 for a discussion on future groundwater monitoring.

### 2.2 SCREENING OF REMEDIAL ACTION TECHNOLOGIES

Initially, remedial actions were considered in terms of technologies that could be implemented based on site-specific conditions. Those technologies determined to be impractical were eliminated from consideration. This section addresses the group of technologies that were screened and evaluated as potentially applicable to the site.

#### Option #1 Natural Bioremediation

This option was determined to be unfeasible because high levels of chlorinated solvents exist within the unsaturated soil and the groundwater. Also, the chlorinated solvent groundwater plume has migrated off-site.

## **Option #2 Soil Excavation and Groundwater Extraction**

This option would involve the removal of approximately 300 yards of soil that is highly contaminated with chlorinated solvents. The soil is classified as a hazardous waste and would require disposal into a hazardous waste landfill in Belleville, Michigan. The total cost to dispose of 300 yards would be \$130,000.

Approximately, 3 recovery wells would be required to contain the groundwater plume. Groundwater would be treated using a tray-tower air stripper prior to discharge into the sanitary sewer. Implementation costs (\$66,000) and operation & maintenance costs for 4 years (\$108,000) are very high.

These remediation alternatives are cost prohibitive and may not remediate the groundwater plume to levels below the NR 140 Enforcement Standards.

## **Option #3 In-Situ Chemical Oxidation**

This treatment process would involve injecting Fenton's reagent (hydrogen peroxide) through vertical well points into both the soil and groundwater plumes. The hydrogen peroxide would be applied with a catalyst creating a hydroxyl free radical. This hydroxyl free radical is capable of oxidizing chlorinated organic compounds. This oxidation process converts the organic molecules to carbon dioxide and water. This treatment process has proven effective in treating chlorinated organic solvents in soil and groundwater. The treatment process can be completed within several months. Because the Fenton's reaction creates heat and pressure within the subsurface, contaminants may be forced into nearby utility trenches or basements. We feel this treatment method could be cost effective (\$240,000) but would not be safe if applied at this site. Fenton's reaction is best applied at remote sites where vapor migration is not a concern.

## **Option #4 SVE and Groundwater Sparging**

Soil vapor extraction (SVE) is a feasible remediation method for this site based on the loosely compacted silty sand found above 10 feet. The SVE system would consist of several vertical extraction wells. SVE has been proven to remove chlorinated solvents from unsaturated soil. Unfortunately, very high concentrations of PCE (near the source) could extend the operational life of the SVE system. If one were to install either a vertical or horizontal (trenched) SVE system, there would be approximately 45 yards of hazardous waste soil that would have to be disposed.

Groundwater air sparging may not be an efficient option for treating the chlorinated solvent groundwater plume. Air sparging would increase the oxygen levels in the groundwater, thereby enhancing natural biodegradation of the petroleum contamination only. Air sparging has proven to be moderately effective in remediating chlorinated solvents.

### **Option #5 Limited Soil Excavation, SVE & Enhanced In-Situ Anaerobic Bioremediation**

Based upon the feasibility assessment, these combined treatment options are deemed the most cost-effective and feasible means to remediate the PCE found in the soil and groundwater. Option #5 consists of the following remedial activities:

- Install new monitoring well downgradient of the groundwater plume
- Perform baseline groundwater sampling of monitoring wells and piezometers
- Injection of Hydrogen Release Compound (HRC®) to enhance anaerobic bioremediation
- Post-HRC® application groundwater monitoring to evaluate the progress of reductive dechlorination
- Excavate and dispose of approximately 55 yards of soil that is highly contaminated with PCE
- Install horizontal SVE system within existing excavation
- Operation & maintenance of SVE system
- Long term groundwater monitoring

## **2.3 REMEDIATION SYSTEM DESIGN**

Conceptual remedial activities were developed based on the present degree and extent of contamination and the magnitude of potential threats to human health and the environment. The soil remediation shall be accomplished by excavating approximately 55 yards of highly contaminated PCE soil and operating a SVE system. The groundwater shall be remediated by injecting a HRC® solution into the groundwater plume. The remediation of soil and groundwater shall be completed in a phased approach. The remediation steps, as they will be implemented, are discussed in detail within the following subsections. Table 1 displays the estimated costs to remediate the PCE within the soil and groundwater.

### **2.3.1 Install New Monitoring Well**

A new monitoring well shall be installed downgradient of the PCE groundwater plume. This well is necessary to monitor the in-situ dechlorination in the groundwater plume. Monitoring results from this well will determine if PCE breakdown products have migrated downgradient from the site. The well shall be installed in the sidewalk on the south side of Main Street and approximately 90 feet west of MW-8 (MSA). See Figure 9 for the proposed location of the new

**TABLE 1  
REMEDIATION COST SUMMARY  
REEDBURG CLEANERS**

REMEDIATION ACTIVITY	CONSTRUCTION <sup>(1)</sup>	CONSULTING <sup>(2)</sup>	TOTAL
Install New Monitoring Well	\$2,000	\$800	\$2,800
Baseline Groundwater Sampling	\$2,200	\$2,300	\$4,500
Injection of HRC® Solution	\$28,500	\$10,500	\$39,000
Post-HRC® Application Monitoring (7 events)	\$17,000	\$8,800	\$25,800
Limited Soil Excavation <sup>(3)</sup>	\$24,800	\$2,800	\$27,600
Installation of SVE System	\$21,000	\$6,100	\$27,100
Operation & Maintenance of SVE System (2 years of operation)	\$4,400	\$9,200	\$13,600
Long Term Groundwater Monitoring (8 events)	\$12,200	\$10,500	\$22,700
<b>Totals</b>	<b>\$112,100</b>	<b>\$51,000</b>	<b>\$163,100</b>

Notes: (1) Construction costs include: drilling, lab, excavation, & remedial equipment, etc.

(2) Consulting costs include: oversight, reporting, & field equipment, etc.

(3) Excavation costs do not include removing, cleaning & disposing of the USTs, because these costs are not reimbursable.

monitoring well. This new well shall be installed to a depth of 20 feet and intersect the sandstone aquifer.

### 2.3.2 Baseline Groundwater Sampling

Ten monitoring wells and three piezometers shall be sampled to verify the extent of groundwater contamination and update the groundwater geochemistry prior to implementing the groundwater remediation treatment. Dedicated bailers shall be purchased for these wells to reduce future groundwater sampling costs. If high levels of groundwater contamination are found to exist within the new monitoring well, then the groundwater remediation plan may need to be modified. Groundwater samples shall be analyzed for the following parameters:

- Volatile organic compounds (VOC)
- Methane
- Ethene/ethane
- Chloride
- Sulfate
- Nitrate/nitrite
- Total organic carbon (TOC)

### 2.3.3 Injection of HRC® to Enhance Anaerobic Bioremediation

Hydrogen release compound (HRC®) is a passive treatment option for in-situ bioremediation of chlorinated solvents. HRC® is a proprietary, environmentally safe, food quality, polylactate ester specially formulated for the slow release of lactic acid upon hydration. Microbes metabolize the lactic acid released by HRC® and produce hydrogen, which can be used by reductive dehalogenators, which are capable of dechlorinating chlorinated solvents. HRC® provides a slow-release hydrogen source that is consumed over a 9 to 18 month period. The slow-release mechanism favors dehalogenators over methanogenic bacteria.

HRC® is a highly viscous liquid that is typically injected (1,000 psi) under pressure through small diameter Geoprobe rods, directly into the groundwater plume. HRC® will remain near the injection point and generate highly diffusible hydrogen slowly over time.

We propose to inject the HRC® at 43 locations on-site and in the sidewalk along Main Street (see Figure 9). The injection points would be spaced between 10 to 15 feet apart. The tightest spacing will be used where the highest PCE concentrations are present. The injection points would be installed with an air rotary drill hammer. The sandstone formation cannot be penetrated with a Geoprobe or an auger. The boreholes would be 3" in diameter and 27 feet deep. If the boreholes caved in above the sandstone, a PVC sleeve shall be placed from the surface down to the top of the sandstone. We intend to inject the HRC® by slowly pumping, not under pressure, it through a tremie pipe directly into the sandstone aquifer.

Approximately, 80 lbs of HRC® would be pumped into each injection point. A total of 3,500 lbs of HRC® would be pumped between 17 and 27 feet deep across the site. The initial response time within the groundwater plume is expected to be between 100 and 200 days after the injection period.

Injection of the HRC® would be conducted over a 4 day period. During the injection period, nearby utility corridors would be monitored. Vapor monitoring would determine if explosive vapors from petroleum or PCE were being forced into the utility corridors. We do not anticipate any vapors to migrate into utility corridors. The injection process would be halted if conditions in the utility corridors significantly changed. The corridors would be monitored several times a day for the following: photo-ionization detector (11.7 lamp), oxygen, carbon dioxide, and combustible gases.

A careful watch shall be placed on whether the in-situ groundwater treatment and the ensuing changes in the groundwater plume characteristics (lower redox potential/reducing environment) has an effect on the petroleum groundwater plume. The petroleum plume should remain stable during the HRC® application period. HRC® will not react with the existing petroleum plume. In fact, the presence of the petroleum will enhance the remediation of the PCE. Once the HRC® has been used up (approximately 18 months), the groundwater conditions should change from being very reducing to either slightly reducing or aerobic.

HRC® is manufactured by Regenesi Bioremediation Products. Positive remediation results have been demonstrated throughout various parts of the U.S. In 2001, HRC® was applied at 5 sites in Wisconsin. HRC® has proven to be an effective in-situ technology to bioremediate chlorinated solvents in groundwater.

#### 2.3.4 Post-HRC® Application Groundwater Monitoring

Once the injection of the HRC® solution has been completed, groundwater monitoring must be conducted to evaluate the HRC® enhancement of reductive dechlorination. At a minimum, several wells within the plume and several wells downgradient of the plume shall be monitored. The monitoring events shall be conducted every other month for the first 6 months and then quarterly for one year. Bailed water from contaminated wells shall be placed in drums and properly disposed. We shall also be watching for any changes in the petroleum plume.

This monitoring program will allow one to closely watch the progression of PCE breaking down into its daughter products, the metabolic acid availability, geochemical reactions and the effect on the petroleum plume. The following groundwater field and laboratory parameters shall be monitored during this phase:



### Laboratory Parameters

VOCs  
Chloride  
Sulfate  
Nitrite/nitrate  
TOC  
Methane  
Ethene/ethane  
Metabolic acids (lactic, pyruvic,  
acetic, propionic & butyric)

### Field Parameters

Water depth  
Dissolved oxygen  
Oxidation reduction potential (ORP)  
Temperature  
Conductivity  
pH

#### 2.3.5 Limited Soil Excavation

Approximately 55 yards of PCE contaminated soil shall be removed from a single L-shaped excavation (see Figure 10). The northern portion of the excavation would have approximate dimensions of 14' x 9' x 10' deep. The northern portion would remove the soil with very high PCE concentrations and MW-1. We do not plan on reinstalling MW-1. The southern portion of the excavation would focus on removing the three previously abandoned gasoline USTs. The southern portion would probably have dimensions of 20' x 10' x 8' deep. Based on the soil samples collected during the investigation, we anticipate that the soil surrounding the USTs is contaminated with PCE. The excavation would be left open to allow for installation of the SVE pipe system.

Because the excavated material will be considered a hazardous waste, the soil will need to be hauled to a hazardous waste facility in Belleville, Michigan, operated by EQ Corporation. Prior to placing the soil into a subtitle C landfill, the soil would be chemically oxidized (hydrogen peroxide type method) to remove a majority of the PCE contamination.

We would like to propose that approximately 20 yards of the least contaminated excavated soil be placed back into the excavation and treated utilizing the SVE system. The contaminated soil would be mixed with clean sand (low moisture content) and placed back into the excavation near the SVE piping. We feel this method could be effective. If it would be acceptable to the DNR, hauling and landfill disposal costs could be reduced by \$7,500.

#### 2.3.6 Installation of SVE System

We feel the residual soil contamination left after the limited soil excavation can be remediated by installing a horizontal SVE system. We expect that the SVE system will remediate any residual petroleum contamination in the soil. We propose to install a network of 4-inch PVC slotted piping within the excavation mentioned in Section 2.3.5. See Figure 10 to view the proposed SVE piping layout. The excavation would be backfilled up to 6 feet with pea gravel or a like material that allows maximum air flow. The slotted pipe would be placed 6 feet deep and

covered with one foot of pea gravel, a filter fabric, three feet of sand and then 1.5 feet of ¾-inch crushed rock. At the surface, the excavation would be sealed with plastic sheeting and either concrete or asphalt.

In addition to the piping network in the excavation, two 20 foot horizontal SVE wells will be installed into the sides of the excavation (see Figure 10). The 4-inch PVC slotted pipes would be installed by using a backhoe to push the pipes into the subsurface soil. These horizontal SVE wells will be installed approximately six feet deep. Because the water table is located about 17 feet deep, we do not anticipate that the horizontal piping network will get flooded.

The SVE piping network shall be trenched, a short distance to the north, toward a small remediation building (see Figure 10). The building would contain a soil venting unit that would include a centrifugal blower and a moisture knockout tank. The blower motor would be explosion-proof. A centrifugal blower performs best in high flow and low vacuum applications. These blowers require less maintenance. Centrifugal blowers are mainly used in sand/gravel zones or trenched systems with a long length of perforated pipe.

Mid-State Associates (MSA) conducted a SVE pilot test on four monitoring wells in December 1996 at Spellman Monument. Their test showed a radius of influence of 120 feet and an average flow of 2 scfm/ft of screen. Their wells were screened within the sandstone. The unsaturated soil (fine sand) at Reedsburg Cleaners should be equally permeable to the sandstone. For design purposes, we shall use a conservative radius of influence of 25 feet. At 25 feet, the SVE system could pull vapors from every portion of the soil contamination plume.

There is not a monitoring well with sufficient open screen within the unsaturated sand to conduct a pilot test at this time. After the piping network has been installed and the excavation properly backfilled, a pilot test shall be performed. The pilot test shall determine the proper blower size and what the discharge vapor concentration shall be. We anticipate that the SVE system will not exceed air emission standards.

Based on calculations made during the investigation, the soil cleanup standard for PCE at this site is 15 ug/kg. We shall use this value as our cleanup goal for the SVE system.

In order to save money, a search shall be made to locate a used remediation building and used SVE equipment that would satisfy the remediation plan. Because a new building and new equipment could cost around \$15,000, the use of used equipment could be a large savings to the project.

### 2.3.7 Operation & Maintenance of SVE System

We anticipate that the SVE system would operate approximately 12 hours per day on a timer. Pulsing the SVE system would reduce the production of preferential air-flow pathways. The site is also located next to a residential area and would probably be operated only during the day.

The schedule of vapor sample collection would begin with the startup of the SVE system. Air samples would be collected daily for the first 3 days of operation, weekly for the first 3 weeks and monthly thereafter. All the air samples would be analyzed for total VOCs.

During air sampling events, the following field readings would be taken: air flow rate, air temperature and vacuum pressure. Every quarter during operation, the following would be tested: methane and carbon dioxide. Also during monthly visits, maintenance checks of the blower and knockout tank shall be conducted.

We anticipate that the SVE system would remain operational for approximately 2 years. After 3 consecutive months of extremely low air emissions, the SVE system will be shut down. Soil samples shall be collected from approximately 3 previously impacted soil locations to confirm that soil cleanup goals have been achieved.

### 2.3.8 Long Term Groundwater Monitoring

Approximately 1.5 years after the HRC® solution has been injected into the groundwater plume, long term groundwater monitoring shall be implemented. The purpose of the groundwater monitoring is to further evaluate the reductive dechlorination of PCE, monitor the end-product dissolved gases (methane, ethene, & ethane), and monitor trends of chlorinated solvent and petroleum concentrations within the monitoring wells. Bailed water from contaminated wells shall be placed in drums and properly disposed.

The following parameters will be collected quarterly from approximately 13 wells (both on-site & off-site):

#### Laboratory Parameters

VOCs

#### Field Parameters

Water depth  
Dissolved oxygen  
Oxidation reduction potential (ORP)  
Temperature  
Conductivity  
pH

The following parameters will be collected every 6 months from approximately 13 wells (both on-site & off-site):

Laboratory Parameters

VOCs  
Chloride  
Sulfate  
Nitrite/nitrate  
Methane  
Ethene/ethane

Field Parameters

Water depth  
Dissolved oxygen  
Oxidation reduction potential (ORP)  
Temperature  
Conductivity  
pH

VOC samples may need to be collected from various off-site monitoring wells to verify if contaminant concentrations have changed. Also, various off-site downgradient wells may need to be monitored for biological parameters.

The long term groundwater monitoring program shall continue until it is determined that remaining chlorinated solvent concentrations are not a threat to the environment. Long term groundwater monitoring will also determine if the petroleum contamination plume is stable and if natural attenuation will be successful in remediating the plume. We anticipate that long term groundwater monitoring may be necessary for 2 years.

### 3.0 SCHEDULE OF REMEDIAL ACTIVITIES

The following schedule of remedial activities for the Reedsburg Cleaners site will be initiated upon receiving approval of the RAOR by the WDNR. Prior to initiating any remedial activities, permission shall be obtained from the Dry Cleaner Environmental Response Program. Installation of a new monitoring well and conducting the baseline groundwater sampling will commence upon the WDNR's approval.

Proposed schedule of activities:

- April 2002           WDNR approval of remedial option
- April 2002           Consultant selection process
- May 2002            Install new monitoring well
- May 2002            Baseline groundwater sampling event
- June 2002           Implement HRC® injections into groundwater
- Aug. 2002           Initiate post-HRC® groundwater monitoring
- Sept. 2002          Conduct limited soil excavation
- Sept. 2002          Install SVE piping network
- Nov. 2002          Perform SVE pilot test & size SVE equipment
- Jan. 2002          Install remediation shed & SVE equipment
- Feb. 2002          Startup SVE system & conduct performance testing

Periodic status reports shall be submitted to the WDNR to inform them of the remediation progress. The availability of remediation contractors and SVE equipment may modify the above timeframe.

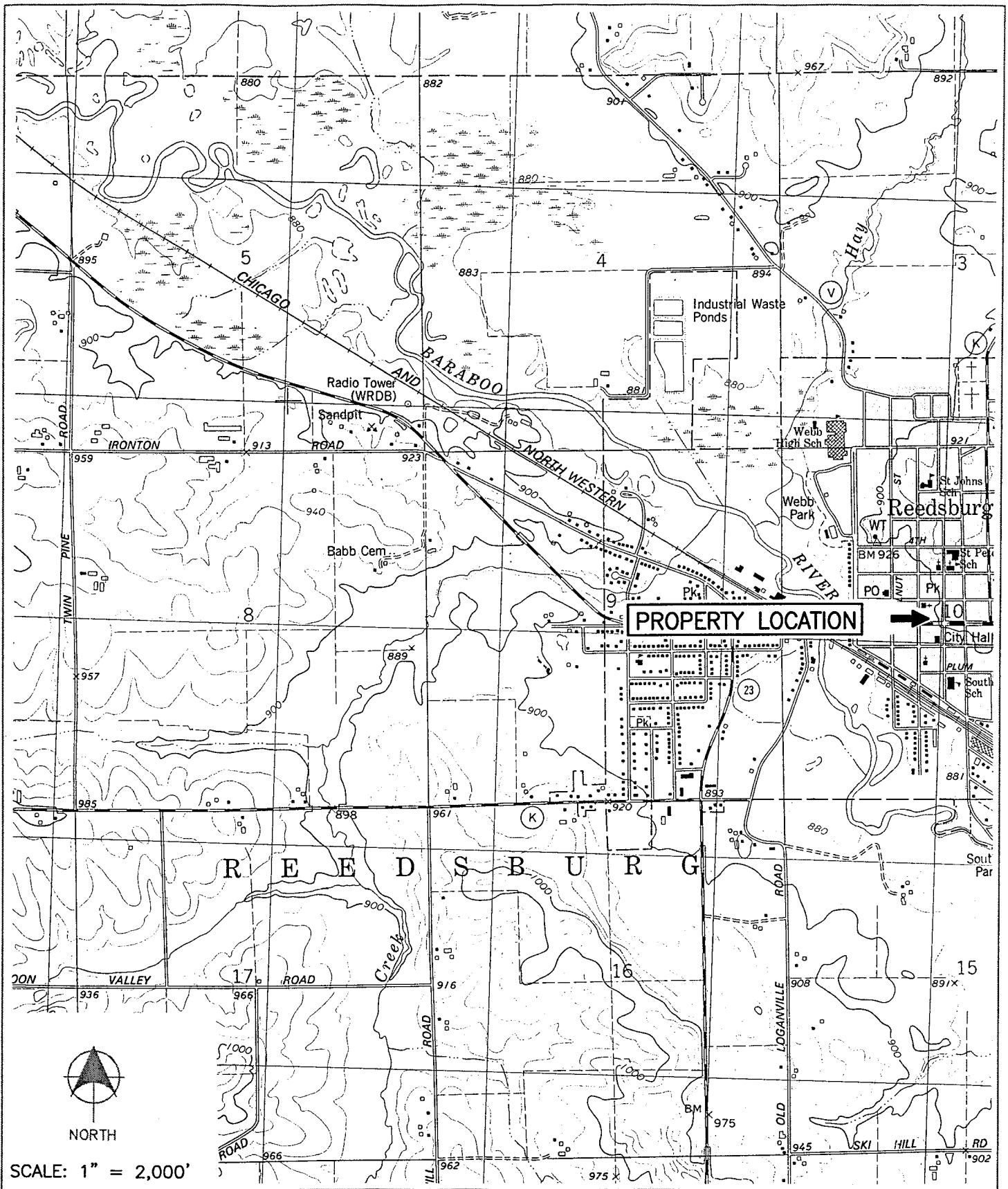
#### 4.0 LIMITATIONS OF ASSESSMENT

The conclusions presented in this report were derived using generally accepted hydrogeologic, engineering, and analytical practices. The recommendations presented herein, represent our professional conclusions based upon the data collected at the time of the sampling, at the specific locations described in this report. Conditions at other locations may be different than described in this investigation.

The findings of this report are valid as to the present time of the investigation. However, changes in the conditions of a property can occur with the passage of time, whether due to natural processes or the works of man on this or adjacent properties. In addition, changes in applicable or appropriate standards may occur, whether they result from legislation, the broadening of knowledge, or other reasons. Accordingly, the findings of this report may be invalidated wholly or partially by changes outside our control.

The interpretations and conclusions contained in this report are based upon the result of independent laboratory analysis, intended to detect the presence and concentration of certain chemical constituents in samples obtained from the subject property. Vierbicher Associates, therefore has no control over such testing and disclaims any responsibility for errors and/or omissions arising therefrom.

G:\DATA\ENVENG\Butz Cleaners 76008676\Remedial Action Report.doc



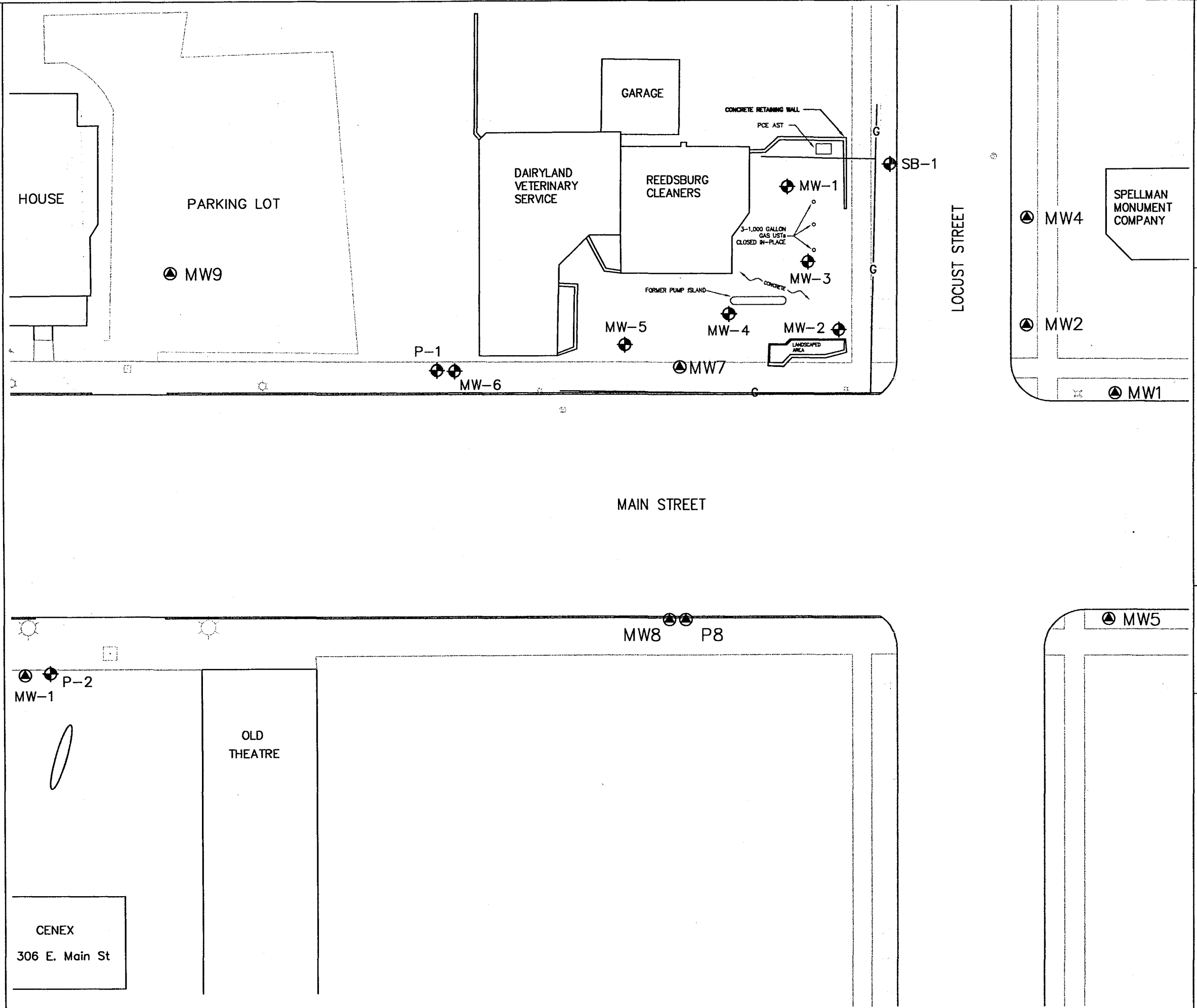
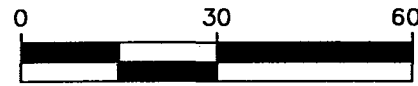
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REEDSBURG CLEANERS  
 349 E. MAIN STREET  
 REEDSBURG, WISCONSIN

FIGURE 1  
 SITE LOCATION MAP

**LEGEND**

- ⊙ = ELEC. MANHOLE
- ⊙ = TRAFFIC LIGHT
- ⊙ = LIGHT POLE
- ⊙ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊙ = STORM MANHOLE
- ⊙ = SAN. MANHOLE
- ⊙ = FIRE HYDRANT
- ⊙ = MONITORING WELL (Butz)
- ⊙ = MONITORING WELL (others)



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EXISTING SITE LAYOUT

FIGURE #  
2

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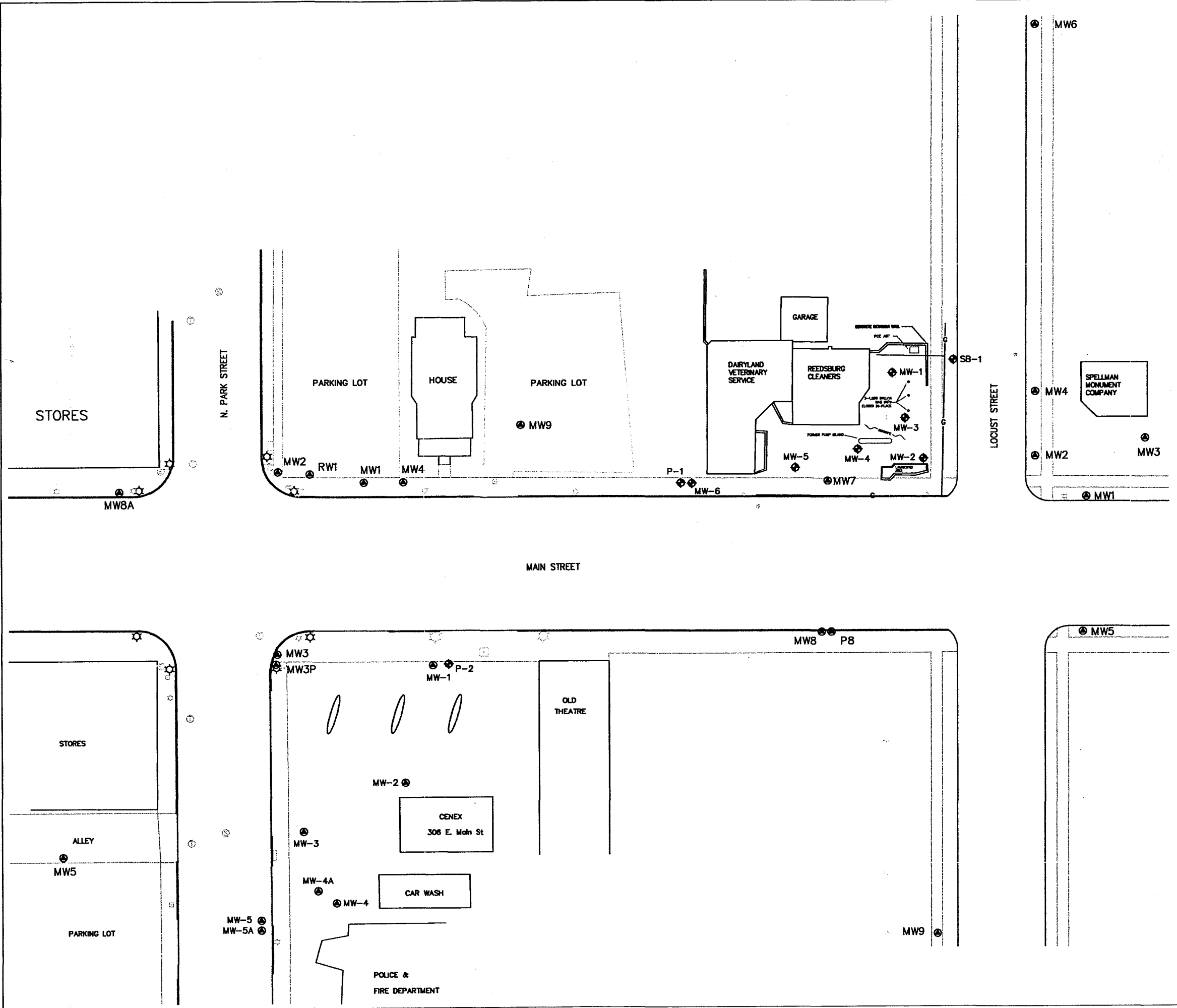
CENEX  
306 E. Main St

OLD  
THEATRE



**LEGEND**

- ⊙ = ELEC. MANHOLE
- ⊛ = TRAFFIC LIGHT
- ⊙ = LIGHT POLE
- ⊠ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊙ = STORM MANHOLE
- ⊙ = SAN. MANHOLE
- ⊙ = FIRE HYDRANT
- ⊙ = MONITORING WELL (Butz)
- ⊙ = MONITORING WELL (others)

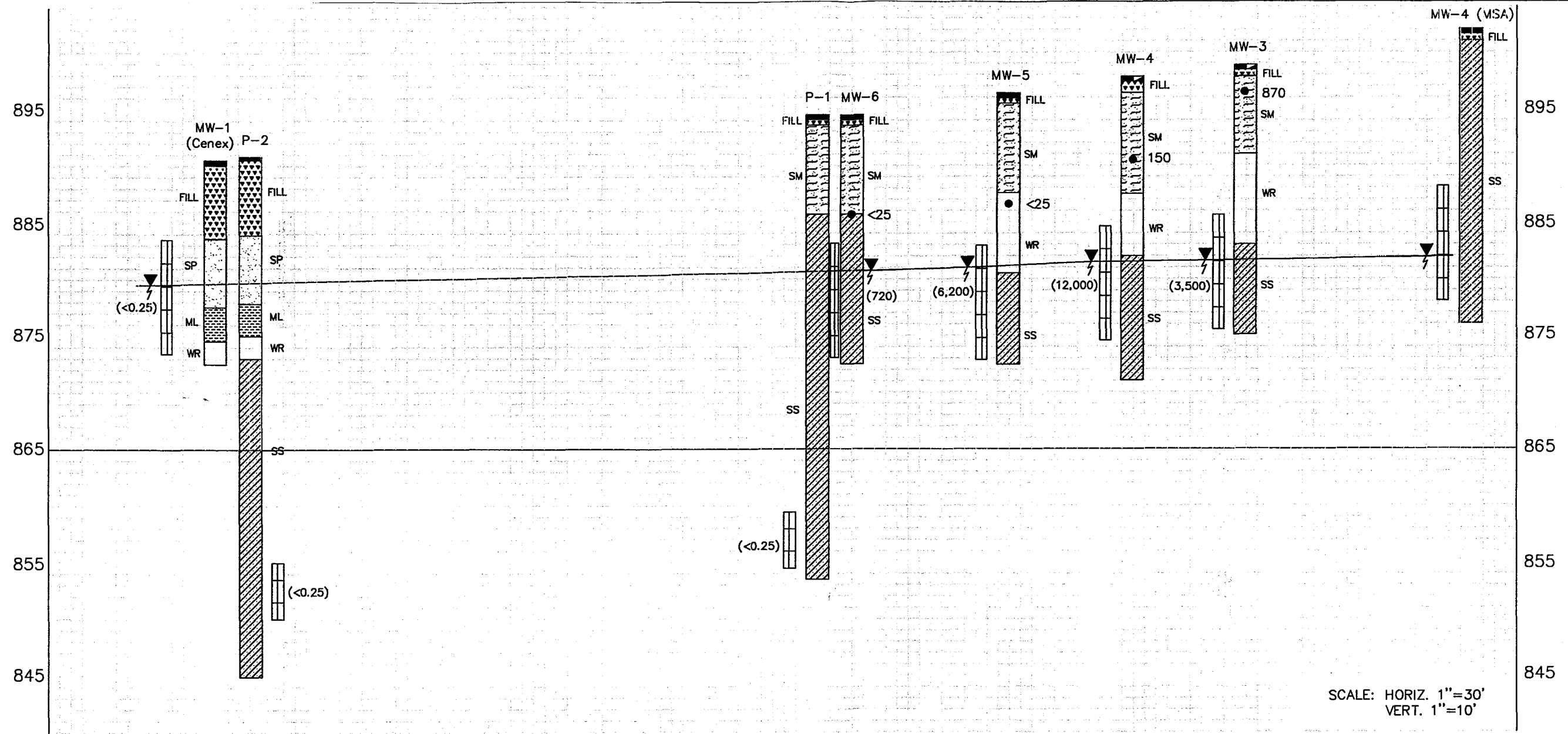


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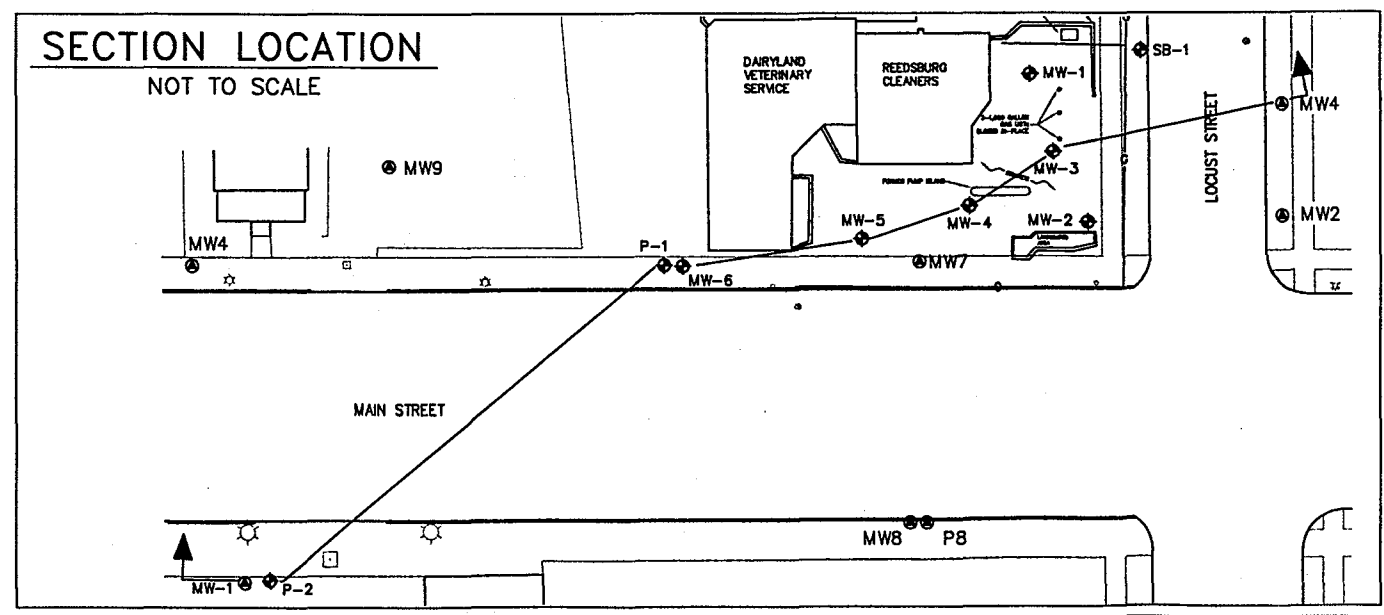
FIGURE # SOIL BORING AND MONITORING WELL LOCATION MAP  
3

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SCALE: HORIZ. 1"=30'  
VERT. 1"=10'



- LEGEND**
- CONCRETE
  - GRAVEL/CLAY (FILL)
  - SAND (SP)
  - SILT (ML)
  - SCREEN LOCATION
  - SILTY SAND (SM)
  - WEATHERED SANDSTONE (WR)
  - SANDSTONE (SS)
  - SOIL SAMPLE LOCATION INDICATING THE PCE CONCENTRATION (ug/kg)
  - (3,500) GROUNDWATER PCE CONCENTRATION (ug/L)
  - GROUNDWATER TABLE (August 13, 2001)

REEDSBURG CLEANERS  
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REEDSBURG, WISCONSIN

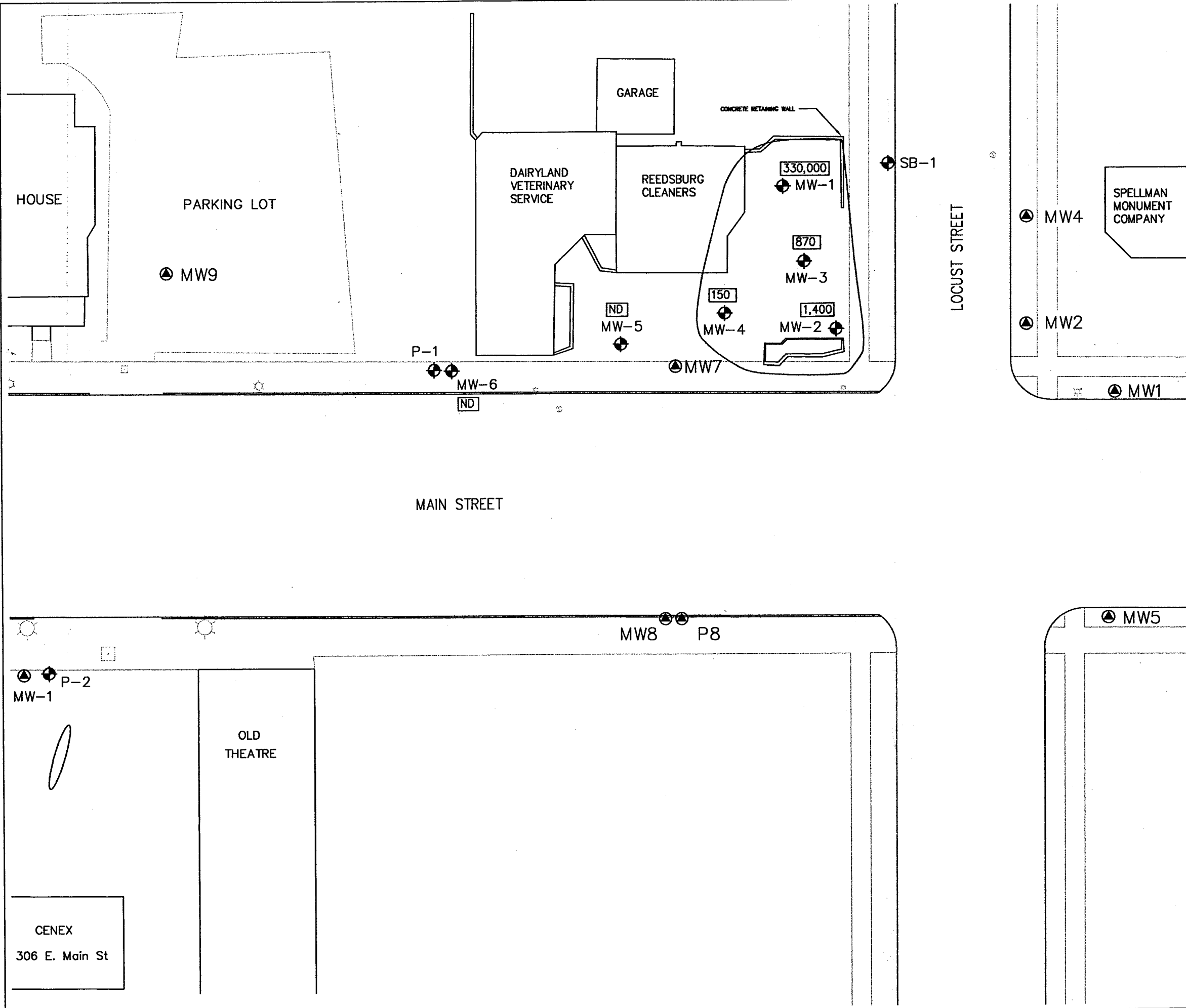
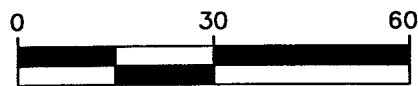
GEOLOGIC CROSS SECTION  
WEST/EAST

FIGURE #  
5

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**LEGEND**

- ⊙ = ELEC. MANHOLE
- ⊗ = TRAFFIC LIGHT
- ⊙ = LIGHT POLE
- ⊙ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊙ = STORM MANHOLE
- ⊙ = SAN. MANHOLE
- ⊙ = FIRE HYDRANT
- ⊕ = MONITORING WELL (Butz)
- ⊕ = MONITORING WELL (others)
- 900 = PCE Concentration (ug/kg)
- = EXTENT OF PCE CONTAMINATION



CENEX  
306 E. Main St

REEDSBURG CLEANERS  
349 E. MAIN STREET  
REEDSBURG, WISCONSIN

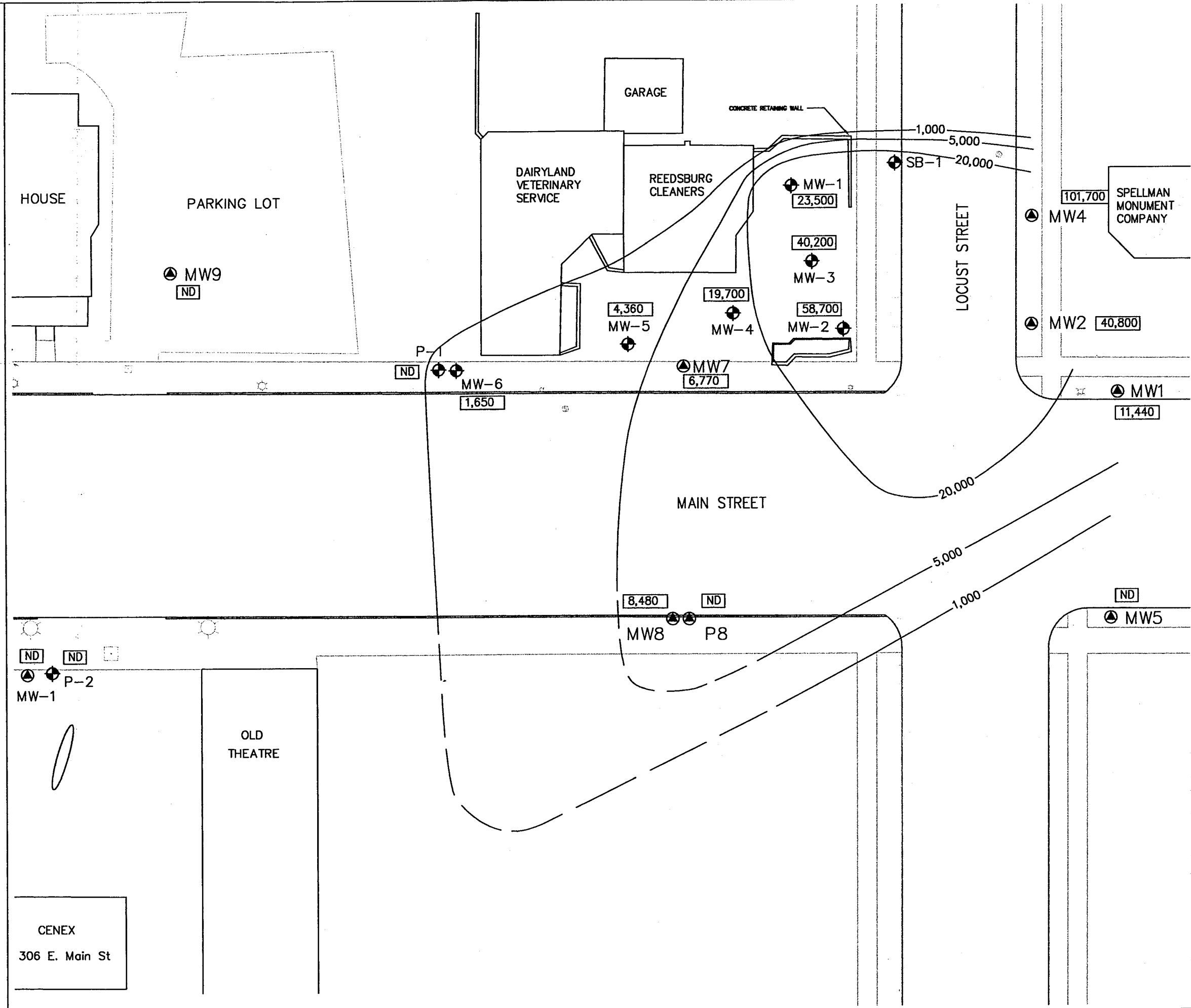
EXTENT OF PCE SOIL  
CONTAMINATION

FIGURE #  
6

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- TR = ELEC. TRANSFORMER
- ⊙ = STORM MANHOLE
- ⊙ = SAN. MANHOLE
- ⊙ = FIRE HYDRANT
- ⊕ = MONITORING WELL (Butz)
- ⊕ = MONITORING WELL (others)
- 900 = Total BTEX Concentration (ug/L)



REEDSBURG CLEANERS  
349 E. MAIN STREET  
REEDSBURG, WISCONSIN

GROUNDWATER ISO-  
CONCENTRATION MAP - BTEX

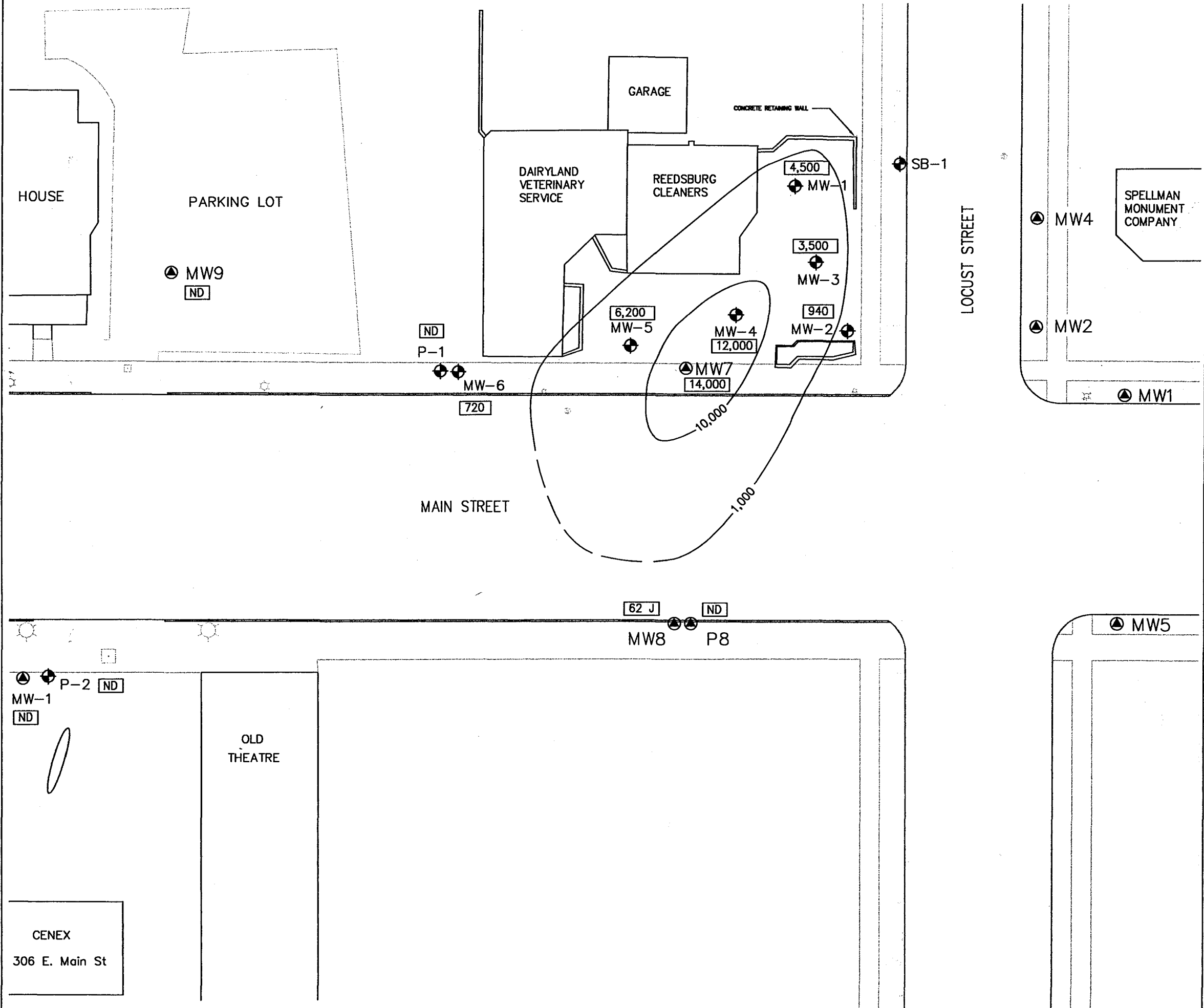
FIGURE #  
7

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CENEX  
306 E. Main St

**LEGEND**

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- ⊙ = LIGHT POLE
- ⊠ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊙ = STORM MANHOLE
- ⊙ = SAN. MANHOLE
- ⊙ = FIRE HYDRANT
- ⊙ = MONITORING WELL (Butz)
- ⊙ = MONITORING WELL (others)
- 900 = PCE Concentration (ug/L)



REEDSBURG CLEANERS  
349 E. MAIN STREET  
REEDSBURG, WISCONSIN

GROUNDWATER ISO-  
CONCENTRATION MAP - PCE

FIGURE #  
8

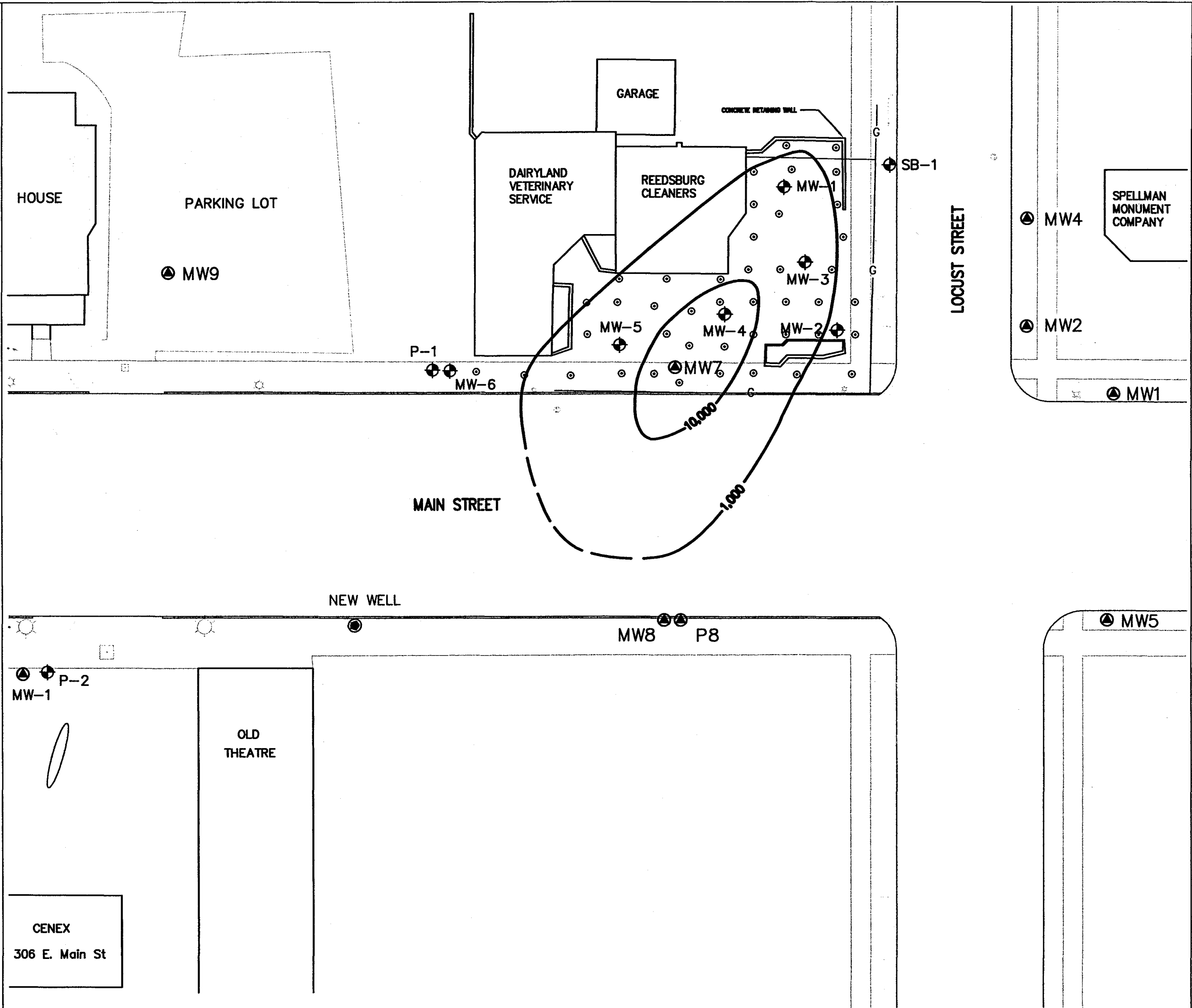
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- ⊙ = TRAFFIC LIGHT
- ⊛ = LIGHT POLE
- ⊠ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊖ = STORM MANHOLE
- ⊗ = SAN. MANHOLE
- ⊛ = FIRE HYDRANT
- ⊕ = MONITORING WELL (Butz)
- ⊙ = MONITORING WELL (others)
- ⊙ = HRC INJECTION POINT



NORTH



REEDSBURG CLEANERS  
349 E. MAIN STREET  
REEDSBURG, WISCONSIN

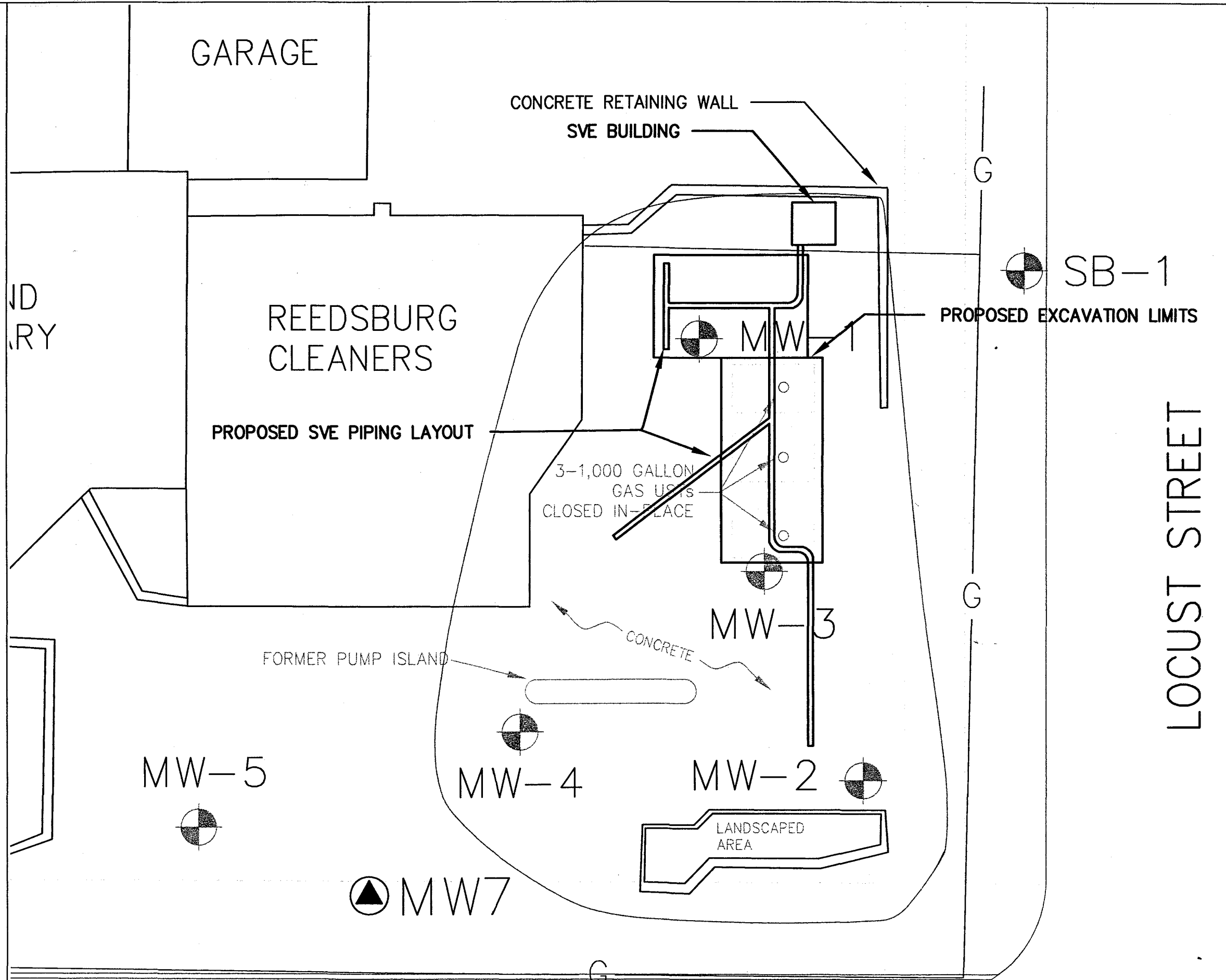
PROPOSED HRC INJECTION  
LAYOUT

FIGURE #  
9

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- ⊛ = LIGHT POLE
- ⊠ = ELEC. BOX
- TR = ELEC. TRANSFORMER
- ⊖ = STORM MANHOLE
- ⊗ = SAN. MANHOLE
- ⊛ = FIRE HYDRANT
- ⊕ = MONITORING WELL (Butz)
- ⊙ = MONITORING WELL (others)



REEDSBURG CLEANERS  
349 E. MAIN STREET  
REEDSBURG, WISCONSIN

PROPOSED EXCAVATION LIMITS  
& SVE PIPING LAYOUT

FIGURE # 10

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LOCUST STREET

SB-1



March 19, 2002

Mr. Randy Maas  
Remediation and Redevelopment Program  
Wisconsin Department of Natural Resources  
3911 Fish Hatchery Road  
Fitchburg, WI 53711

Re: Remedial Action Options Report  
Reedsburg Cleaners  
349 E. Main Street, Reedsburg  
BRRTS # 03-57-002801  
02-57-001682

Dear Mr. Maas:

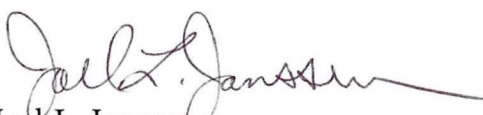
Enclosed please find a copy of the Remedial Action Options Report for the Reedsburg Cleaners.

Conceptual remedial activities were developed based on the present degree and extent of contamination and the magnitude of potential threats to human health and the environment. The soil remediation shall be accomplished by excavating approximately 55 yards of highly contaminated PCE soil and operating a SVE system. The groundwater shall be remediated by injecting a HRC® solution into the groundwater plume. The remediation of soil and groundwater shall be completed in a phased approach.

I have separately enclosed literature on the HRC® technology that was developed by Regensis Bioremediation Products.

If you have any questions or would like to discuss our recommendations, please feel free to give me a call at (608) 233-5800.

Sincerely,  
VIERBICHER ASSOCIATES, INC.

  
Joel L. Janssen  
Hydrogeologist

Enclosure

cc: Wayne Butz

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Fax (715) 359-4753

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(608) 326-1051  
Fax (608) 326-1052

▼ [www.vierbicher.com](http://www.vierbicher.com)

## REMEDIAL ACTION USING HRC UNDER A STATE DRY CLEANING PROGRAM

*David Anderson* (Oregon DEQ, Portland, Oregon, USA)  
Mark Ochsner (Ecology and Environment, Inc., Portland, Oregon, USA)  
Craig Sandefur (Regenesis, Inc., San Clemente, California, USA)  
Steve Koenigsberg, (Regenesis, Inc., San Clemente, California, USA)

**ABSTRACT:** Hydrogen Release Compound (HRC™) was installed at a dry cleaning site in May 1999 to help accelerate and promote biodegradation of chlorinated compounds under the Oregon Dry Cleaning Fund. HRC was chosen because it is cost effective, is easy to install, and requires little or no operation and maintenance. Cost effectiveness is important due to limited funding available from the Oregon Dry Cleaning Fund. Groundwater monitoring has taken place at the site to ensure that chlorinated compounds are degrading. The monitoring has revealed that chlorinated compounds are degrading, but slower than originally anticipated. The slow degradation rate may be attributed to the relatively flat groundwater gradient across the site for approximately 6 months following HRC injection and for approximately six months until fall, when wet weather returned. Closure of the site within a year had been anticipated by the Department of Environmental Quality, but additional monitoring is still necessary. It is too early to determine if additional remedial measures may be necessary, or if additional HRC product is required. However, initial evaluation and positive mass removal and degradation of chlorinated solvents may have been enough for DEQ to consider HRC use as a state dry cleaner presumptive remedy.

### INTRODUCTION

In 1995, Oregon's Environmental Cleanup Laws were revised to provide specific requirements and exemptions from cleanup liability for dry cleaning owners and operators. The State Dry Cleaner Fund is used to investigate and clean up contamination at dry cleaners. After DEQ determines a facility is eligible for funding, the order of investigations or cleanup efforts for all participating sites is determined. Priority is based on the potential risks to human health or the environment, and the availability of funds. DEQ funds and manages a group of contractors that provide the dry cleaner environmental services to DEQ. All of the funding for investigation and cleanup of the facilities comes from the Dry Cleaner Fund. Hayden Island Cleaners is one of the facilities accepted into the Dry Cleaner Program.

Hayden Island Cleaners is an active dry cleaning facility located on Hayden Island, an island located in the Columbia River, north of the city of Portland, Oregon. The groundwater flow direction and gradient at the site change depending on time of year and because the shallow groundwater at the site is in direct communication with the river. Responses related to river stage and tidal

*This is a preprint of a paper to appear in proceedings of The 2nd International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 22-25, 2000. © Battelle Press, Columbus, OH*

changes are observed. The result is that groundwater beneath the site fluctuates in direction and magnitude.

Investigations at the site indicate that soil and groundwater have been impacted by chlorinated solvent contamination near the dry cleaning building. Tetrachloroethene (PCE) contamination occurs in soil at concentrations of 1,500 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ) beneath the facility. Shallow groundwater has been impacted by PCE contamination above the Federal Drinking Water Maximum Contaminant Level (MCL) of 5 micrograms per liter ( $\mu\text{g}/\text{L}$ ) and the United States Environmental Protection Agency (EPA), Region IX, Preliminary Remediation Goal (PRG) of 1.1  $\mu\text{g}/\text{L}$ . Trichloroethene (TCE) and cis-1,2-dichloroethene (cis-DCE) have also been detected in the groundwater. The highest concentrations of PCE have historically been detected in MW-1, located near the northwest corner of the site (Figure 1).

Hydrogen Release Compound (HRC), manufactured by Regenesis, of San Clemente, California was used and evaluated as an Interim Remedial Action Measure (IRAM) to help accelerate and promote biodegradation of chlorinated compounds. HRC was chosen because it is cost-effective, is easy to install, and requires little or no operation and maintenance. HRC is also being considered by the DEQ as a presumptive remedy in the State of Oregon Dry Cleaning Fund.

## **MATERIALS AND METHODS**

**Description of Technology.** HRC is a passive, treatment option for in-situ bioremediation of chlorinated aliphatic hydrocarbons (CAHs). HRC is a proprietary, environmentally safe, food quality, polylactate ester specially formulated for slow release of lactic acid upon hydration. Bioremediation with HRC is a multi-step process. Microbes metabolize the lactic acid released by HRC, and produce hydrogen, which can be used by reductive dehalogenators, which are capable of dechlorinating CAHs.

**Bench Scale Testing.** To determine if indigenous bacteria at the site were capable of reducing PCE, soil samples were collected for bench scale testing. A representative soil sample was collected from the saturated zone beneath the dry cleaners site at approximately 25 feet below ground surface (BGS), at an interval where HRC could be applied.

The soil sample was shipped to Applied Power Concepts, Inc., (APC) laboratory where the sample was split into six discrete samples for the bench scale testing. The samples were tested using a protocol designed by Regenesis and outlined in their *Bench Scale Experiments* manual. The bench scale test provides an accelerated response to anaerobic remediation. The focus of the test was to determine whether the soil contains a population of bacteria that are not only suitable to perform the remediation, but could also respond to an increase in the carbon compound biochemical energy and the hydrogen generated from HRC.

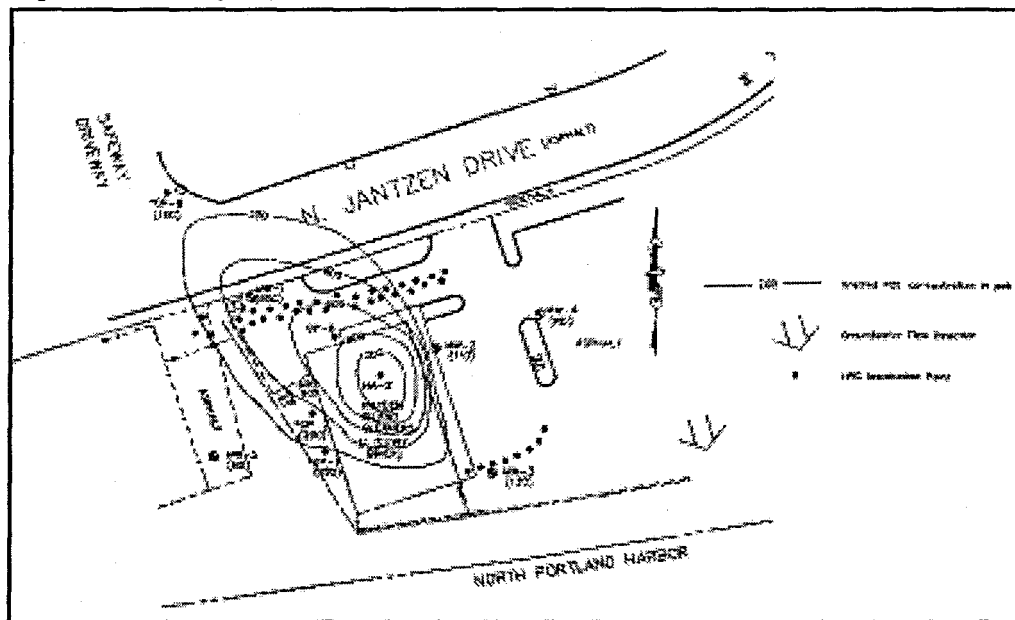
**Field Application.** Based on the results of the bench scale testing, the site configuration, the groundwater flow direction and gradient, and the groundwater

sampling data, two barrier arrays were determined to be able to provide the best coverage of HRC at the site. HRC was installed at the Hayden Island Cleaners site in May 1999. A standard van mounted Geoprobe® rig equipped with a 1.25-inch outside diameter drill rod was used to inject the HRC. The HRC was pumped from buckets, through an application hose, and injected through the drill rods using a specially designed pump provided by Regenesis. The HRC was placed along the entire vertical saturated interval of the aquifer from approximately 25 to 40 feet BGS.

An 80-foot barrier array was installed downgradient of MW-1 along the northern property boundary. The array consisted of 34 HRC delivery points, offset in two rows, and spaced at 5-foot intervals (Figure 1). Forty-eight pounds of HRC was injected per hole (3.2 pounds per vertical foot [lbs./vertical foot]) for a total of 1,680 pounds. The 3.2 lbs./vertical foot was at the low end of an application range of 2 to 10 lbs./vertical foot as defined by Regenesis. Monitoring well MW-1 was used as a monitoring point along this northern barrier array.

The second barrier array was oriented along the south portion of the property. This array consisted of eight injection points, spaced at 5-foot intervals (Figure 1). Forty-eight pounds of HRC was injected per hole (3.2 lbs./vertical foot) for a total of 624 pounds. Monitoring well MW-3 was used as a monitoring point along this southern barrier array.

Figure 1. Site Layout, HRC Probe Points



**Groundwater Monitoring.** Baseline groundwater samples were collected from six upgradient and downgradient monitoring wells prior to HRC installation. Groundwater samples were analyzed using EPA Method 8260 for Volatile Organic Compounds (VOCs). Natural attenuation parameters were also analyzed and included total and dissolved iron, nitrate, nitrite, sulfate, sulfide, methane,

ethane/ethene, chloride, phosphorous, and manganese. In addition, field chemical parameters were collected for dissolved oxygen (DO), oxidation/reduction (redox) potential, pH, and temperature.

## RESULTS AND DISCUSSION

**Bench Scale Testing Results.** The bench scale samples were run from 11/9/98 to 12/4/98. TCE was added to the soil samples at concentrations of 10 mg/L and 25 mg/L along with 1.5 grams of HRC (sorbitol polylactate). The results of the test indicated that significant reductions of TCE were observed in all of the samples nine days into the test, including the production of cis-DCE and vinyl chloride (VC). By the end of the test, the sample set that began with a low TCE value (10 mg/L) had been reduced to an average of 1.00 mg/L. The sample set with the highest TCE value (25 mg/L) was reduced to an average value of 5.29 mg/L. However, no degradation of TCE was indicated after the first 15 days of the test. Cis-DCE and VC still were produced and apparently degraded for the length of the test.

Results of organic acid analysis (lactic and pyruvic) indicated an increase in acid concentration, especially lactic acid, indicating that HRC was continuing to be available for degradation. Bacterial counts of the samples indicate a healthy population of aerobic, anaerobic, and sulfate reducing bacteria in the subsurface soils at the site.

Based on comparisons of the bench scale testing data to other test data, the Hayden Cleaners site was determined to have suitable microbes in the subsurface to be a good candidate for a pilot field test.

**Groundwater Monitoring Results.** Groundwater samples were collected from site monitoring wells prior to and following placement of the HRC product.

PCE concentrations have decreased approximately 75% from the initial sampling event in March 1998 in monitoring wells MW-1 and MW-3 (Figure 2). The initial decrease in MW-1 and MW-3 may be attributed to dilution based on the fluctuations of the shallow groundwater. However, it is believed that biodegradation/natural attenuation of the parent PCE compound was occurring at a slower rate before installation of HRC. Concentrations in MW-2 have decreased approximately 30% and represent the slower natural background aquifer conditions.

Following injection of HRC, significant degradation of PCE were observed in the wells, particularly at MW-3, where the daughter degradation products, TCE and cis-DCE concentrations have increased and appear to be accumulating (Figure 3). Monitoring wells MW-1 and MW-2 showed a similar decrease in PCE, but a slower increase in TCE concentrations and no production of cis-DCE. Vinyl chloride has not been detected in any of the site wells.

A review of selected geochemical parameters measured at the site confirms that degradation is occurring (Table 1). Baseline conditions at the site indicate an aquifer with low DO (<1.5 mg/l) and redox conditions (<100 mV).

Nitrate concentrations at the site have been decreasing with time, indicating that the site aquifer is depleted with respect to nitrate. Total iron and total manganese concentrations have been increasing with time, indicating iron and manganese reducing environments. Sulfate concentrations have increased with time, have stabilized, and are beginning to decrease, indicating possible sulfate reduction. The presence of methane beginning approximately three months after HRC injection may indicate that the terminal electron donor processes for nitrate, iron, and sulfate have begun to be depleted and that a move toward methanogenic conditions is occurring.

Figure 2. PCE Concentrations in Monitoring Wells

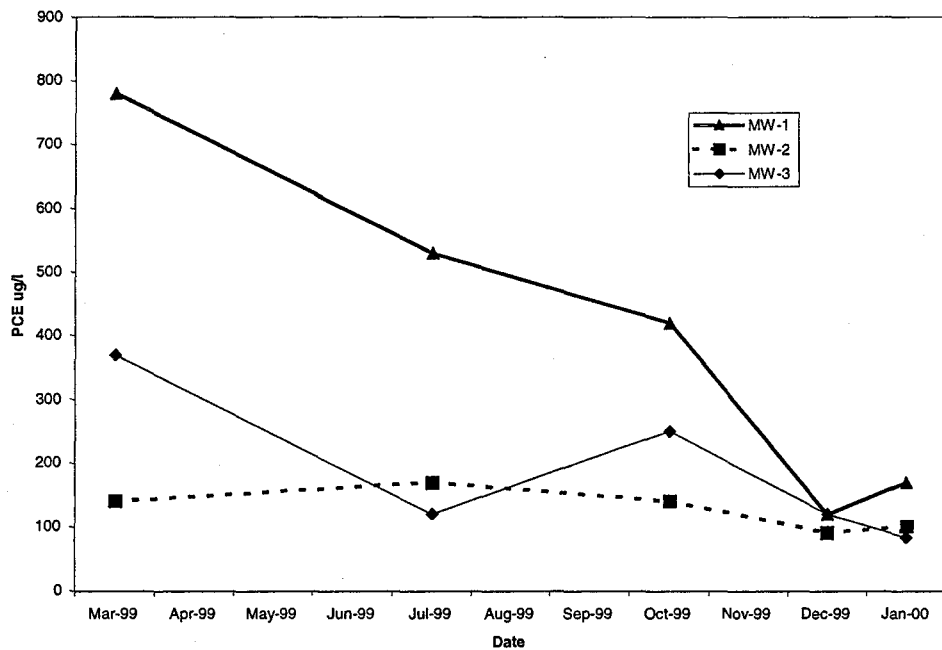


Figure 3. Volatile Organic Compounds detected in MW-3

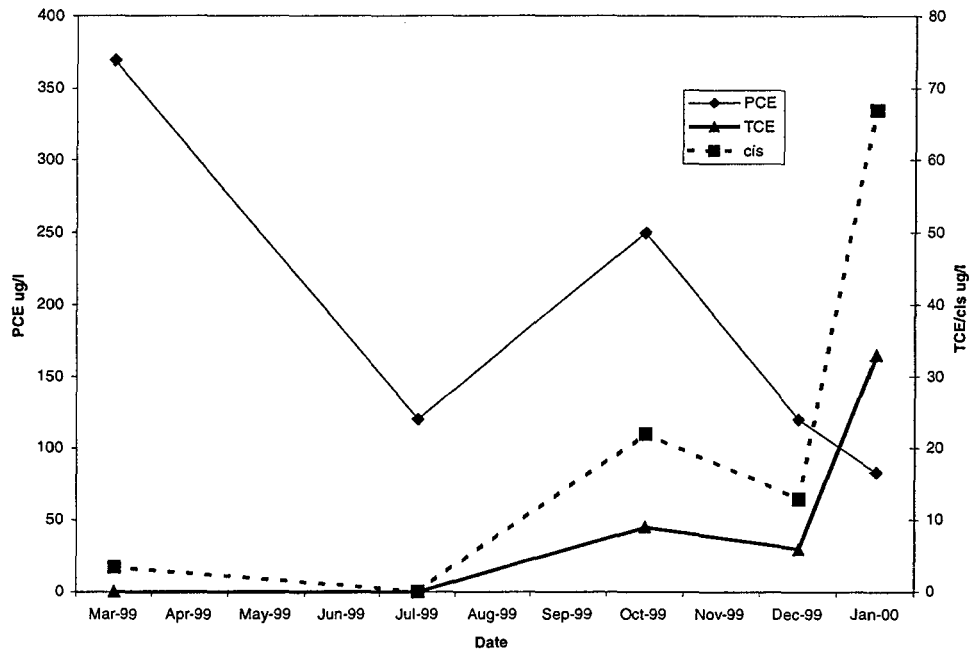


Table 1. Selected Geochemical Parameters in Groundwater (mg/l)

Well	Date	Nitrate	Iron (Total)	Mn (Total)	Sulfate	Methane
MW-1	12/28/98	2.1	0.315	NA	18	NA
	07/12/99	9.2	0.288	0.0635	24	ND
	10/07/99	6	0.012	0.0458	22	ND
	12/17/99	0.7	0.124	1.39	23	0.0042
	01/18/00	ND	0.667	3.04	24	0.0005
MW-2	12/28/98	2.3	NA	NA	6	NA
	07/12/99	4.5	0.081	0.0233	17	NA
	10/07/99	5.2	0.077	0.0159	14	NA
	12/17/99	0.4	0.148	0.0526	8.5	0.0224
	01/18/00	1.2	0.02	0.0481	7.7	ND
MW-3	12/28/98	2.1	NA	NA	4	NA
	07/12/99	0.5	0.997	0.0688	36	ND
	10/07/99	ND	3.95	1.27	22	0.11
	12/17/99	0.2	7.91	1.29	30	0.504
	01/18/00	0.25	8.74	1.28	25	0.612

NA = not analyzed. ND=Not detected

**Project Costs.** The costs associated with the HRC installation are outlined below. HRC was selected as an IRAM for the Hayden Island site with the primary objective to increase contaminant mass removal and reduce remaining concentrations to below risk-based concentrations. Also, DEQ was interested in reviewing HRC as a cost-effective means compared to other, more common remedies such as soil vapor extraction (SVE) and air sparging. Following are the actual costs incurred at the site, excluding site investigation activities, contractor costs, and DEQ oversight:

HRC product	\$6.00 per pound x 2,310 pounds = \$14,000
Regenesis Pump Rental	\$900
Bench Scale Testing	\$2,000 per sample
Drilling Subcontractor	\$4,000
<u>4 quarters of monitoring</u>	<u>\$10,000</u>

**Total Costs** **\$31,000**

Because of the limited amount of funding the state receives to investigate and cleanup dry cleaner sites, DEQ is evaluating the use of HRC as a presumptive remedy to help manage site prioritization, characterization, and eventual cleanup or no further action determination. At a similar dry cleaning site considered for HRC use, DEQ plans to spend an estimated \$150,000 for installation of a multiphase extraction system. If successful in achieving site closure at the Hayden Island site, HRC would save approximately \$120,000.

**CONCLUSIONS.** Specific conclusions that can be drawn from the use of HRC at the Hayden Island site are as follows:

- Shallow groundwater contaminated with PCE has shown degradation to TCE and cis-DCE;
- A general decline in PCE was observed across the site before installation of HRC, probably because of groundwater flushing and dilution from the adjacent river;
- Approximately seven months following HRC installation, a reduction of PCE by 75 % at the site was observed in wells MW-1 and MW-3 adjacent to the HRC injection arrays;
- Degradation rates observed in MW-2 are indicative of natural degradation rates for the site;
- Approximately seven months following HRC installation, an increase in associated production of daughter products (TCE and cis-DCE) is observed at the site;
- Based on the apparent success of HRC to reduce contaminant mass and stimulate degradation of chlorinated solvents, DEQ likely will continue to use HRC as a presumptive remedy.



## ENHANCED CAH DECHLORINATION USING SLOW AND FAST RELEASING POLYLACTATE ESTERS

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**ABSTRACT:** This paper compares the results of two separate field tests using slow and fast releasing polylactate esters to remediate chlorinated aliphatic hydrocarbon (CAH) contamination in groundwater by enhancing reductive dechlorination. The two polylactate esters generate molecular hydrogen in groundwater at different rates to serve as electron donors for reduction-oxidation reactions. At both sites, both the fast and slow releasing polylactate esters have been shown to effectively change groundwater conditions to enhance reductive dechlorination of CAHs by first reducing competing electron acceptors. However, the time required to reduce the competing electron acceptor concentrations was greatly different at the two sites - approximately one month for Site 2 compared to seven months for Site 1. After one year, elevated levels of hydrogen continue to be present within the source area at Site 1. Along with quickly providing conditions favorable for reductive dechlorination at Site 2, the high levels of hydrogen produced by the fast releasing compound also induced conditions favorable for methanogenesis. A dramatic increase in methane concentration was measured at Site 2 following the injections. At Site 1, low concentrations of hydrogen produced by the slow releasing compound only slightly increased methane levels. Hydrogen is wasted in methanogenesis because it does not assist in accelerating reductive dechlorination.

### INTRODUCTION

Sites 1 and 2 are located within 10 miles of each other in Santa Clara County, California. The geology at both sites consists of interbedded layers of clay, silty sand, and sand (clay is the predominant soil type above the water-bearing zone). The water-bearing unit at both sites is primarily composed of silty sand. At both sites, groundwater flow has been measured consistently to the north and northeast at a gradient of 0.001 to 0.002 feet per foot.

In the mid-1960s both sites began using tetrachloroethene (PCE) and trichloroethene (TCE) for manufacturing activities. Compounds detected in soil and groundwater include PCE and TCE and their daughter (degradation) products: cis-1,2-dichloroethene (DCE) and vinyl chloride. The primary releases to groundwater at both sites consisted of TCE. Initial concentrations of TCE in groundwater within each site's source area were approximately five milligrams per liter (mg/L). In 1985, a pump and treat system was installed at Site 2 to contain the migration of contaminants to a down-gradient property. Prior to the field tests using polylactate ester, TCE concentrations in groundwater at Site 2 had decreased to approximately one mg/L. At Site 1, no remediation activity was

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conducted prior to the field test and TCE levels in groundwater within the source area remained around five mg/L.

To date, one of the most widely used substrates to enhance anaerobic bioremediation is lactic acid. For the field tests CDM used an environmentally safe, food quality, polylactate ester that releases lactic acid upon biological degradation. Lactic acid occurs naturally in milk and other foods and is formed in muscles during exercise. It is the major product in most fermentation processes utilized by the dairy industry in the manufacturing of buttermilk, sour cream, yogurt, and some types of cheese (Gaudy and Gaudy, 1980).

The released lactic acid acts as a nutrient source for anaerobic microbes. These microbes metabolize the lactic acid into pyruvic acid and then acetic acid. In addition, in the presence of molecular hydrogen lactic acid will absorb hydrogen to form butyric acid and then propionic acid. These five acids are classified as fatty acids. Typically, in the conversion of lactic acid to acetic acid by the anaerobic microbes (acetogens), one mole of lactic acid produces two moles of molecular hydrogen. Butyric and propionic acid will also degrade and release hydrogen. Dissolved hydrogen is the most reduced of all molecules under anaerobic conditions. Since hydrogen gives up an electron so readily, it is the preferred electron donor for microbes that reduce electron acceptors such as oxygen, nitrate, iron, sulfate, and CAHs (Hemond and Fechner, 1994).

The difference between the slow and fast releasing polylactate esters is that the slow releasing compound is bound in a highly viscous polymer that slowly releases the lactic acid, while the fast version is not. The fast version is less viscous and completely water-soluble. Because of its low viscosity (similar to water), it can be injected more easily and can spread over a larger aquifer volume more rapidly than the slow releasing compound. The fast releasing polylactate ester releases lactic acid about an order of magnitude faster into the groundwater and therefore generates higher initial concentrations of hydrogen in groundwater. Regensis' standard HRC<sup>TM</sup> product was used as the slow releasing polylactate ester and Regensis' HRC<sup>TM</sup>-primer product was used as the fast releasing polylactate ester.

The most thermodynamically favored electron acceptor used by microbes for the degradation of organic carbon is dissolved oxygen (DO). Anaerobic bacteria, critical for reductive dechlorination of CAH compounds, generally cannot function at DO concentrations greater than one mg/L. After DO is depleted, anaerobic microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis). Generally, the rate of methanogenesis increases with higher hydrogen concentration (Hemond and Fechner, 1994).

Oxidation-reduction potential (ORP) of groundwater is a measure of electron activity and is an indicator of the relative tendency of a substance to accept/donate electrons. Oxidation is defined as the loss of electron(s) from a substance; while reduction is the gain of electron(s). Reduction-oxidation (redox) reactions in groundwater are usually biologically mediated; therefore, ORP is affected by and exerts an influence on rates of biodegradation. Low or negative

ORP measurements are indicative of an anaerobic environment while high ORP measurements [greater than 300 millivolts (mV)] indicate an aerobic environment.

Reductive dechlorination of CAHs is the process by which anaerobic microbes (dehalogenators) substitute a hydrogen atom for a chlorine atom. Through this process, the more chlorinated CAHs can be degraded to form less chlorinated compounds (e.g., PCE to TCE to cis-1,2-DCE to vinyl chloride and finally to ethene). Reductive dechlorination occurs most readily in conditions between sulfate reduction and methanogenesis. However, dechlorination of PCE and TCE also may occur in the ORP range associated with denitrification or iron (III) reduction. Dechlorination of cis-1,2-DCE and vinyl chloride are generally inhibited by the presence of sulfate (Weidemeier et al., 1998).

### **FIELD TESTS**

Field tests at both sites were conducted within the contamination source areas. The polylactate esters were injected into the water-bearing zones using a pump and a truck-mounted Geoprobe™ apparatus. The injection locations were spaced approximately 10 feet apart and covered a total injection area of approximately 4,200 and 5,000 square-feet at Site 1 and 2, respectively.

For each injection location, the Geoprobe™ advanced a probe to the bottom of the water-bearing zone. Then the point on the probe was detached, allowing the polylactate ester to be pumped into the subsurface through the unit's hollow push rods. Additional polylactate ester was injected into the water-bearing zone during retraction of the probe and discontinued at the top of the water table. A few days after the injections, following dispersement of the polylactate ester into the groundwater, all the locations were grouted with neat cement.

At Site 1, the slow releasing polylactate ester was injected at a rate of approximately 6 pounds of polylactate ester per linear foot and at pressures between 500 to 1,500 pounds per square inch (psi). At Site 2, the fast and slow releasing polylactate esters were injected in adjacent injection locations. The fast releasing polylactate was injected into the groundwater first at a rate of three pounds per linear foot. A few hours later, subsequent to the dispersement of the fast releasing polylactate ester, the slow releasing polylactate ester was injected into an adjacent location at a rate of three pounds per linear foot.

Prior and subsequent to the injections, monitoring wells within and adjacent to the source area (upgradient, downgradient, and crossgradient with respect to groundwater flow direction) were monitored for:

- General environmental parameters such as temperature, pH, conductivity, ORP, alkalinity, turbidity, and total organic carbon (TOC)
- Dissolved hydrogen
- Fatty acids (lactic acid and its degradation acids)
- Electron acceptors such as DO, nitrate/nitrite, sulfate, and total iron
- Metabolic by-products such as ferrous iron, dissolved manganese, sulfide, chloride, methane, ethane, and ethene
- CAHs such as chlorinated ethenes and chlorinated ethanes.

## RESULTS AND DISCUSSION

Tables 1 through 5 present the analytical data from groundwater samples collected from monitoring wells within each site's source area prior and subsequent to the injections. The tables show data for days prior to the injections as negative valued days and after the injections as positive valued days. Day 0 corresponds to the injection day: December 15, 1999 for Site 1 and October 2, 2000 for Site 2. Both sites continue to be monitored at six to ten week intervals.

Following the injection of the polylactate esters at both sites, increased levels of TOC, fatty acids, and hydrogen were observed. Fatty acids were not detected at either site prior to the injections. The presence of TOC represents solubilization of the polylactate ester into the groundwater. The presence of fatty acids demonstrates the breakdown of lactic acid (to pyruvic and acetic acid) and formation of butyric and propionic acid.

**TABLE 1. Selected General Environmental Parameters Values within the Source Areas at Site 1 and 2 Prior and Subsequent to the Field Tests.**

Day from Injection (Day 0)	Temperature (°C)	pH	ORP (mV)	TOC (mg/L)	Dissolved Hydrogen (nM)
Site 1					
-23	17.7	7.29	170	--	--
35	17.3	7.12	-235	--	0.86
103	17.1	7.11	-190	7.6	4.80
151	17.3	6.82	-303	28	4.17
209	17.8	6.41	-293	62	2.13
264	18.4	6.09	-301	87	98
328	17.1	6.72	-303	55	26
Site 2					
-7	21.0	6.92	18	<2.0	1.65
43	20.6	6.57	-341	220	240
85	19.7	6.52	-239	390	41

**TABLE 2. Fatty Acid Values Within the Source Areas at Sites 1 and 2.**

Day from Injection (Day 0)	Propionic Acid (mg/L)	Butyric Acid (mg/L)	Lactic Acid (mg/L)	Pyruvic Acid (mg/L)	Acetic Acid (mg/L)
Site 1					
-23	<1.0	<1.0	<25	<10	<1.0
35	<1.0	<1.0	<25	<10	<1.0
103	2.0	<1.0	<25	<10	13
151	17	6.7	<25	<10	40
209	14	3.9	<25	<10	77
264	45	14	<25	<10	120
328	30	<1.0	<25	<10	91
Site 2					
-7	<1.0	<1.0	<25	<10	<1.0
43	180	16	<25	<10	290
85	320	77	<25	<10	400

**TABLE 3. Electron Acceptor Values Within the Source Areas at Sites 1 and 2.**

Day from Injection (Day 0)	Dissolved Oxygen (mg/L)	Nitrate/Nitrite (mg/L)	Sulfate (mg/L)	Total Iron (mg/L)
Site 1				
-23	0.14	5.2	260	0.055
35	0.08	1.3	300	0.058
103	0.07	<0.05	270	0.30
151	0.35	<0.05	88	1.7
209	0.07	<0.05	51	7.3
264	0.07	<0.10	60	13
328	0.03	<0.10	6.3	7.1
Site 2				
-7	0.24	1.2	290	0.44
43	0.01	<0.1	<1.0	3.4
85	0.00	1.6	<1.0	32

**TABLE 4. Metabolic Byproduct Values Within the Source Areas at Sites 1 and 2.**

Day from Injection (Day 0)	Sulfide (mg/L)	Ferrous Iron (mg/L)	Dissolved Manganese (mg/L)	Methane (µg/L)	Ethene (µg/L)
Site 1					
-23	<1.0	<1.0	0.79	5.8	0.026
35	<2.0	<1.0	1.4	3.9	0.046
103	<2.0	<1.0	2.5	4.3	0.125
151	<2.0	<1.0	4.1	34.3	0.447
209	<2.0	1.7	6.4	1,943	0.395
264	2.0	2.4	8.8	5,556	0.319
328	<2.0	7.0	9.7	1,600	0.046
Site 2					
-7	<2.0	<1.0	0.56	1,000	16
43	6.9	3.2	11	2,200	16
85	<2.0	29	1.9	180,000	120

**TABLE 5. Selected CAH Results Within the Source Areas at Sites 1 and 2.**

Day from Injection (Day 0)	PCE (µg/L)	TCE (µg/L)	cis-1,2-DCE (µg/L)	Vinyl Chloride (µg/L)
Site 1				
-23	<50	3,500	500	<50
35	<50	3,200	470	<50
103	<50	2,400	1,400	<50
151	<5.0	1,400	2,742	<5
209	3.4	370	3,439	<1.0
264	2.9	340	4,442	<1.0
328	<1.0	<2.0	4,952	4.4
Site 2				
-7	71	450	1,719	180
43	<1.0	11	2,315	300
85	<1.0	2.9	62.3	1,000

As expected with the higher rate of solubilization of the fast releasing polylactate ester, larger increases in TOC, acetic acid, and hydrogen concentrations were measured at Site 2. With the increase in hydrogen to sustain reduction-oxidation reactions, ORP decreased at both sites to  $-200$  to  $-300$  mV, indicative of highly reducing conditions in groundwater. The use of the slow releasing polylactate ester at Site 1 produced a low constant concentration of hydrogen between two and five nanomolar (nM) for the first seven months following the treatment. This slow generation of hydrogen contributed first to the decrease in nitrate level and then to the gradual decreases in sulfate concentration in groundwater. In contrast, at Site 2 the high concentration of hydrogen generated by the fast releasing polylactate ester reduced nitrate and sulfate to non-detect levels within the first monitoring event (Day 43).

Hydrogen concentrations decreased dramatically at Site 2 between the first and second monitoring events after the treatment. As the fast releasing polylactate ester degrades and releases all of its hydrogen, the slow releasing polylactate ester at Site 2 will continue to produce hydrogen at low concentrations. Over time it is anticipated that hydrogen concentrations at Site 2 will begin to stabilize to levels observed at Site 1. Hydrogen concentrations at Site 1 increased substantially after the reduction of sulfate levels (Day 264) and may be attributed to the reduction of electron acceptors (nitrate and sulfate) in the groundwater.

Due to the reduction of nitrate and sulfate at Site 2 and the high influx of hydrogen into the groundwater, conditions became favorable for complete reductive dechlorination to ethene. TCE and cis-1,2-DCE levels at Site 2 prior to the treatment had been between 300 to 700 micrograms per liter ( $\mu\text{g/L}$ ) ( $450 \mu\text{g/L}$  just prior to the injections) and 1,000 and 3,000  $\mu\text{g/L}$  ( $1,719 \mu\text{g/L}$  just prior to the injections), respectively. Following reduction of competing electron acceptors, TCE concentrations at Site 2 decreased to 11  $\mu\text{g/L}$  during the first monitoring event (Day 43) and 2.9  $\mu\text{g/L}$  during the second monitoring event (Day 85).

At Site 2, the reduction of TCE was correlated with an increase in cis-1,2-DCE concentration to 2,315  $\mu\text{g/L}$  at Day 43. However with decreased concentration of TCE, cis-1,2-DCE became a favorable electron acceptor in the groundwater and concentration of cis-1,2-DCE dropped to 62.3  $\mu\text{g/L}$  at Day 85. With the degradation of cis-1,2-DCE, increases in vinyl chloride were measured. In addition, degradation of vinyl chloride to ethene is inferred with the increasing concentration of ethene between Day 43 and 85.

At Site 1, initial TCE levels were higher than Site 2. The TCE level at Site 1 prior to the injections was 3,500  $\mu\text{g/L}$ . Under sulfate reducing conditions observed at Site 1 subsequent to the injections, concurrent reduction of TCE to cis-1,2-DCE was evident. Thermodynamically, the reduction of PCE and TCE is as favorable as reduction of sulfate (similar releases of energy). However, the reduction of cis-1,2-DCE and vinyl chloride is not as favorable and is inhibited under sulfate reducing conditions. The first indication of reduction of cis-1,2-DCE to vinyl chloride did not occur until sulfate levels fell to 6.3 mg/L on Day 328 when 4.4  $\mu\text{g/L}$  of vinyl chloride was detected at Site 1. This was the first historical detection of vinyl chloride within the source area of Site 1.

With the reduction of competing electron acceptors at Site 1 and continued release of hydrogen from the slow releasing polylactate ester, it is anticipated that continued reductive dechlorination will drive remaining cis-1,2-DCE to vinyl chloride and eventually to ethene. At Site 2, the accelerated reduction of TCE and cis-1,2-DCE to vinyl chloride and ethene, is expected to continue as hydrogen continues to be generated by the slow releasing polylactate ester.

Methanogenesis (reduction of carbon dioxide to methane) occurs at the same reductive (ORP) conditions as reductive dechlorination. Typically levels of above 10 nM are needed to induce methanogenesis. Initial concentrations (prior to the injections) of methane at Site 2 were higher than Site 1 (1,000 versus 5.8 µg/L). Increased levels of methane were seen at both sites, but only with high hydrogen levels. At Site 2, with the use of the fast releasing polylactate ester and high hydrogen concentrations, methane levels increased to 180,000 µg/L 85 days after the injections.

At Site 1, with the low levels of hydrogen produced, methane levels increased only slightly to 34.3 µg/L 151 days after the injections. However with the higher hydrogen concentrations observed after Day 151 (98 nM), increased levels of methane (5,556 µg/L) were observed at Site 1. During this period at Site 1, ORP levels were fairly constant between -293 and -303 mV but reductive dechlorination of TCE to cis-1,2-DCE slowed. Prior to the high hydrogen concentrations observed after Day 151, TCE concentrations were reducing at a rate of approximately 15 µg/L/day. After Day 151, TCE concentration reduction decreased to a rate of approximately 0.4 µg/L/day. With higher hydrogen concentrations, the favorable reduction process in the groundwater at Site 1 became methanogenesis as evidenced by the higher methane concentrations.

## CONCLUSIONS

Both the fast and slow releasing polylactate esters have been shown to effectively change groundwater conditions to enhance reductive dechlorination of CAHs at both sites by first reducing competing electron acceptors. Sulfate concentrations at both sites are now below inhibitory levels, and the continued release of hydrogen from the slow releasing polylactate ester is anticipated to facilitate the reductive dechlorination process at both sites. However, the time required to reduce the competing electron acceptor concentrations was greatly different at the two sites - approximately one month for Site 2 compared to seven months for Site 1. After one year, elevated levels of hydrogen continue to be present within the source area at Site 1.

Similar to Site 2 where the initial high hydrogen concentrations produced high methane levels, Site 1 also showed that high levels of hydrogen in groundwater will induce methane production. Hydrogen is wasted in methanogenesis because it does not assist in accelerating reductive dechlorination. After reduction of competing electron acceptors, reductive dechlorination proceeds at a faster rate with lower concentrations of hydrogen.

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