

FULL SCALE CHEMICAL OXIDATION OF MANUFACTURED GAS PLANT HYDROCARBONS IN SOIL AND GROUNDWATER USING FENTON'S REAGENT

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ABSTRACT

Chemical oxidation of manufactured gas plant hydrocarbons in soil and groundwater is currently being conducted at the Burlington MGP site. The Geo-Cleanse[®] Process involves simultaneous injection of Fenton's reagent (hydrogen peroxide and trace quantities of an iron catalyst) under pressure into the impacted soil. The process provides non-selective oxidation of typical MGP organic compounds such as volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). A total of 352 shallow, intermediate and deep injectors have been installed on the Burlington MGP site. A geomembrane has been installed over a portion of the site to provide a barrier above a silty layer of soil to prevent short-circuiting to the surface and allow proper contact between the reagents and contaminants. Chemical injection began on August 9, 2000, and continued through December 9, 2000 when cold weather conditions no longer allowed efficient chemical delivery. Chemical injection resumed on April 16, 2001 and was discontinued on September 12, 2001. This paper will discuss the efficacy of the process, the groundwater cleanup accomplished, and lessons learned during the implementation.

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INTRODUCTION

Wisconsin Electric Power Company currently owns a former MGP site in the City of Burlington, Wisconsin. The 2.1 acre site is located along the Fox River in an industrial area of the city. From 1907 to 1946, one of Wisconsin Electric's predecessor companies manufactured gas using the Lowe carburetted water gas processes. The Burlington plant was closed and the manufacturing equipment dismantled in 1948. In 1995, most of the buried piping, foundations, and slabs were removed and 12,000 tons of contaminated soil from the upper five feet of the site was excavated, taken off-site for treatment and disposal, and the area was covered with a layer of clean fill material. Further remediation is necessary to accommodate the City of Burlington's riverfront redevelopment plans, the related widening of Calumet Street which borders the site, and the construction of a highway across the southern portion of the site.

Wisconsin Electric determined that the Geo-Cleanse[®] in-situ chemical oxidation treatment process, a technology that has been used successfully to clean up many other contaminated sites, was the most cost-effective process to successfully treat the soil and groundwater at the Burlington site.

GEO-CLEANSE PROCESS DESCRIPTION

Chemical oxidation of organic contaminants is accomplished by injection of hydrogen peroxide and a catalyst formulation into the soil at various elevations under carefully controlled conditions. The Geo-Cleanse[®] process is a technology that simultaneously injects reagents under pressure into the impacted media via a patented methodology and equipment. This in-situ oxidation system is capable of complete, non-selective oxidation of organic compounds in soil and groundwater.

The Fenton's reaction is: $\text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{OH}\cdot + \text{Fe}^{+3} + \text{OH}^-$

The hydroxyl free radical (OH•) is an extremely powerful oxidizer of organic compounds. Residual hydrogen peroxide, due to its unstable characteristics, rapidly decomposes to water and oxygen in the subsurface environment. Soluble iron amendments added to the aquifer during the Geo-Cleanse[®] process in trace quantities are precipitated out during conversion to ferric iron. During the reaction sequence, the organic compounds are successively converted to shorter chain mono- and di-carboxylic (fatty) acids. These compounds are non-hazardous, naturally occurring substances, and are further degraded into carbon dioxide and water by subsequent reactions.

PILOT TEST

In May, 1999, a pilot test was conducted on site to determine the efficacy of the treatment method with soil and groundwater at the site. A total of 7,696 gallons of 50% hydrogen peroxide solution were injected through nine injectors over nine days of treatment. Injection to the shallow silt zone was hindered by the lack of a confining, native overburden layer. The pilot test was successful in significantly reducing both volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) in the lower sand and gravel zone to levels below Wisconsin

regulatory soil cleanup levels and groundwater standards in nearly all injector locations. Injection into the upper silt zone was not successful due to permeability contrasts in the backfill to ground surface. This problem would be addressed in the full scale design through the use of a geosynthetic membrane that would overlay the silty areas. Based on the pilot test results, a decision was made to proceed with full scale remediation.

REGULATORY APPROVAL FOR FULL SCALE TREATMENT

A Design Report was submitted to the Wisconsin DNR for full scale treatment on site on January 12, 2000. Approval to proceed was obtained on May 25, 2000. DNR required a significant number of conditions in order to proceed due to questions raised during their evaluation. For example, a perimeter vent well system with frequent gas monitoring was required to address questions about the potential for airborne release of VOCs. Existing abandoned utility piping was removed to prevent trenches acting as conduits. Additional on-site and off-site groundwater monitoring wells were installed. Temporary wells were required along the riverbank to detect potential migration of hydrocarbons into the river. Modeling was conducted to show that water quality standards would be met before, during and after remediation of the site. Initially, injection pressure was limited to 20 psi, and injection rate was limited to 1.6 gpm per injector. Additional field monitoring of groundwater quality, vapor concentrations in vent wells, and HCN gas monitoring was required.

The design of the injection system was based on baseline organic concentrations measured during site soil boring activities. Figure 1 below shows the concentrations of total organic

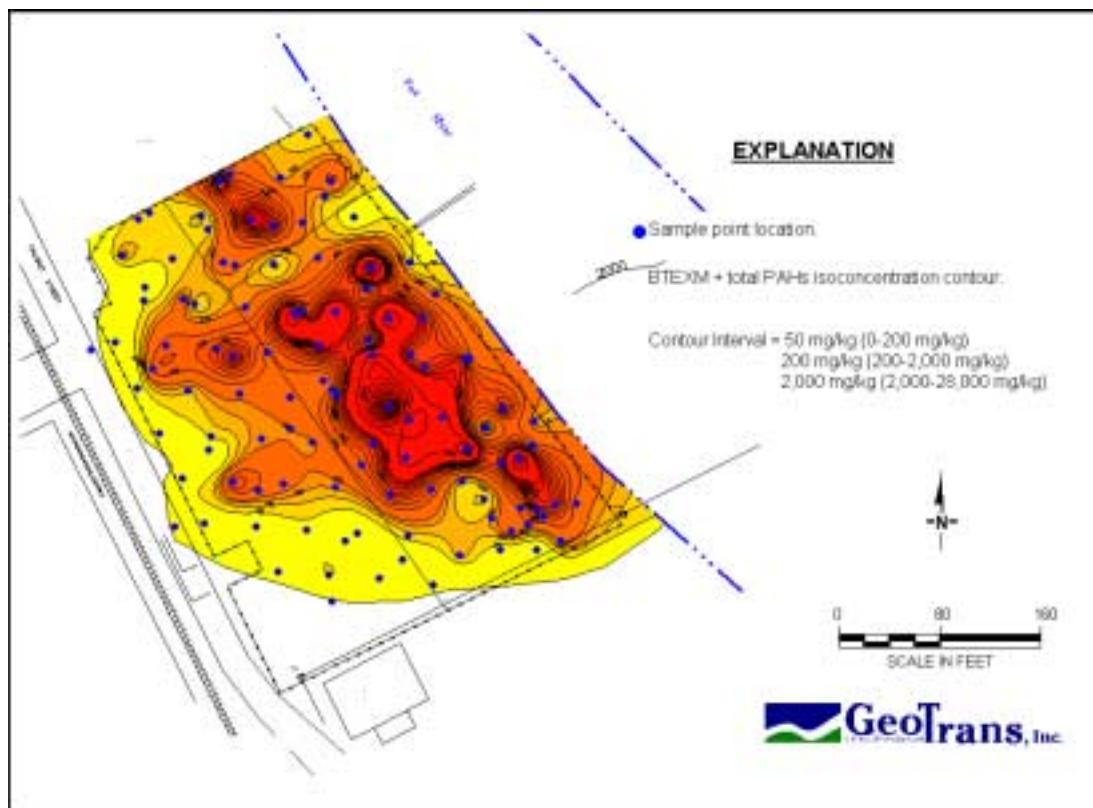


Figure 1
Baseline Soil Concentration Contours

contaminants calculated as the sum of benzene, ethylbenzene, toluene, xylene, trimethylbenzene, (BETXM) and polycyclic aromatic hydrocarbons (PAHs) that were measured during the site evaluation phase.

SITE CONSTRUCTION ACTIVITIES

Mobilization to the site began on July 10, 2000. The perimeter vent well system was installed, soil grading and excavation was conducted, and chemical injectors were installed. Soil over approximately 1/3 of the site was stripped, rocks and debris were removed, and 47,400 square feet of geomembrane were placed on the site to ensure contact of oxidants within the zone of contamination. Boots were installed around all injectors and monitor wells protruding through the membrane. Approximately 7000 tons of granular fill were placed over the geomembrane. The shallow injector array, including the geomembrane area, are shown in Figure 2 below.

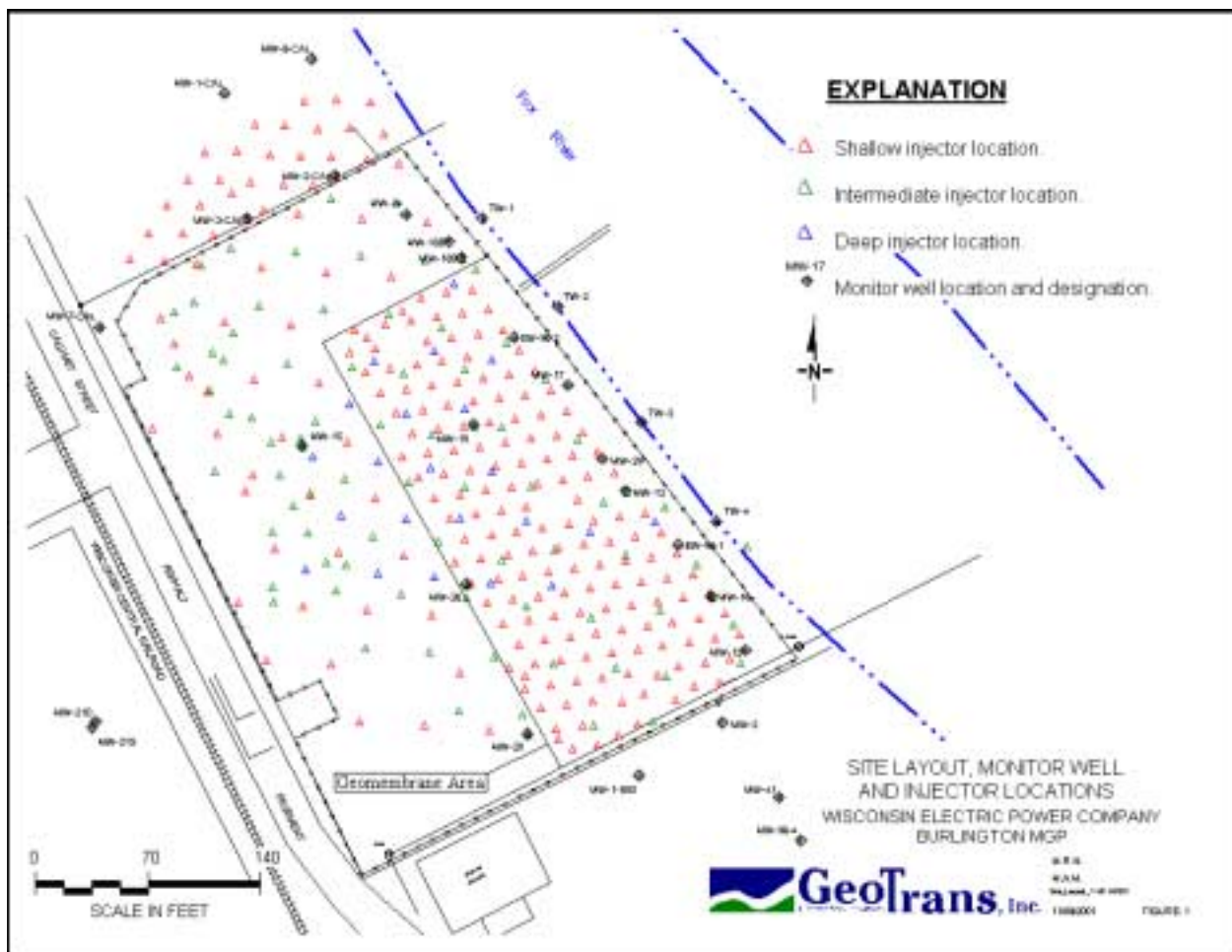


Figure 2
Shallow Injector Array Layout

Injector Installation

Chemical injectors were installed in shallow, intermediate, and deep zones on site. The injector wells were screened at approximately 2-6, 8-12, and 14-18 feet below the groundwater table,

respectively. Figure 3 shows a schematic view of the cross sectional injector array. Each injector contains a mixing head that promotes mixing of reagents and stimulates circulation of groundwater. The injector heads are specifically designed to control and mix the reagents during the Geo-Cleanse® process which maximizes the dispersion and diffusion of the reagent through the soil and affected aquifer. A cross section of the injector well is shown on Figure 4.

Based on the results of the pilot test, a conservative radius of influence for the injectors is 10 feet in the shallow organic silt layer and 25 feet in the remaining sand and gravel areas. The injectors are spaced to provide a 20% overlap in the radius of influence. A total of 198 shallow injectors, 75 intermediate injectors, and 27 deep injectors were installed for the full scale oxidation of the site. An additional 28 injectors were installed on the adjacent property to the north in order to clean up an area of additional contamination.

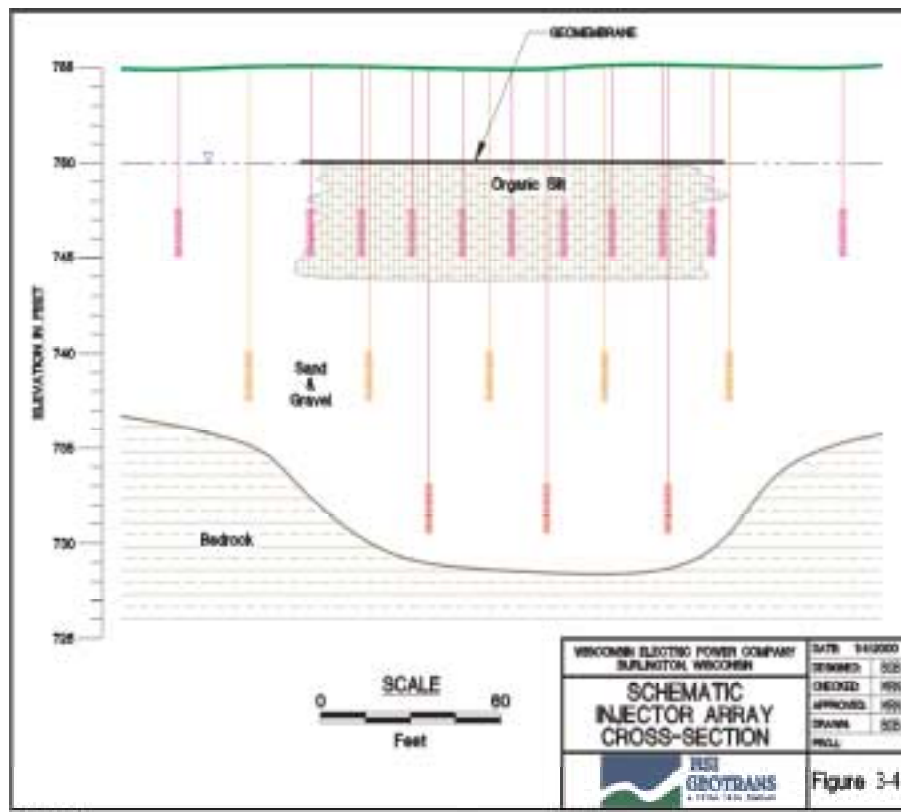


Figure 3
Schematic of Chemical Injector Array

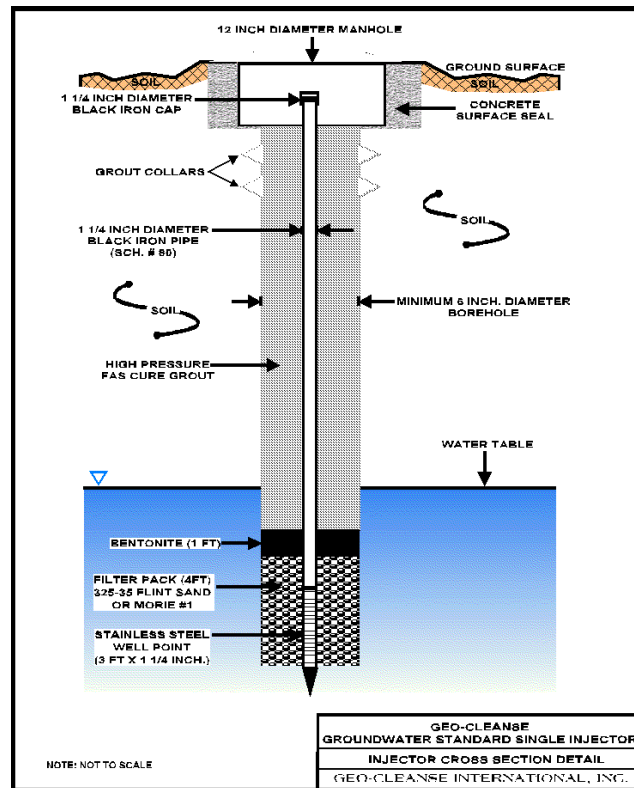


Figure 4
Injector Cross Section Details

Chemicals Used

Based on the results of the bench and pilot tests, an oxidant (50% hydrogen peroxide) to contaminant ratio ranging from 10:1 to 40:1 was determined for the site, depending upon geological strata. Originally, the site was calculated to contain approximately 50,000 pounds of organic contaminants (total BTEXM & PAHs). Based on an average reagent to contaminant ratio of 25:1, a total of 1,250,000 pounds or 125,000 gallons of reagent was estimated for the full scale treatment of the site. Subsequent soil samples were collected and analyzed during injector installation and the organic mass was recalculated based on weighting the area and depth based on concentration. The new calculations showed that the site contained 110,000 pounds of organic compounds based on total BTEXM and PAHs, over twice the mass originally estimated. A major portion of the organic mass has been associated with a shallow silty soil layer which was underrepresented in the initial soil boring strategy.

RESULTS ACHIEVED TO DATE

Peroxide Injection

Chemical injection activities began on August 21, 2000 and terminated on December 9, 2000 when cold weather conditions forced a shut down of injection activities for the winter. Chemical injection was resumed on April 16, 2001 and was discontinued on September 12, 2001 to evaluate the effectiveness of the program. During 2000, a total of 78,420 gallons of 50%

hydrogen peroxide were injected into the soil and groundwater at the site. During 2001, a total of 125,085 gallons of 50% hydrogen peroxide were injected into the soil and groundwater. A total of approximately 203,500 gallons of 50% hydrogen peroxide has been injected into the site over the thirteen-month period since start-up. To date, this results in an average reagent to contaminant ratio of 18.5:1. Bubble plots representing the location and quantities of peroxide injection for the shallow, intermediate and deep injectors are shown on Figures 5 through 7.

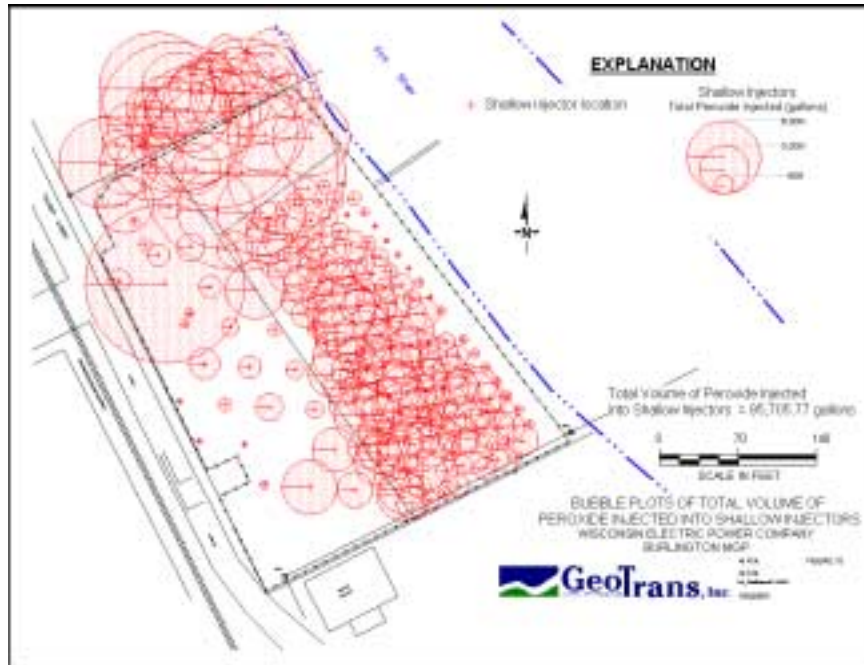


Figure 5
Bubble Plot of Peroxide Injection – Shallow Layer

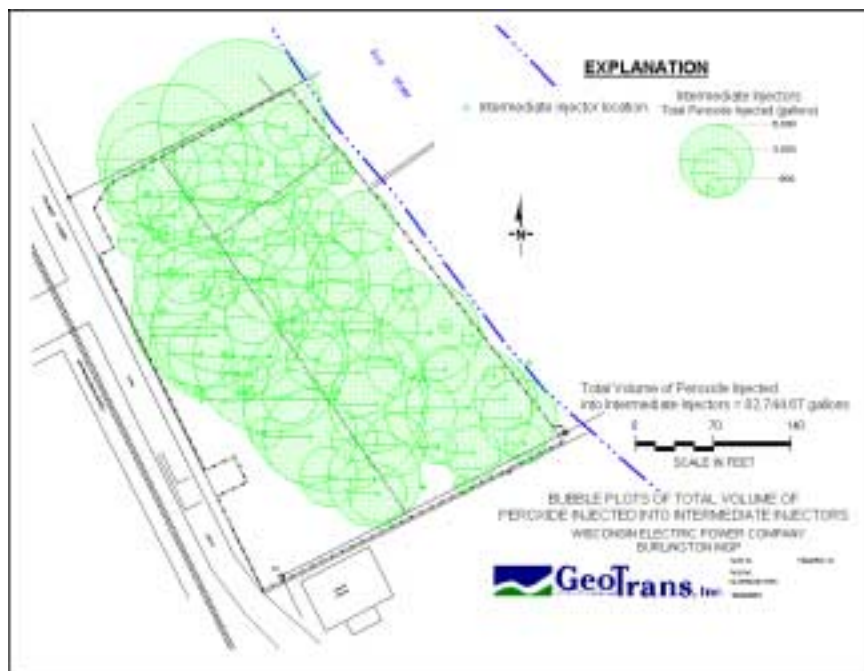


Figure 6
Bubble Plot of Peroxide Injection – Intermediate Layer

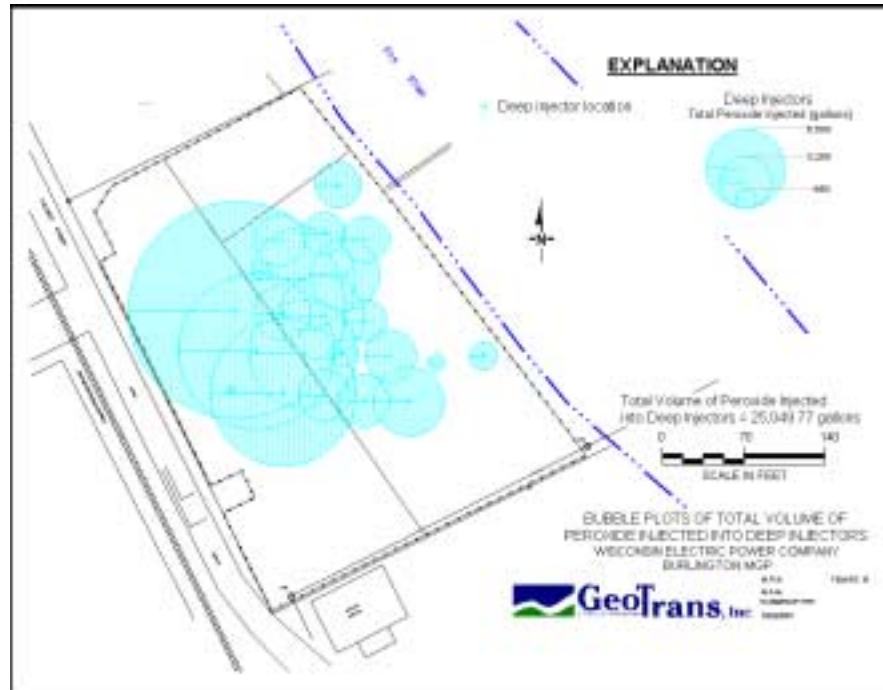


Figure 7
Bubble Plot of Peroxide Injection – Deep Layer

Most of the peroxide was injected through the shallow and intermediate injectors and to a lesser extent through the deep injectors. A limited amount of oxidant was injected near the river due to concerns raised by the DNR about peroxide entering the river. Unfortunately, the area along the riverbank is also where a number of groundwater monitoring wells are located.

Field Monitoring Observations

During the course of injection to many areas both inside and outside the Burlington MGP site, monitoring of groundwater and gases from the treatment zone have confirmed a good dispersal of oxidants and other reagents. Monitoring of groundwater from adjacent locations surrounding an active injector permits an evaluation of a radius of influence from each injector. Samples of groundwater were collected and evaluated for performance criteria (pH, peroxide concentration, iron, and headspace PID) as well as other parameters to evaluate and adjust for the effectiveness of the injection to that region. Based on groundwater performance criteria, peroxide was found throughout the groundwater in the treatment zone with the proper levels of iron and the desired slightly acidic pH of the groundwater. These are the proper conditions for oxidation to occur as was confirmed by the associated carbon dioxide increase and VOC decrease observed in the vent/monitoring points within the treatment zone. During the injection, carbon dioxide levels ranged from 2 to 25%, with many of the higher contaminant zones in excess of 25%. In addition, VOCs (measured via groundwater headspace with a PID), were reduced in various areas to non-detectable levels. Monitoring of degassing materials and groundwater not only provided an effective indirect measurement of radius, but also provided a means to determine when to terminate injection and commence discrete sampling and analysis of groundwater within an area.

Additionally, real-time air monitoring instruments were situated around the perimeter of the site to measure any potential volatilization and migration of airborne contaminants. As expected, the air monitoring data obtained did not identify any VOC emissions related to the chemical oxidation process during the first stage of injection (2000). The real-time instruments were replaced during 2001 with periodic spot air monitoring using a hand-held gas chromatograph as a check during the remainder of the project.

Groundwater Sampling Results

Figure 8 shows the location of the groundwater monitoring wells on the site.

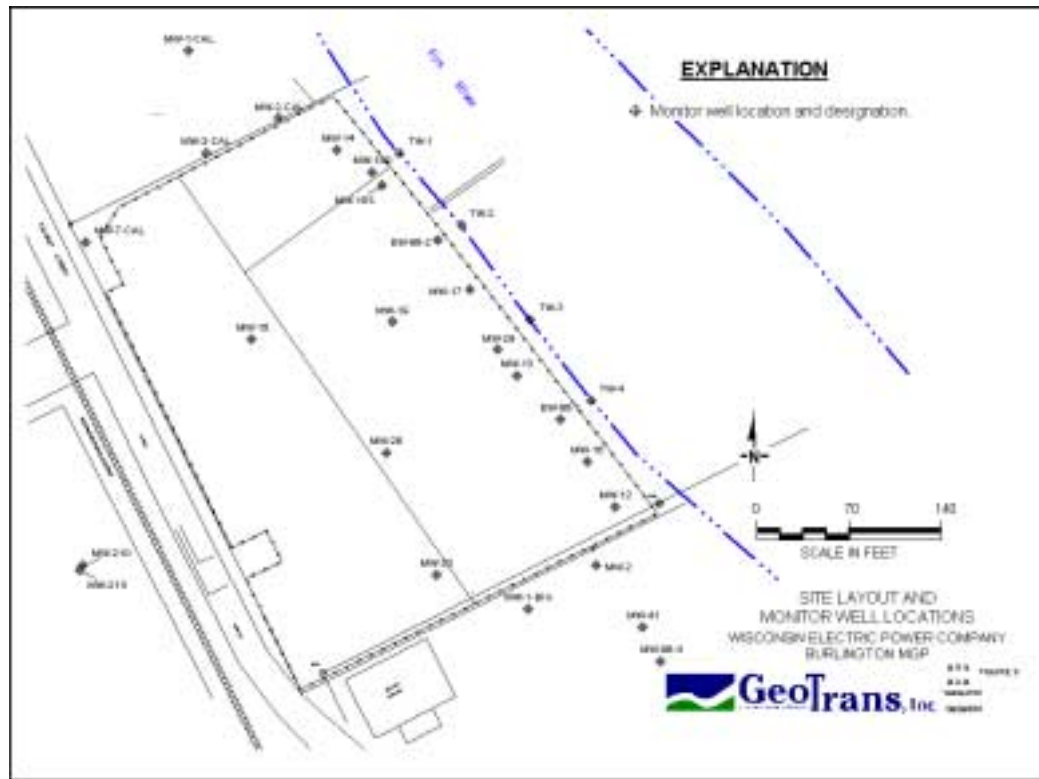


Figure 8
Groundwater Monitoring Wells

Time-concentration charts of BTEXM and PAH concentrations in selected wells are presented in Figures 9, 10, 11 and 12. Total BTEXM and PAH concentrations in MW-15, which is within the sandy soil area west of the silty soil layer, has declined dramatically as is shown in Figure 9. The same pattern is apparent in MW-26 which is located in the center of the site. At both of these wells contaminant concentrations decreased by approximately 97%. A decreasing, then slightly increasing trend is apparent in MW-19 which is located 60 feet from the river in the center of the silty soil area. The total reduction at this well is 80% to date. The total BTEXM and PAH concentrations decreased 93% in MW-13 which is located 12 feet from the river.

MW-15

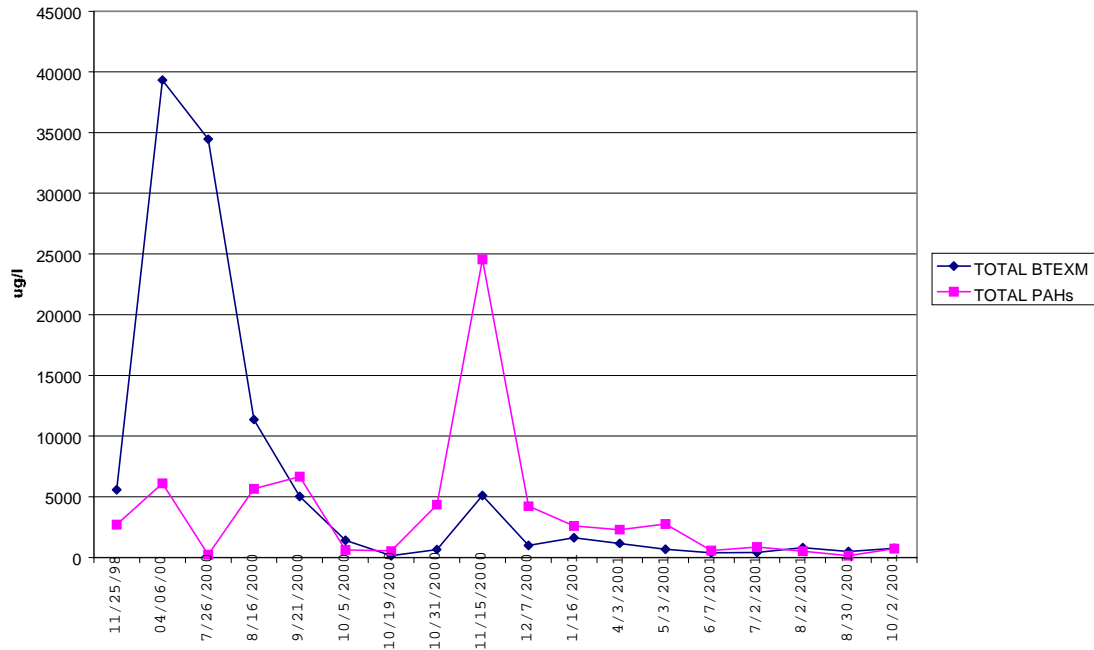


Figure 9
MW-15 Groundwater Concentrations

MW-26

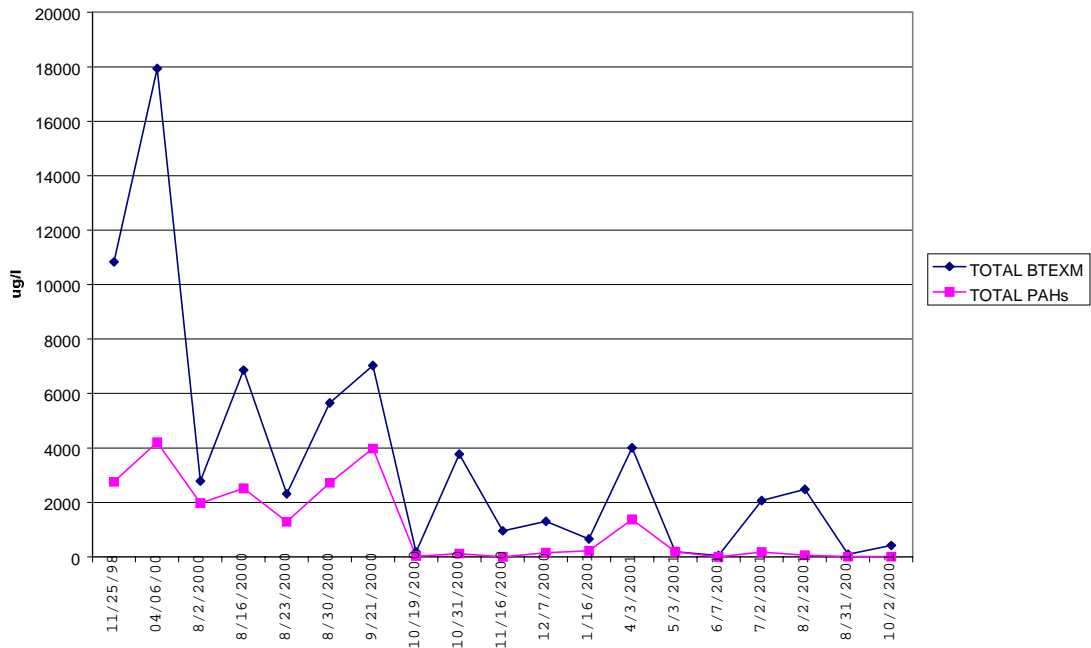


Figure 10
MW-26 Groundwater Concentrations

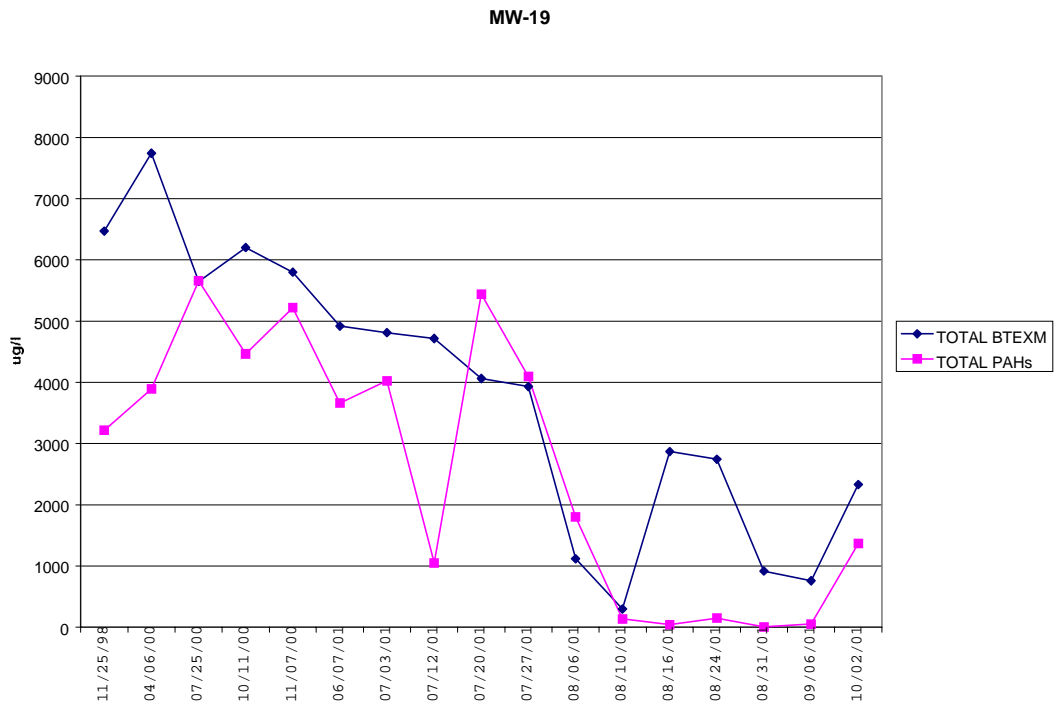


Figure 11
MW-19 Groundwater Concentrations

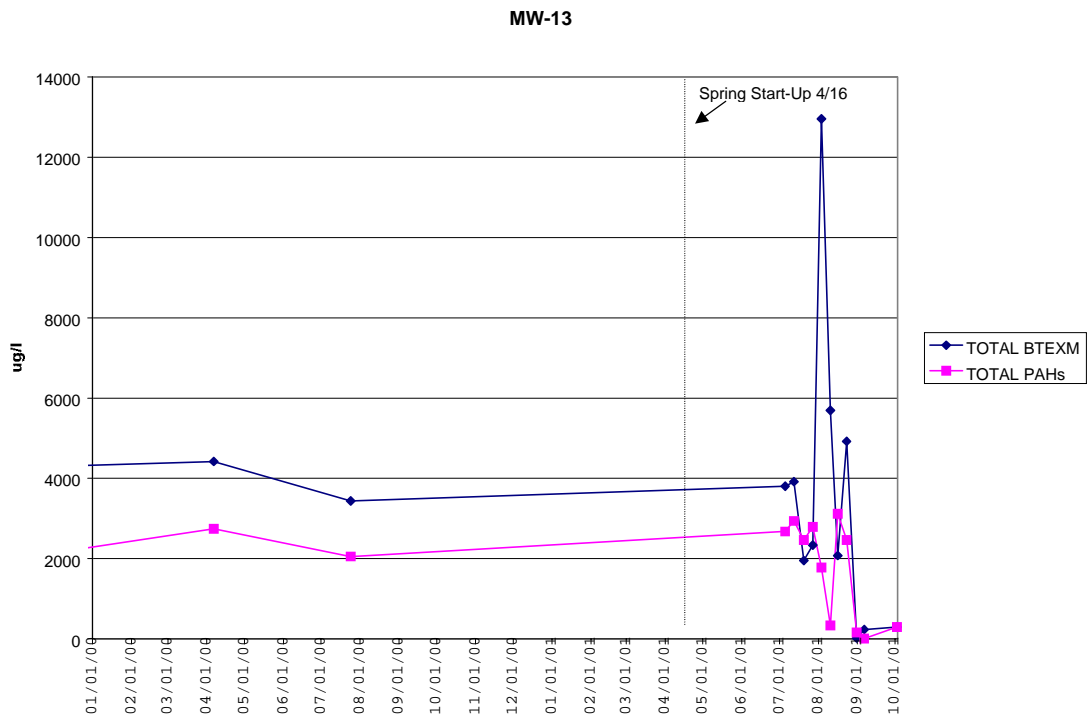


Figure 12
MW-13 Groundwater Concentrations

As shown on these figures, an increase in the total BTEXM and PAH concentrations occurred in the samples collected in late October, 2000. During the last week in October, a City contractor installed and operated a dewatering system along the western edge of the property in order to construct a new sanitary sewer. The contractor operated the dewatering system at an extraction rate of approximately 500 gpm for over a week duration in order to lower the water table in the construction trench by at least six feet to a total depth of 13 feet below ground surface. Although steps were taken to prevent impacts to the oxidation project by concurrently extracting water from a row of injectors at the edge of the treatment area, they were largely ineffective. Consequently, contaminated groundwater from the untreated portion of the site was drawn into the treated area resulting in the observed increase. Fortunately the groundwater concentrations dropped quickly after additional chemical oxidant was injected into that area.

PRE & POST REMEDIATION GROUNDWATER MONITORING

Isoconcentration maps were prepared of the BTEXM and PAH concentrations in groundwater before and after chemical oxidation. Figure 13 (pre-oxidation) and 14 (post-oxidation) provide a graphical representation of the concentration reductions across the site. Pre-treatment data were based on averaged April and July, 2000 groundwater data and the post treatment data were based on averaged September and October, 2001 data.

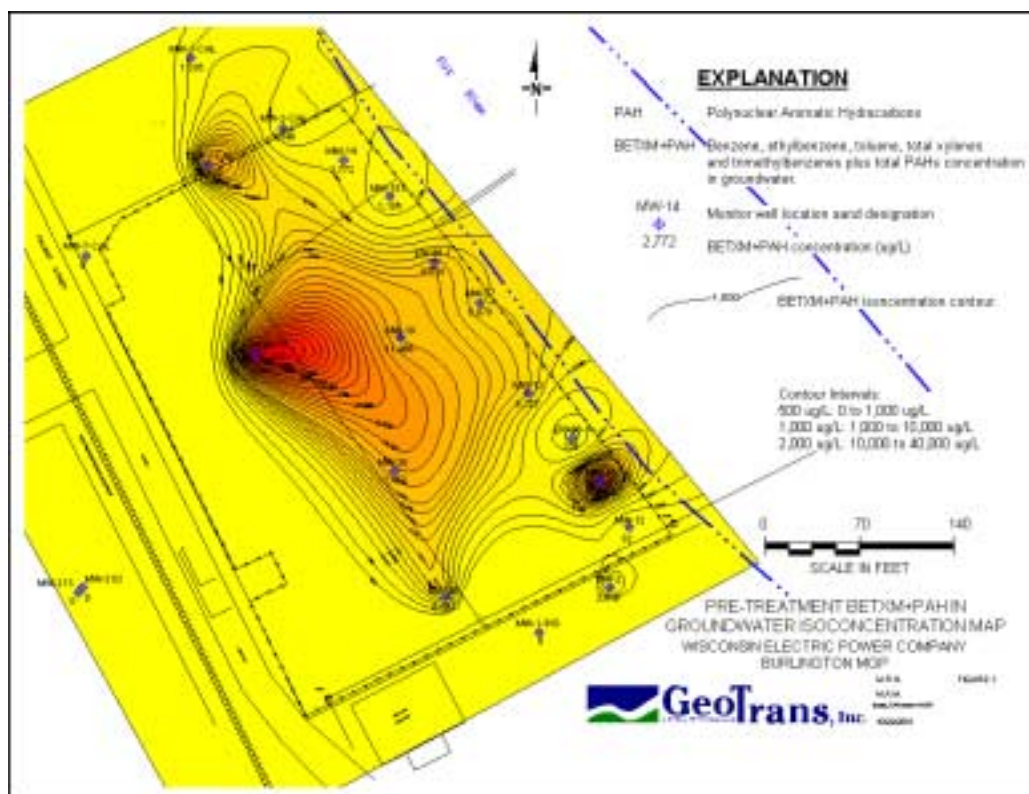


Figure 13
Pre-treatment BTEXM and PAH Concentrations in Groundwater

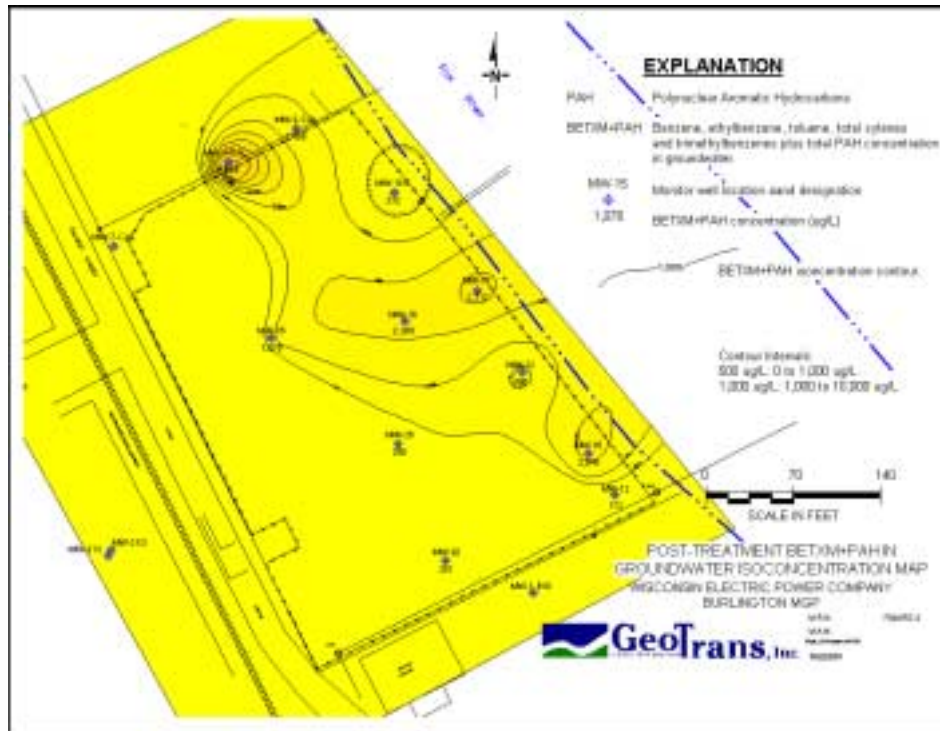


Figure 14
Post-Oxidation BTEXM and PAH Concentrations in Groundwater

A comparison was also made of the pre- and post-remediation groundwater data for a variety of wells. Figure 15 provides a comparison of benzene and Figure 16 provides a comparison of the naphthalene concentrations. The figures show that the chemical concentrations decreased significantly in all wells for benzene and all wells except one for naphthalene. These comparisons indicate that contaminants in the sand and gravel materials along the western portion of the site and beneath the shallow silt layer have been reduced to near non-detectable levels in the groundwater.

Comparison of Pre- and Post-Treatment Benzene in Groundwater

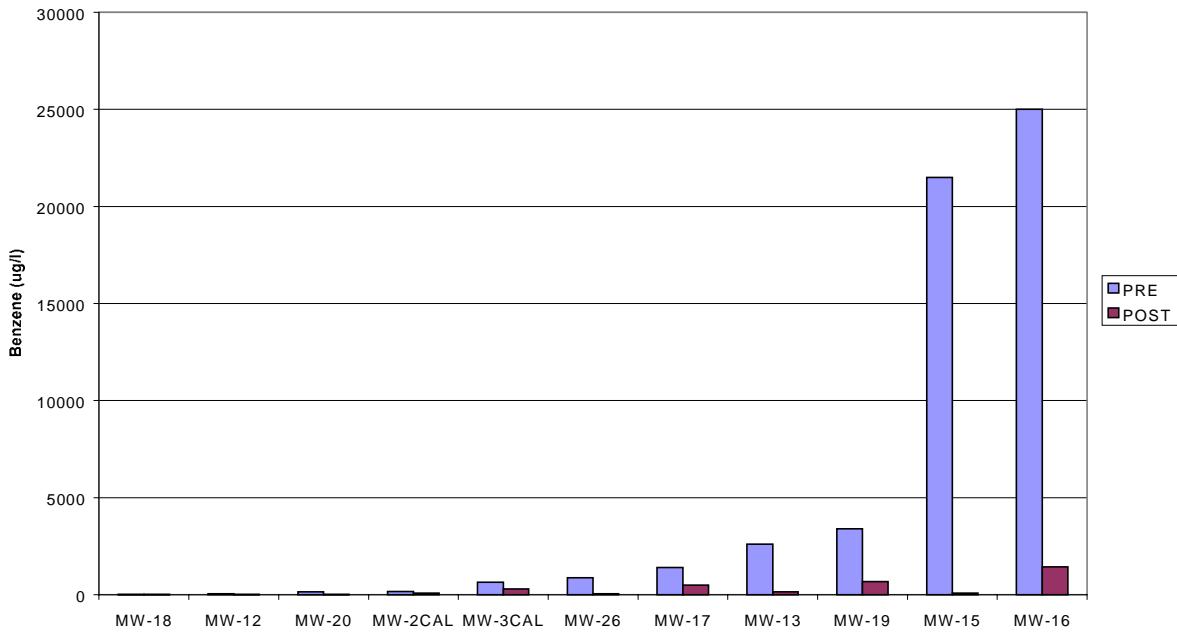


Figure 15
Pre-and Post-Treatment Benzene Concentrations in Groundwater

Comparison of Pre- and Post-Treatment Naphthalene in Groundwater

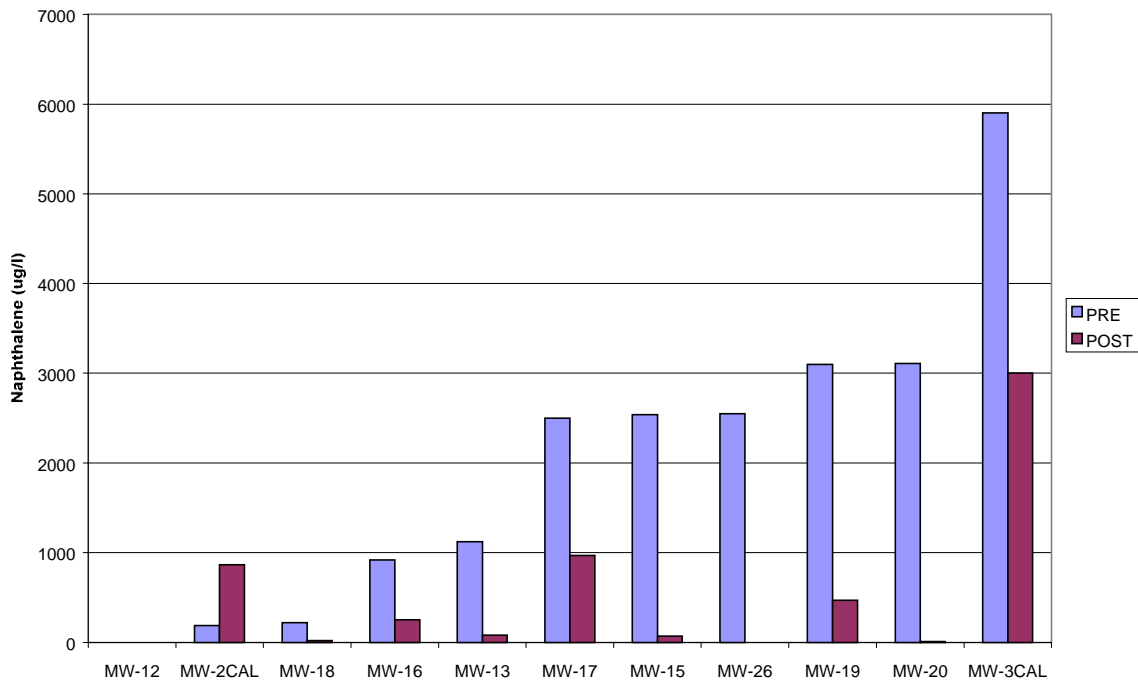


Figure 16
Pre- and Post-Treatment Naphthalene Concentrations in Groundwater

By contouring the intervals and calculating the changes between Figures 13 and 14, it is estimated that the total BTEXM and PAH concentrations were lowered across the site as a whole by approximately 80%. The residual contaminants that remain occur within the shallow silt zone along the edge of the Fox River and in a hot spot area on the southeast side of the site. Figure 17 shows the hot spot area and is a plot of PID headspace analyses performed on groundwater samples obtained from nearly all shallow injectors in the silt zone (geomembrane area) after chemical oxidation was terminated in September, 2001.

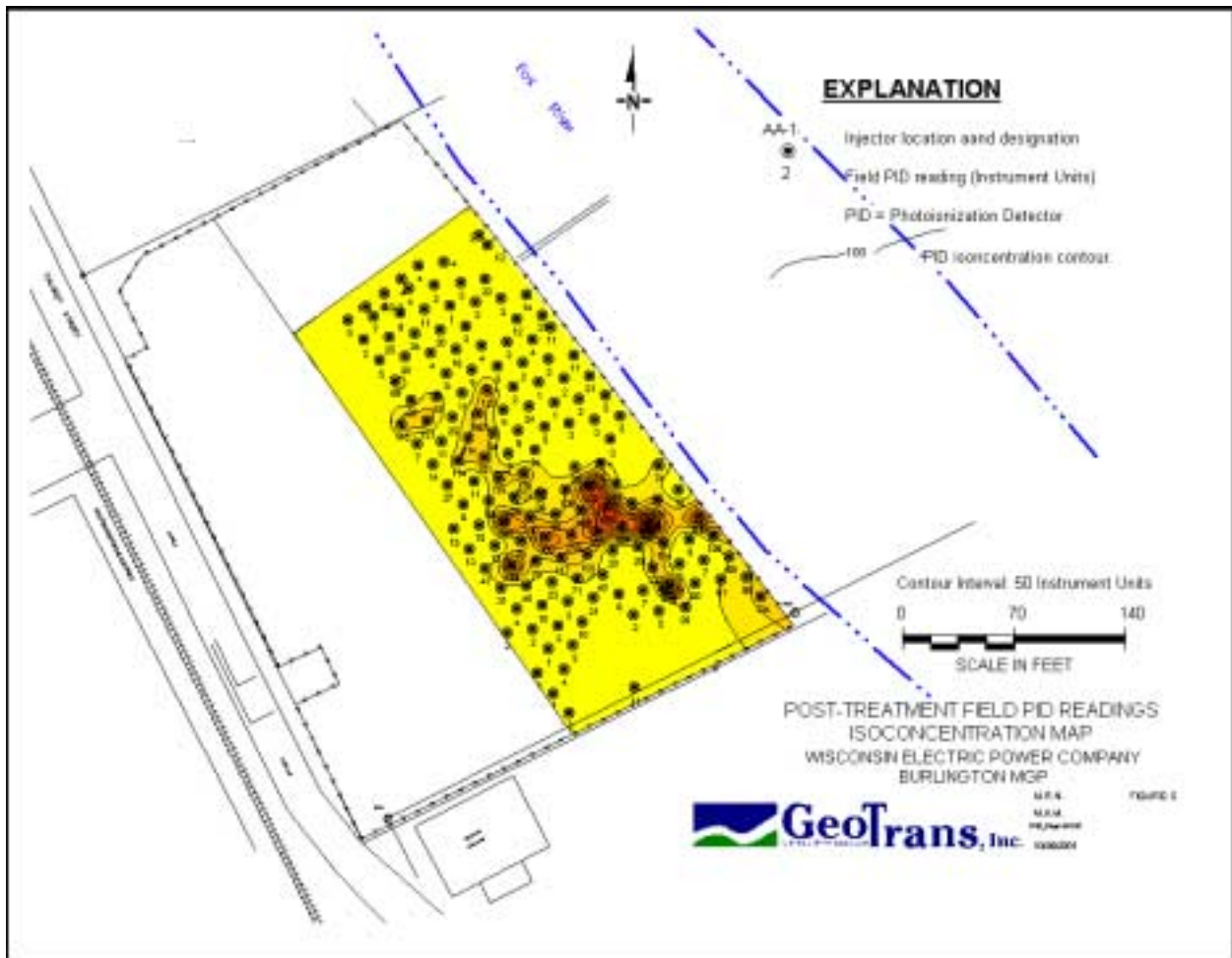


Figure 17
Hot Spot Areas Based on PID Groundwater Readings

The southeast hot spot area corresponds to locations where chemical oxidant dosages were lower due to leaking boots that sealed the geomembrane to the injector pipes. Only limited reagents could be placed in those areas without leakage. The contaminants along the bank of the Fox River could also not be aggressively addressed because of concerns raised by the DNR regarding the potential discharges of peroxide or hydrocarbons to surface water. Plans are currently being evaluated to address the soils in both the river bank and residual hot spot areas.

CONCLUSIONS

Full scale remediation of the Burlington MGP site has been conducted using the Geo-Cleanse® Process. The process involved subsurface injection of Fenton's reagent in 352 chemical injectors located across the treatment area. Approximately 203,500 gallons of 50% hydrogen peroxide have been injected into the site thus far for an average reagent to contaminant ratio of 18.5:1. Chemical oxidation has decreased the hydrocarbon concentration in groundwater at the site as a whole by approximately 80%. Oxidation of hydrocarbons within the sand and gravel portions of the site has been nearly 100%. Residual hydrocarbons that remain occur in the shallow silt zone along the bank of the river and in a hot spot in the southeast portion of the site. These areas could not be aggressively treated with oxidation due to DNR concerns regarding the river and due to leaky membrane seals around selected injectors. Plans are being developed to address both of these concerns during 2002.