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Chapter 17

CASE STUDIES: CLOSING SOLVENT SITES USING ACTIVATED CARBON IMPREGNATED WITH IRON

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ABSTRACT

Sites impacted by even extremely high concentrations of chlorinated solvents (indicative of dense non-aqueous phase liquid, i.e. DNAPL) are being closed using a specially-prepared, activated carbon impregnated with an iron salt that is pyrolyzed into nano-sized deposits of porous, metallic iron. Contaminants are adsorbed by the carbon catalyst and quickly and efficiently treated via reductive dechlorination by the iron. LT Environmental, Inc. (LTE) has pioneered the TerraCert[®] program for implementing remedies using this carbon-iron injectate, known as BOS 100[®]. Three case studies are presented to document the effectiveness of this innovative technology.

Keywords: chlorinated solvents, DNAPL, carbon adsorption, carbon-iron injectate, closure

1. INTRODUCTION

Activated carbon is carbon that has been treated with oxygen to open up millions of micropores between the carbon atoms. The result is an interstitial surface area which is increased enormously, ranging from 300 to 2,000 square meters per gram (m²/gm) (independent laboratory data). The effectiveness of activated carbon as an adsorbent of constituents of concern (COCs) is well documented in the literature and is a process that has been used to treat wastewater for centuries. Other uses date back to antiquity, when the Romans and Egyptians used carbon to purify water.

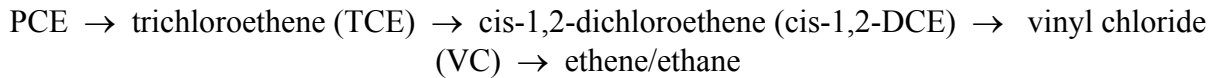
2. TECHNOLOGY DISCUSSION

The essence of remediating chlorinated COCs using the BOS 100[®] technology is coupling the carbon adsorption properties with the dechlorination process of iron (a stepwise function that produces a variety of byproducts, i.e. “daughters”). Based on applicable half-cell reactions and associated Gibbs Free Energy of Reaction, the impregnated elemental iron serves as an electron

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donor (being oxidized in the process) and the aliphatic chloroethenes/chloroethanes serve as the principal electron acceptors.

For instance, if perchloroethene (PCE) is the “mother product” of concern, the stepwise degradation into daughter products occurs primarily through the following steps:



It should be noted that some trans-1,2-dichloroethene and 1,1-DCE can be formed during the kinetic reaction, but these species are not thermodynamically favored in the sequence. The final step is the generation of end-product hydrocarbons (ethene or ethane) which, due to very high vapor pressures and low affinity, escape the matrix and allow for “fresh” contaminant to be adsorbed by the carbon catalyst.

Until the advent of the BOS 100[®] technology, reactive iron alone was the material most commonly used to induce reductive dechlorination. Although effective in reducing mother products such as PCE or TCE, placing “raw iron” in the subsurface can result in slow or incomplete treatment because the period of time in which the solute and iron are co-located is primarily dependent upon seepage velocities. If the contact time is insufficient, then the dechlorination process can be prematurely interrupted leaving derivative daughter products (e.g. VC) that can cause greater health risks and/or increase cleanup costs. These deficiencies are avoided by the innovative combination inherent to BOS 100[®] in that the carbon carrier ensnares the initial contaminant (and continues to hold kinetically-generated derivatives) during the cleanup cycle. The resident solutes are then reduced to innocuous end products via adequate contact with the interstitial iron.

When the carbon-iron injectate is placed in the subsurface where chloroethenes/chloroethanes and elemental iron co-exist in the carbon pore network, the dechlorination process is a surface reaction whereby iron molecules are oxidized and the chlorine molecules are replaced by hydrogen molecules derived from hydrolyzed slurry water. The rate of reaction is dictated by the local concentration of the solute and the amount of available surface area of the iron.

As chloroethenes/chloroethanes diffuse into the carbon, the solute concentrations within the pore network are substantially higher than concentrations that existed in the surrounding soil or groundwater. Thus, the rates of dechlorination within the activated carbon are significantly faster than rates commonly observed using reactive iron alone or other dechlorinating reagents due to the concentrating effect and the substantial surface area offered by the reactive iron. The surface area of iron varies, depending on the product used, as evident in the following examples:

- Typical iron powder used in reactive iron treatment has a surface area is less than 1 m²/gm to 2 m²/gm (independent laboratory data).
- The nano iron impregnated in the BOS 100[®] matrix has a surface area that ranges from approximately 200 m²/gm to 300 m²/gm (RPI laboratory data).

3. PERFORMANCE MONITORING

Tracking the overall treatment progress of this innovative remedy is accomplished by monitoring decreases in groundwater concentrations of chlorinated hydrocarbons, as shown on Figures 1 and 2, and increases in groundwater concentrations of chloride (generated as a result of reductive dechlorination) and ferrous iron (generated as the nano iron is oxidized), as shown on Figure 3. Other gaseous byproducts, including propene and 2-methylpropene, can also be used to document that (reductive dechlorination) treatment is occurring and that the disappearance of COCs is not simply a result of uptake by the carbon.

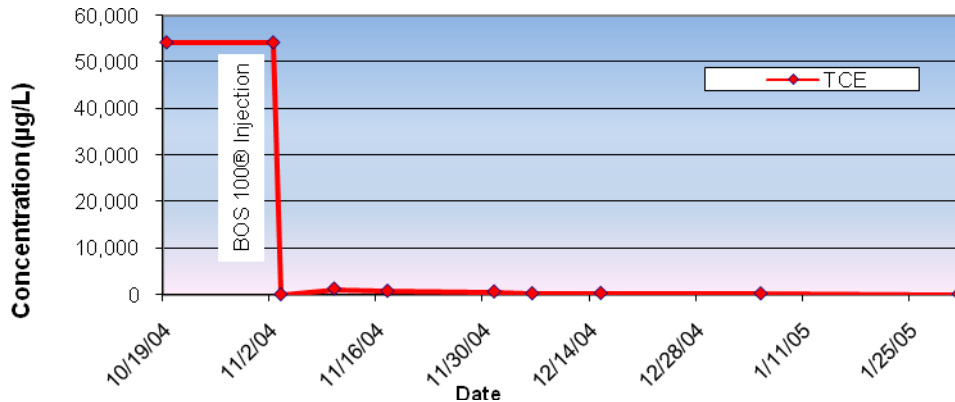


Figure 1. TCE Reduction

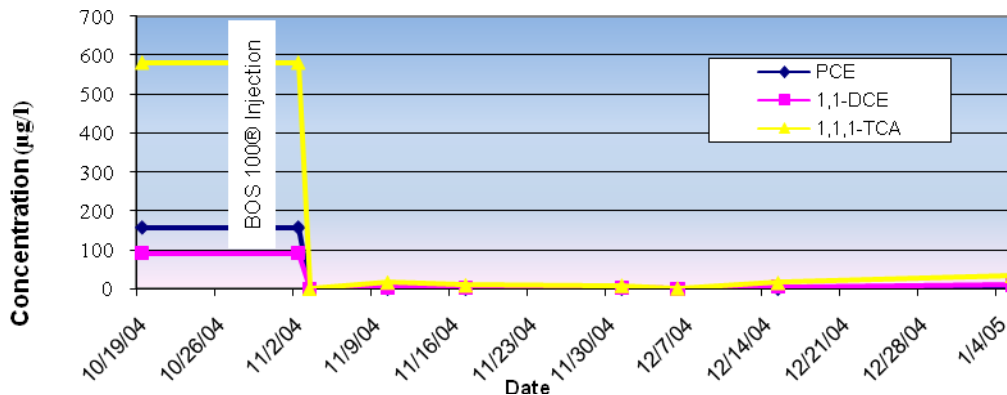


Figure 2. PCE, 1,1-DCE and 1,1,1-TCA Reductions

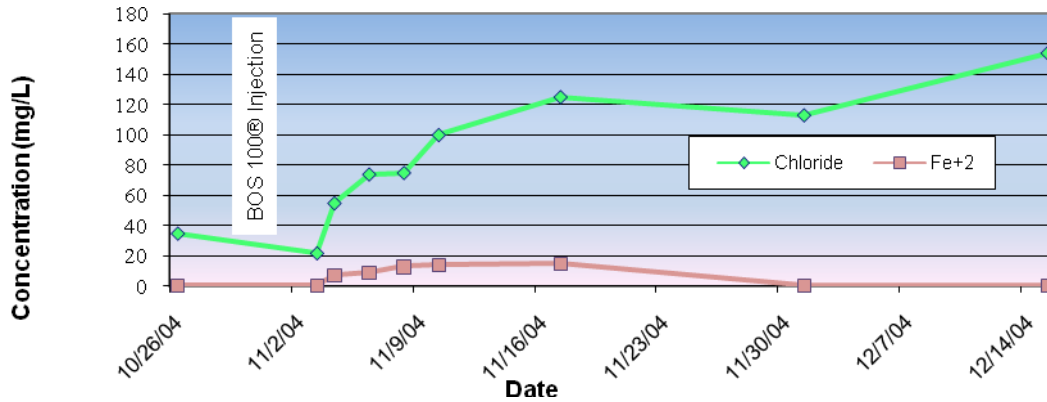


Figure 3. Chloride and Fe⁺² Generation

Other evidence that treatment is occurring is shown by activity testing, as seen on Figure 4. Initial TCE concentrations of 500,000 micrograms per liter (µg/L) in over 20 bench-scale samples were reduced by almost 100 percent after just one hour, having been converted to 20 percent of the theoretical mass of chloride after only 24 hours (RPI 2005).

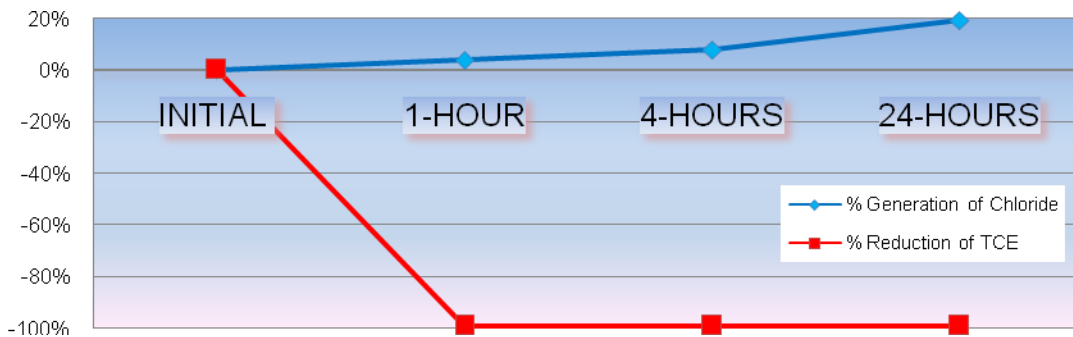


Figure 4. Tce-Chloride Activity

4. CASE STUDIES

LTE’s implementation of the TerraCert[®] program using the carbon-iron injectate has resulted in the closure of or the initiation of closure monitoring at all contracted sites in months rather than years. Case studies involving field-scale applications include a former industrial property, a former dry cleaner site and an active dry cleaner facility.

4.1 Site # 1: Former Industrial Property

In February 2005, LTE used the TerraCert[®] program to remediate TCE-laden groundwater emanating from several sources that had comeled into a large, main plume at a former manufacturing facility (Figure 5). The project was high profile and required rapid closure due to impending redevelopment of the site. As a result of the sales-purchase agreement, the property was divided into two parcels (north and south) under a Voluntary Cleanup Program (VCUP). The site was ideal for the TerraCert[®] evaluation, design and installation process because of the client's desire to obtain a No Action Determination (NAD); the severity of the COC concentrations; and the fast-track nature of the project.

Sources included an underground storage tank (south parcel) containing TCE used in manufacturing processes conducted from 1923 to 1971. Another source (north parcel) was TCE-laden sludge, discovered in a former disposal area. The tank was removed in the 1970's and LTE removed the characteristically-hazardous sludge via excavation for incineration in 2006.

4.1.1 Evaluation

The initial discovery of TCE-impact groundwater was based on results for groundwater samples collected from monitoring wells installed by a third party, independent consultant between July 2004 and March 2005. As part of the TerraCert[®] program, LTE went on to install an extensive, yet inexpensive, network of vertical-profile borings and groundwater-monitoring points to fully characterize the lithology of and the solute distribution within the geologic setting and to determine the geometry of the groundwater plume.

The soil matrix consisted primarily of river alluvium (well graded sands and gravels with varied densities) more than 50 feet thick, underlain by sedimentary bedrock. Groundwater occurred in an unconfined aquifer with a piezometric surface ranging from approximately 26 to 30 feet below ground surface (bgs). As shown on Figure 5, the main groundwater plume covered an area of approximately 175,000 square feet (ft²), or just over four acres, and contained TCE at dissolve-phase concentrations up to 1,280,000 µg/L, which is greater than the solubility of TCE (water solubility $w_s = 1,100,000$ µg/L, Pankow and Cherry 1996). Given the extreme aqueous concentrations, it is likely that free-phase TCE, i.e. DNAPL, had been present at one time as ganglia or pooled product within the interbeds of fine-grained materials (silts and clays) which underlain the primary source area, although DNAPL was never observed in the network of soil borings or groundwater monitoring points.

LTE determined the concentration of chlorinated solvents both spatially and with depth throughout the site. Based on the analytical data, LTE designed a pilot test program to evaluate the efficacy of the carbon-iron injectate. Though an Underground Injection Control (UIC) permit was not necessary, a Rule Authorization (RA) was required and obtained from the U.S. Environmental Protection Agency (EPA).

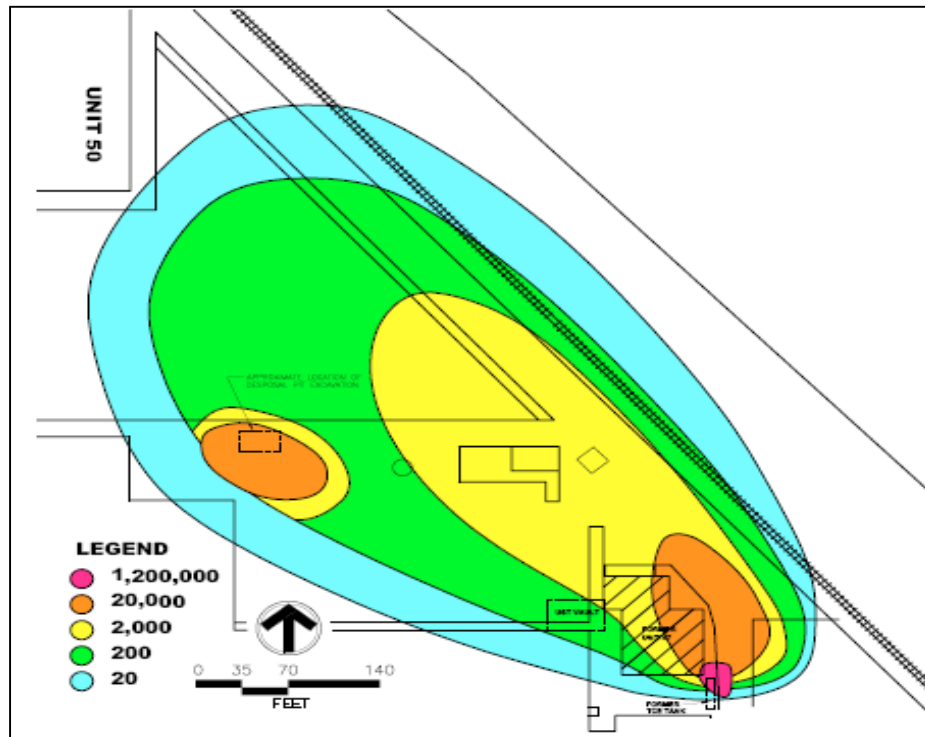


Figure 5. Site # 1, TCE Plume

The pilot test was performed using Direct Push Technology (DPT) and specialized mixing and pumping equipment. An 11-point, off-set Cartesian-type grid, was laid out over an area of approximately 225 ft² at a location (MW-7) where TCE concentrations of 54,135 µg/L were observed. The injection slurry consisted of approximately 3,000 pounds of BOS-100® and 3,300 gallons of organic-free, potable water. LTE conducted a performance sampling program following the completion of injection activities to observe contaminant reduction and to obtain other response information regarding mass-removal rates. Within five weeks, TCE concentrations in the pilot-test area had equilibrated to levels below 5 µg/L.

4.1.2 Design/Installation

Implementation of the full-scale remedy program began in April 2005. The goals for the injection design were to: 1) protect the property boundaries; 2) prevent “hydraulic push” effects which might exacerbate the footprint of the plume; and 3) to achieve cleanup goals.

The site (north and south parcels) was sub-divided into 14 treatment regions, each with specific detailed injection plans. Injection locations were laid out in off-set Cartesian-type grids with 5- to 15-foot spacings in order to create a series of “staggered” lines of injectate that intercepted the groundwater flow regime. The carbon-iron slurry was injected at multiple depths (from 1- to 3-foot intervals throughout the vertical extent of the plume at any given location) either using “top-down” or “bottom-up” techniques depending on the lithology. Approximately

164,000 pounds of injectate was placed at over 2,500 locations during the installation phase of the project.

4.1.3 Results

Groundwater samples were collected from the extensive network of monitoring wells and temporary points throughout the installation phase in order to monitor remedy performance. Results for key wells are shown in Table 1.

Table 1. TCE Reduction

Key Wells	Before Treatment (µg/L)	After Treatment (µg/L)
Source/Near-Source Wells		
MW-7	54,136	<0.5
MW-7 deep	546	5.7
GMW-4R	3,511	1.0
MW-29 deep	454	<0.5
MW-30	1,280,000	<0.5
Property Boundary Wells		
GMW-2R	2,700	<0.5
MW-3	1,800	<0.5
MW-14	224	<0.5
MW-22	24	<0.5
MW-25	336	<0.5
MW-28	744	<0.5

All the goals of the project were met using the TerraCert[®] process, including the client's expectation of meeting regulatory requirements within the constraints of the property transaction. Not only was clean-up achieved very quickly, but at a cost well below both conventional approaches and newly developed *in-situ* biological methods for treating chlorinated solvents in groundwater.

4.1.4 Closure

An NAD was issued by the State for the north parcel in just 20 months (which included one year of closure monitoring). An NAD was also issued for two-thirds of the south parcel, with closure pending for the remainder of the site, following a 2-year, closure-monitoring program to be completed by mid 2010.

4.2 Site # 2: Former Dry Cleaner

PCE was released to the subsurface as a result of historical leakage from a dry-cleaning solvent tank formerly located at this small, urban site (Figure 6). The facility had been a dry cleaner from 1952 to 1998 and was remediated under the auspices of a VCUP. Impacted soil within the “release halo” was removed by LTE via excavation in 2005 and the resultant groundwater plume was remediated using the TerraCert[®] program. Access to off-site impacts was limited to street right-of-ways in this residential neighborhood.

4.2.1 Evaluation

The initial discovery of PCE impacts was based on results for soil and groundwater samples collected during a site assessment conducted by a third party, independent consultant between October 2001 and May 2004. LTE completed additional vertical-profile borings and installed a network of groundwater-monitoring points to fill in data gaps, as part of the TerraCert[®] program.

The soil matrix consisted primarily of clayey residuum underlain by claystone bedrock. Groundwater occurred in an unconfined aquifer with a piezometric surface ranging from approximately 6 to 12 feet bgs. The fate and transport of the PCE groundwater plume was dictated by a hillside setting, which caused a fairly steep gradient (0.064 feet/foot) and incised drainage features filled with sandy colluvium, long since paved or built over during urban development. As shown on Figure 6, dissolve-phase concentrations of PCE in groundwater ranged up to 122,000 µg/L in the source area, which is near the solubility (PCE_{ws} = 200,000 µg/L, Pankow and Cherry 1996). DNAPL was never observed in the network of soil borings or groundwater monitoring points, though free-phase solvent likely had been present at one time as ganglia or pooled product within the clayey residuum.

Once LTE obtained an RA from the EPA, a series of pilot tests were performed to: 1) demonstrate the performance of BOS-100[®]; 2) evaluate the delivery system (DPT equipment) in fine-grained soil and fractured bedrock; and 3) monitor potential hydraulic push that may be caused by groundwater mounding (temporarily increasing the gradient) during injection activities.

4.2.2 Design/Installation

Implementation of the full-scale remedy program began in March 2008. The site was subdivided into 11 treatment regions (nine on site and two off site), each with specific detailed injection plans.

Injection locations were laid out in off-set Cartesian-type grids with 7.5- to 10-foot spacings in order to create a series of “staggered” lines of injectate that intercepted the groundwater flow regime. The carbon-iron slurry was injected at multiple depths (at 2-foot intervals) using top-down techniques. A total of 9,450 pounds of injectate were placed at 225 locations during the installation phase of the project.

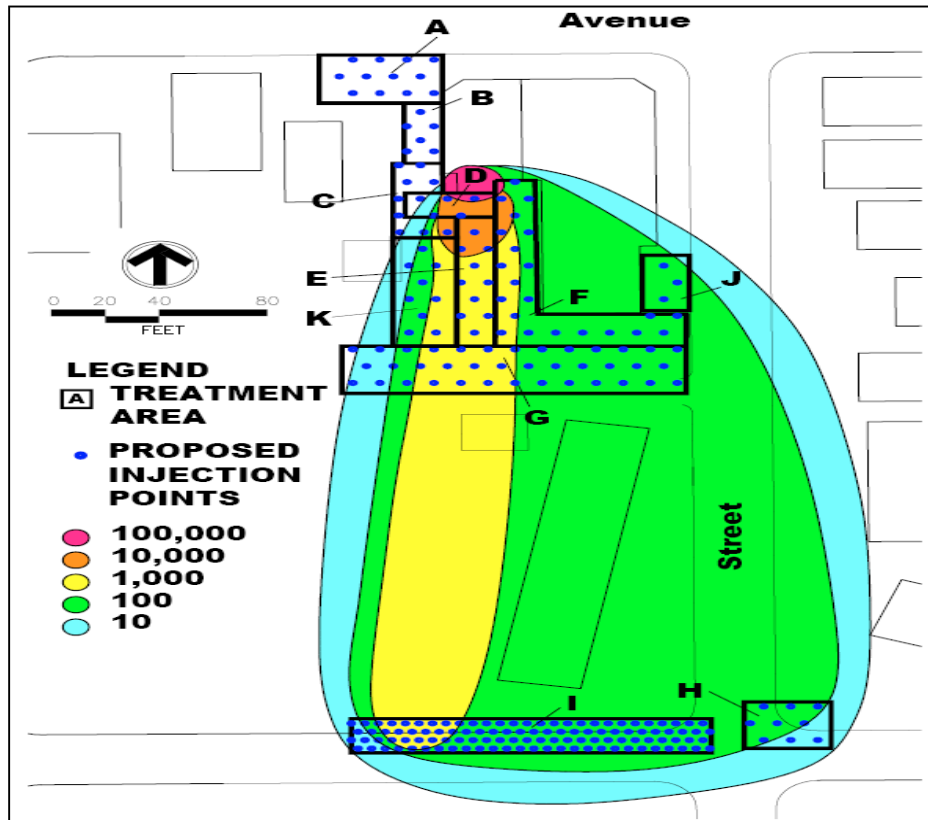


Figure 6. Site # 2, PCE Plume

4.2.3 Results

Groundwater samples were collected from the extensive network of monitoring wells and temporary points throughout the installation phase in order to monitor remedy performance. Results for key wells are shown in Table 2.

Target clean-up levels, per the VCUP, were achieved upon the completion of the 2-week injection program. As with Site #1 above, not only was clean-up achieved very quickly, but at a cost well below other remedies considered for the site.

4.2.4 Closure Monitoring

Per the VCUP, post-treatment sampling will be conducted on a quarterly basis for a period of one year. Closure via an NAD is expected from the State by mid 2009.

Table 2. PCE Reduction

Key Wells	Before	After
	Treatment (µg/L)	Treatment (µg/L)
Source/Near-Source Wells		
PZ-1	122,000	<0.5
PZ-4	29,200	<0.5
PZ-5	12,202	<0.5
PZ-7	9,870	<0.5
PZ-9	11,072	<0.5
GW-4	22,700	<0.5
Property Boundary Wells		
GW-1	2,700	<0.5
GW-2	1,800	<0.5
Off-Site Wells		
GW-8	6,919	<0.5
GW-9	827	<0.5

4.3 Site # 3: Active Dry Cleaner

The likely cause of PCE impact to the subsurface was historical discharge of solvent from a dry-cleaning machine to a leaking floor drain located within this commercial facility (Figure 7). As is often the case, the releases were likely intermittent and diluted by rinse water transmitted into the drain. Once the fluid exited the leaking drain pipe underneath the building, the PCE-laden water evaporated in the subsurface and generated a PCE vapor plume over the years. Since the PCE vapor plume was heavier (more dense) than the air which occupied the unsaturated pore space of the soil underlying the building, the plume travelled downward, making eventual contact with the water table. This condition, in turn, caused a mass transfer of PCE from the vapor phase to the aqueous phase; hence, impacting shallow groundwater. The resulting groundwater plume was limited in size and intensity, with only low concentrations of PCE detected in site wells, even adjacent and downgradient of the floor drain. LTE’s treatment objective was to address State regulatory concerns regarding impacts at the downgradient property boundary.

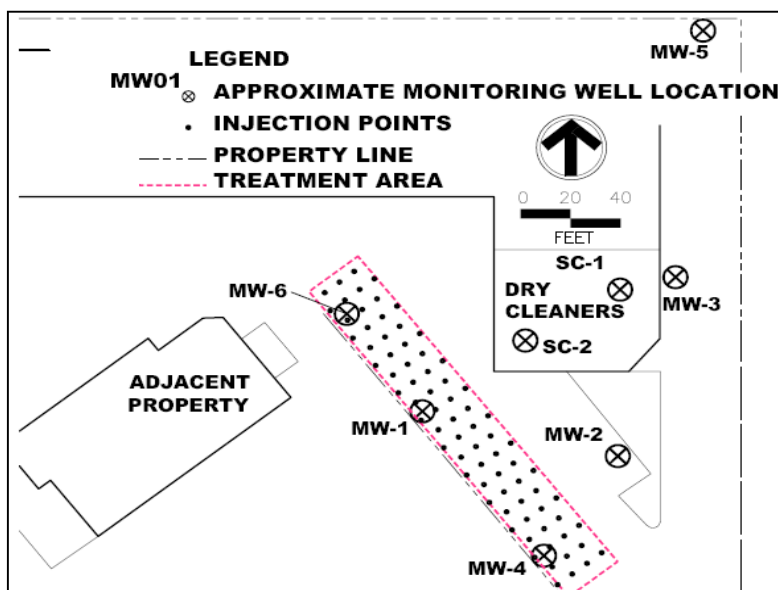


Figure 7. Site # 3, Permeable Reactive Barrier

4.3.1 Evaluation

The initial discovery of PCE impacts was based on results for groundwater samples collected during a site assessment conducted by a third party, independent consultant between June and July 2006. There were no apparent soil impacts.

The soil matrix consisted primarily of sandy, clayey residuum underlain by sandstone and claystone bedrock. Groundwater occurred in an unconfined aquifer with a piezometric surface ranging from approximately 16 to 21 feet bgs. Dissolve-phase concentrations of PCE in groundwater ranged up to 54 $\mu\text{g/L}$ in the treatment area.

4.3.2 Design/Installation

Once LTE obtained an RA from the EPA, LTE implemented a remedy program that consisted of injecting the carbon-iron slurry as a permeable reactive barrier at the property boundary. Installation activities occurred in June 2007.

Injection locations were laid out in off-set Cartesian-type grids with 7.5-foot spacings in order to create a series of “staggered” lines of injectate that intercept the groundwater flow regime. The carbon-iron slurry was injected at multiple depths (at 1 ½-foot intervals) using top-down techniques. A total of 1,260 pounds of BOS-100[®] were placed at 77 locations during the installation phase of the project.

4.3.3 Results

Groundwater samples were collected from monitoring wells within the treatment area and from elsewhere on site, as part of a quarterly-monitoring program required by the State. Results for key wells are shown in Table 3.

Table 3. PCE Reduction

Key Wells	Before Treatment (µg/L)	After Treatment (µg/L)
Property Boundary Wells		
MW-1	54	<0.5
MW-4	42	<0.5
MW-6	16	<0.5

4.2.4 Closure

Four quarterly sampling events were completed to demonstrate that PCE concentrations within the treatment area continued to be undetectable and that concentrations elsewhere on site were downward trending due to natural attenuation. Closure via an NAD was issued by the State in August 2008.

5. REFERENCES

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