Enhanced In Situ Biodegradation of PCE Following Electrical Resistance Heating at a DNAPL Source Area

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ABSTRACT: Area of Concern (AOC) 607 is a former dry cleaner at the Charleston Naval Complex (CNC). During the RCRA field investigation (RFI), soil and groundwater were found to be impacted by tetrachloroethene (PCE). PCE concentrations in groundwater as high as 42,000 mircograms per liter (µg/L) were detected. During a nine-month period, an area defined by monitoring wells with PCE concentrations greater than 2,000 µg/L was treated using electrical resistance heating (ERH). Initial monitoring conducted during the cooling period indicated that a dissolved plume remained in some portions of the treatment zone at concentrations greater than several thousand µg/L. The ratio of biodegradation daughter products to PCE in groundwater was significantly greater than prior to implementation of ERH. To evaluate whether the reductive dechlorination (RD) process could be enhanced, the team implemented an enhanced reductive dechlorination (ERD) pilot study. A soluble substrate was periodically injected into two injection wells in the portion of the original treatment area at which VOC concentrations in groundwater were greatest and downgradient groundwater was monitored to assess the impact on RD. The pilot study indicated a significant enhancement of the RD process.

INTRODUCTION

PCE, a typical dry-cleaning solvent, was used and accidentally released at the former dry cleaner facility. The maximum concentration detected during the RFI (42,000 µg/L) suggested the possible presence of a dense non-aqueous phase liquid (DNAPL) source area. Trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), trans-1,2-dichloroethene (trans-1,2-DCE), and vinyl chloride were also detected in soil and groundwater samples.

PCE appears to have migrated vertically downward as a DNAPL through fill and shallow soils, until it encountered a clay unit at 9.5 to 11.5 feet (feet) (2.9 to 3.5 meters [m]) below land surface (ft bls). The uppermost portion of the site is comprised of fill and the interface between the clay and sand units is where the majority of the contaminant mass was believed to be located and was targeted during ERH implementation.

PCE DNAPL may have accumulated on top of and within the clay layer. This area acts as a residual source for dissolved phase chlorinated solvents that contaminate the groundwater.

ERH SOURCE ZONE TREATMENT

ERH was selected for source zone treatment due to its quick construction (i.e., 6 weeks), relatively short operation (i.e., 10 months) and potential effectiveness for elimination/removal of DNAPL. From October 2001 to July 2002, the area of the site within which PCE concentrations in groundwater exceeded 2,000 µg/L received in situ thermal treatment using ERH. The soil from approximately 4 ft (1.2 m) to the top of the clay layer approximately 11 ft (3.4 m) bls was heated. Depth to groundwater was approximately 5 ft (1.5 m) bls. The ERH target treatment area (TTA) was approximately 16,525 ft^2 (1,535 m^2). Figure 1 shows an aerial view of Building 1189 and the extent of ERH treatment. A description of the ERH technology with a summary of the design, construction, and operation of the system at the former dry cleaner was previously documented (Hudson et al., 2002).

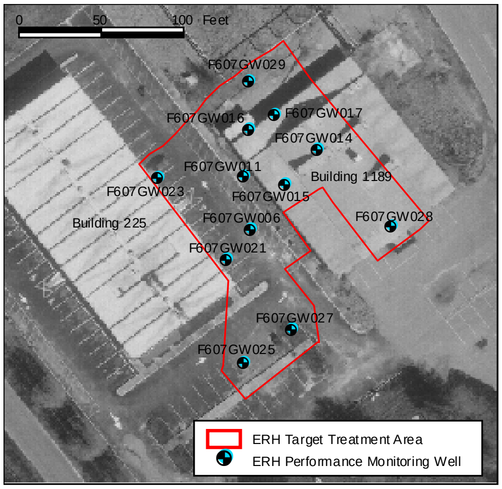

FIGURE 1. ERH TTA.

ERH RESULTS

The operation of the ERH system increased from the original design duration of 124 days to 279 days. The major cause of extended duration was drying of soils in the immediate area around each electrode, making the saturated zone less conductive. As a result, various improvements were made to the electrode design and spacing to include the installation of additional ground rods and cyclic operation of the power control units.

SVE influent results were used to evaluate ERH system performance and the mass of contaminant removed during operation. Total summation of chlorinated volatile organic compounds (CVOCs) and PCE mass recovered via SVE during ERH system operation was calculated at 247 and 234 pounds (lbs) (112 and 106 kilograms [kg]), respectively. The total CVOC concentration is a summation of PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, 1,1-dichloroethene (1,1-DCE), and vinyl chloride concentrations.

To evaluate ERH performance, groundwater samples were collected from 12 shallow monitoring wells within the ERH TTA and analyzed for volatile organic compounds (VOCs). These wells were sampled in September 2001 prior to ERH system start-up, monthly from February 2002 until immediately following system shut-down in July 2002, and six months following shut-down in January 2003. When comparing the analytical results from the January 2003 sampling event to the initial event conducted in September 2001, the overall reduction in the total CVOC summation of detected concentrations was only 21 percent. However, overall PCE reduction was 64.8 percent.

Using September 2001 data, total CVOCs consisted of 76 percent PCE. This decreased to 33.9 percent after six months following ERH system shut-down (January 2003 data). The small overall total CVOC reduction in relation to the larger PCE concentration reduction can be attributed to the increase in cis-1,2-DCE (i.e., 29,000 µg/L) in monitoring well F607GW028 which indicates RD of PCE during the six months (i.e., July to December 2002) since ERH operation.

Accelerated RD is apparent since the overall cis-1,2-DCE concentration increased 288 percent when comparing the September 2001 to the January 2003 results. Cis-1,2-DCE comprised approximately 11 percent of the total CVOCs prior to ERH operation (September 2001) but increased to 54.3 percent six months following ERH system shut-down (January 2003).

ERH CONCLUSIONS

ERH was considered successful in eliminating residual DNAPL, to the extent practicable. The total CVOC dissolved phase mass was calculated as approximately 1.7 lbs (0.77 kg) prior to system start-up. Comparing the 1.7 lbs (0.77 kg) in the dissolved phase with the 247 lbs (112 kg) of CVOC recovered mass from the SVE system, it is clear that the mass recovered cannot have come solely from the dissolved phase. The additional mass could have come from the vadose zone, from adsorbed VOCs, or from DNAPL. The post-ERH total CVOC dissolved phase mass decreased by 33.8 percent, compared to the pre-treatment mass. Post-ERH dissolved phase PCE decreased 41.2 percent. Figure 2 presents the pre- (i.e., September 2001) and post- (i.e., January 2003) 3-D interpretations of PCE in the shallow portion of the surficial aquifer at a concentration of 1,000 μg/L.

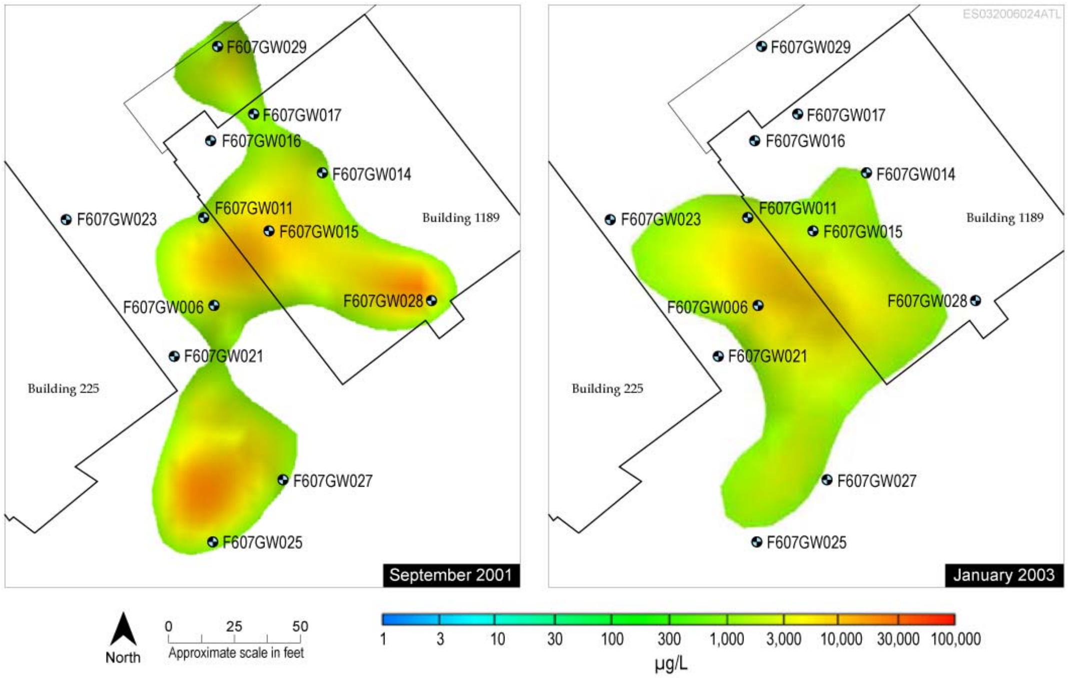

FIGURE 2. PCE Distribution – 3-D Plan View – 2001 and 2003.

ENHANCED REDUCTIVE DECHLORINATION

Post-treatment sampling indicated that the ratio of biodegradation daughter products to PCE was significantly greater than prior to implementation of the ERH. The cause of the daughter product increase is believed to be due to enhanced RD as a result of a release of natural organic carbon from the soil due to heating. Such releases of organic carbon from soil, (ranging from 1 to 8 percent of the sediment bound organic carbon) have been observed during ERH heating of microcosm experiments (Friis et al., 2005). An increase in organic matter would promote RD and boost microbial activity.

ERD PILOT STUDY

To evaluate whether the RD process could be further enhanced, an ERD pilot study was initiated from June 2004 through December 2005. Two new monitoring wells, identified as F607GW032 and F607GW033, were installed within about 10 ft (3 m) hydraulically downgradient of wells F607GW028 and F607GW025, respectively, to monitor performance during the pilot study. Each well was constructed with 5-ft (1.5-m) screens installed to approximately the same depth intervals as the injection wells they were intended to monitor (from 6 to 11 ft [1.8 to 3.4 m] bls for well F607GW025 and from 8 to 13 ft [2.4 to 4 m] bls for well F607GW028). Termination depths were at the top of the competent clay layer.

The overall approach to the pilot study involved the injection of a soluble substrate (potassium lactate) into the shallow aquifer via two wells (F607GW025 and F607GW028), located in the area of the site containing the highest levels of total CVOCs.

The injection approach used a volume adequate to achieve a target radius of influence of approximately 5 to 9 ft (1.5 to 2.4 m) radially from the injection well assuming an injection porosity of 0.10. The potassium lactate dose was selected to satisfy demand from competing electron acceptors (i.e., nitrate, sulfate, dissolved oxygen, dissolved iron, and dissolved manganese) and dissolved CVOCs, with a safety factor of 4.

Table 2 shows the volumes and mass of substrate injected. Six injection events were completed during the 19-month study (June and October 2004; and February, June, September, and December 2005).

TABLE 2. ERD Injection Summary – F607GW025 and F607GW028.

Date	Potassium Lactate lb (kg)	Solution Concentration %	Solution Volume gal (L)
6/9/2004	253 (115)	10	230 (871)
10/13/2004	75.9 (34.5)	3	230 (871)
2/9/2005	75.9 (34.5)	3	230 (871)
6/15/2005	39.6 (18)	0.5	694 (2,627)
9/29/2005	39.6 (18)	0.4	920 (3,482)
12/21/2005	39.6 (18)	0.4	920 (3,482)

ERD PILOT STUDY RESULTS

Post-injection monitoring measured the response of the aquifer and groundwater quality downgradient of the injection. Water quality was measured during 10 performance monitoring events in downgradient wells (F607GW032 and F607GW033) to assess changes in overall biological activity and degree of biodegradation.

F607GW032. Monitoring well F607GW032 was installed downgradient of well F607GW028, located inside the former dry cleaner building. Total CVOC and PCE concentrations from the June 2004 baseline monitoring were 26,021 and 8,090 µg/L, respectively. Results from the December 2005 monitoring event showed total CVOCs and PCE concentrations of 7,356 µg/L and 142 µg/L, respectively. This represents a 72-percent reduction in total CVOCs and a 98-percent reduction in PCE concentration. Vinyl chloride, a RD daughter product of the ERD process, increased an order of magnitude in the December 2005 sample (1,150 µg/L) compared to the baseline monitoring event (June 2004, 151 µg/L). This increase indicates that ERD is successfully progressing. Concentrations of cis-1,2-DCE fluctuated during the ten performance monitoring events and are one order of magnitude lower than the initial baseline condition.

The dissolved gasses methane, ethane, ethene (MEE) were detected at low concentrations in the baseline samples and increased between 1 and 2 orders of magnitude during the performance monitoring period. Baseline methane concentrations of 25 µg/L in June 2004 increased to 6,059 µg/L in August 2005. This indicates methanogenic conditions were created and sustained within the target pilot study area. Ethene, a final dechlorination byproduct of the VOC RD, increased from a baseline concentration of 10 µg/L to 29,562 µg/L in November 2004 to 2,729 µg/L in August 2005, indicating the presence of an effective ERD process. Figure 3 shows CVOC and ethene trends in micromoles (µM) during the 19-month study.

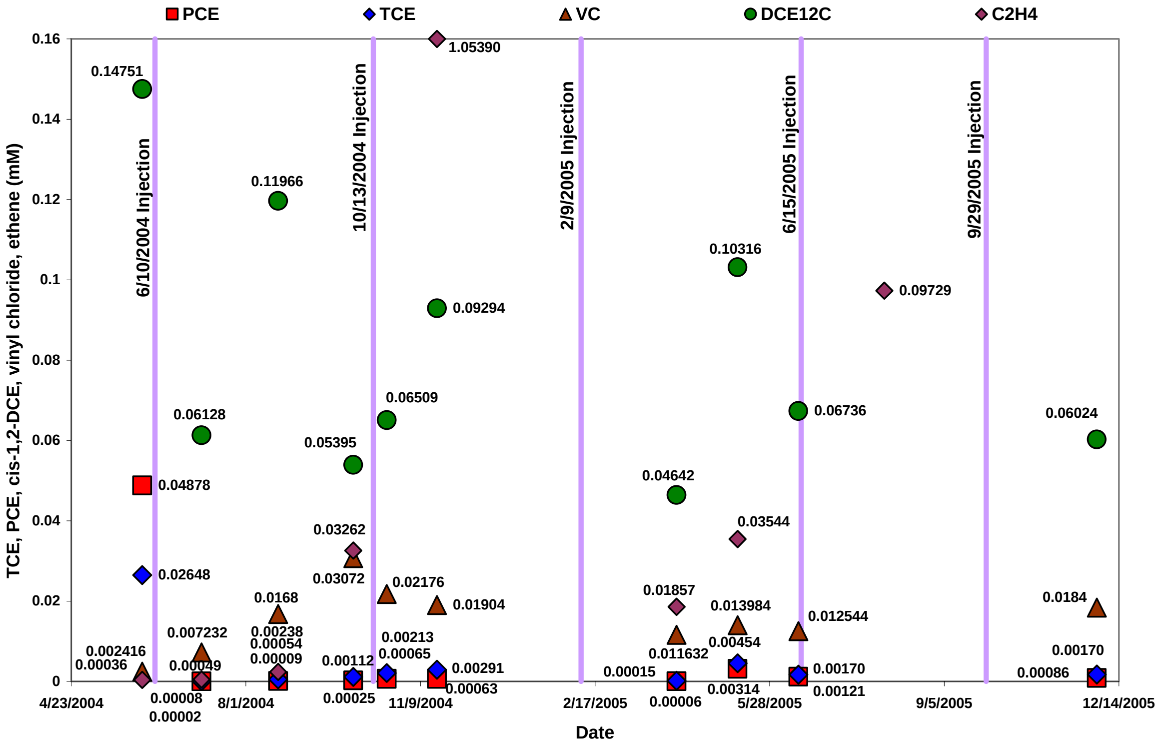

FIGURE 3. CVOCs and Ethene in F607GW032.

Several VFAs (acetic, formic, and propionic acids) were sporadically detected in the post-injection performance monitoring samples, but the VFA concentrations were relatively low overall. This may indicate that the substrate was being effectively consumed and that further substrate addition would be beneficial in this area.

Oxidation/reduction potential (ORP) readings decreased from 80 millivolts (mV) to -152 mV (July 2004), to as low as -181 mV (August 2005), further confirming that more reducing conditions were achieved in this area. As a result of the favorable ORP readings, the concentration of lactate was reduced from 10 percent by volume to 0.4 to 0.5 percent by volume during the final three injection events.

Sulfate concentrations decreased from 231 milligrams per liter (mg/L) during baseline conditions to 102 mg/L in August 2004, indicating that sulfate reduction was likely occurring. Dissolved iron was detected at a concentration of 35,800 µg/L during baseline conditions, indicating that significant iron reduction was occurring in the aquifer. In August 2004 the dissolved iron concentration was 26,900 µg/L, indicating that iron reduction was still occurring to a significant degree.

The presence of the bacteria *dehalococcoides etheneogenes* (DHE) has also been found at sites at which complete transformation of chlorinated alkenes to ethane and/or ethane occurs. The baseline (June 2004) groundwater analysis for DHE (using genomic analytical methods) did detect DHE. However, during the August 2004 monitoring event, the measured DHE concentration in groundwater was 726,000 genomes/mL (gnms/mL), an increase of 5 to 6 orders of magnitude from baseline results. Based on these data, the bacterial strain DHE is not only present but also is responding readily to the ERD stimulation.

F607GW033. Monitoring well F607GW033 was installed downgradient of well F607GW025, which was used as the injection well. Total CVOCs and PCE concentrations from the June 2004 baseline event were 859 and 219 µg/L, respectively. Total CVOCs from December 2005 were 10 µg/L; resulting in a reduction of 98.8 percent. PCE has not been detected since the August 2004 monitoring event. Vinyl chloride increased an order of magnitude in the five samples collected from July 2004 (86.5 µg/L) through November 2004 (131 µg/L). However, only vinyl chloride (2.8 µg/L), cis-1,2-DCE (4.2 µg/L), and trans-1,2-DCE (3 µg/L) were detected during the December 2005 monitoring event.

Dissolved gasses ethane and ethene were not detected in the baseline samples. Ethane was not detected in any of the performance monitoring samples. Ethene was detected in the first monthly sampling event, but not in subsequent sampling events. Methane was detected in the baseline sampling event (June 2004) at a concentration of 16,600 µg/L, increased an order of magnitude in November 2004 sample (286,636 µg/L) before decreasing in concentration in the sample collected in August 2005 (12,900 µg/L). Figure 4 shows CVOC and ethene trends in µM during the 19-month study.

VFAs were not detected in the baseline sampling event. A more diverse variety of VFAs were detected in the post-injection performance monitoring samples at well F607GW033 than were detected at well F607GW032. These data indicate that the lactate injection has stimulated microbial population growth at well F607GW033 but that the fermentative environment at F607GW033 is not yet as robust as at well F607GW032.

ORP readings decreased from -76 mV during the baseline period to -151 mV (July 2004) to as low as -245 mV (August 2005), further confirming that more reducing conditions were achieved in this area.

Sulfate concentrations decreased from 243 mg/L for baseline conditions to 14 mg/L in August 2004, indicating that sulfate reduction was likely occurring. Dissolved iron was detected at a concentration of 30,600 µg/L during baseline conditions, indicating that significant iron reduction was occurring in the aquifer. In August 2004 the dissolved iron concentration had increased to 111,000 µg/L, indicating that iron reduction was significantly stimulated.

The baseline groundwater sample detected only trace levels of DHE. However, during the August 2004 sampling event, DHE was detected at 41,600 gnms/mL; an increase of 4 to 5 orders of magnitude. Based on these data, the bacterial strain DHE is responding readily to the ERD stimulation.

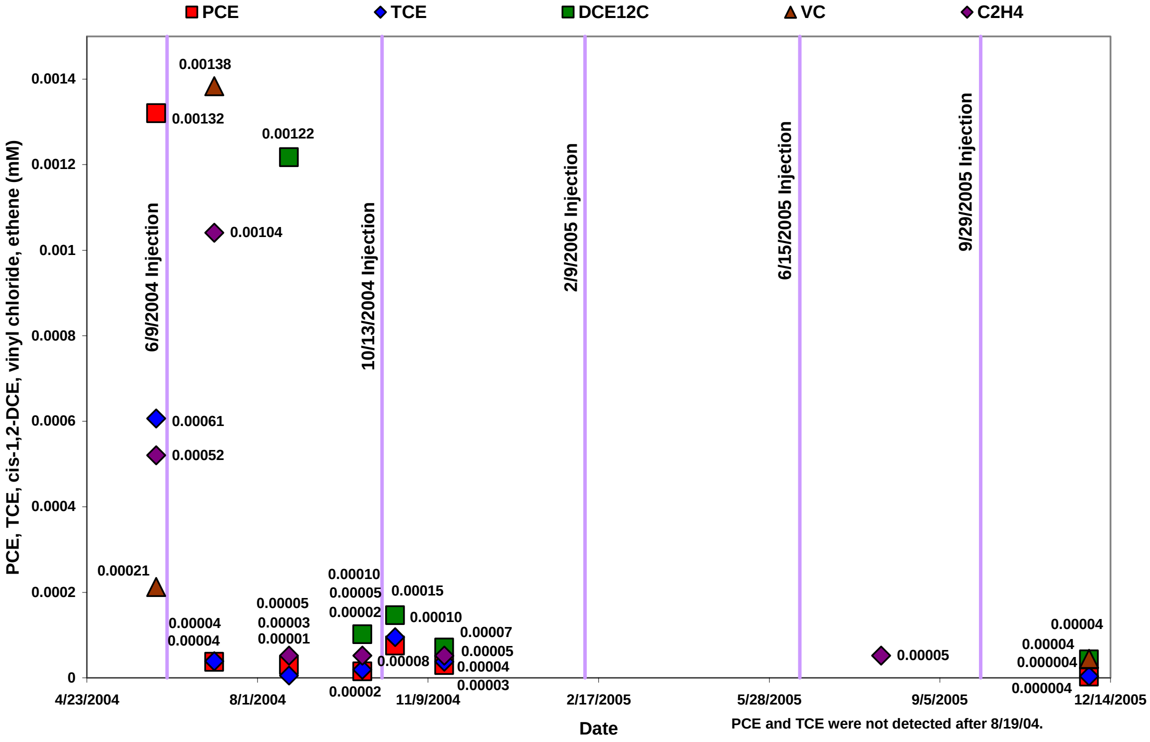

FIGURE 4. CVOCs and Ethene in F607GW033.

ERD CONCLUSIONS

Analytical data from wells F607GW032 and F607GW033 indicate the ERD pilot study achieved significant success in reducing CVOC concentrations and stimulating rapid growth in the native dechlorinating bacterial consortium. Based on the success of the pilot study, a full-scale ERD system was designed and installed. In addition to existing wells F607GW025 and F607GW028 used during the pilot study, ten new injection wells, shown on Figure 5, were installed to impact CVOC contamination in the shallow portion of the surficial aquifer. The initial full-scale injection was completed in February 2006.

Since the six-month post ERH performance monitoring event (January 2003), both the total CVOC and PCE volume and mass have decreased significantly as a result of the success from the focused pilot study and through natural attenuation processes. The total CVOC volume and mass at a concentration of 1,000 µg/L decreased by 44.6 percent when calculated using EVS software since the six-month post-ERH performance monitoring event (January 2003). PCE volume and mass at a concentration of 1,000 µg/L decreased 92 percent.

Figure 5 presents the 3-D interpretation of PCE in the shallow portion of the surficial aquifer at a concentration of 1,000 µg/L using a combined data set from October 2005 to February 2006.

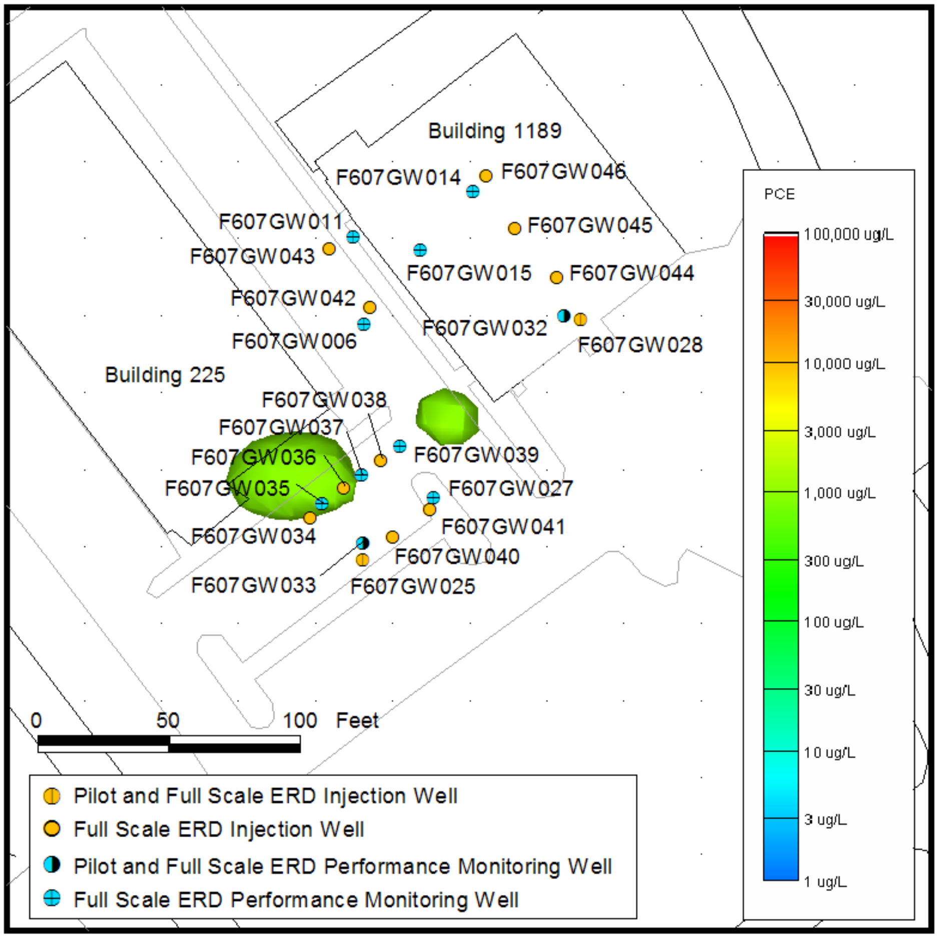

FIGURE 5. PCE Distribution – 3-D Plan View – 2005/2006.

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