

PASSIVE PERMANGANATE REMEDIATION OF A SOLVENT DNAPL SOURCE ZONE

Beth L. Parker (blparker@uwaterloo.ca) and John A. Cherry
(University of Waterloo, Waterloo, ON, Canada),
Tom A. Al (University of New Brunswick, Fredericton, NB Canada)

ABSTRACT: Permanganate remediation was conducted in southern Florida at a small industrial site with TCE and 1,1,1-TCA contamination down to 70 ft bgs in a sand aquifer. The permanganate solution was injected into the DNAPL source zone (30 ft diameter in plan view) where a small mass of residual TCE DNAPL caused this zone to have TCE concentrations exceeding 10,000 ug/L, with small zones approaching TCE saturation. This remediation project comprised three injection episodes, each occurring over several days during which small volumes of KMnO₄ solution were injected at depths between 5 and 65 ft bgs in each of 6-8 direct push holes. During the 2-3 months allowed between injection episodes, the large initial density contrast caused the permanganate to spread out laterally and move downward while fingering and diffusion occurred. The combination of these migration and mixing processes caused complete KMnO₄ coverage of the source zone, even though the coverage immediately after each episode was only 1-8% of the total pore volume of this zone. By keeping the initial injection volumes small relative to the total aquifer pore space within the targeted treatment zone, displacement of TCE mass outward from the source zone was avoided. The post-treatment monitoring showed that the combined effect of the three permanganate injection episodes was a 90% reduction in the aquifer volume where TCE in groundwater was above 100 ug/L and an even larger reduction in volume above 10,000 ug/L. The injections caused the maximum TCE concentration in groundwater to drop from 635,000 ug/L to 56,000 ug/L, with this latter value occurring only in a very small zone. These results indicate that all or nearly all of the DNAPL has been destroyed. These encouraging results are based on groundwater sampling of an exceptionally detailed network of depth-discrete multilevel monitoring systems. Based on the results of this initial phase, we expect that complete remediation of the source zone will be achieved with one additional injection episode focused on the two small zones where moderate TCE concentrations exist.

INTRODUCTION

Inadvertent releases of small volumes of free-product trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) occurred between 1995-early 97 in the vicinity of spigots on an outside wall of an industrial building used to manage waste solvents from a vapor degreaser that was housed in the building located in Broward County, Florida. The site is underlain by medium-grained sand with a shallow water table (< 3 feet bgs). TCE and TCA contaminated soil and groundwater was discovered in April, 1997 at which time solvent use was discontinued and more extensive groundwater investigations were initiated. Initial direct-push (Geoprobe) sampling in 1997 was followed by installation and sampling of a network of conventional 2-inch diameter monitoring wells with 5 or 10-ft long screens to delineate the extent of contamination. This was followed by an

attempt to remediate using *in situ* oxidation by injecting a Fenton's-type reagent into 30-ft screened injection wells in 1998 and early 1999. The site owner discontinued this trial after detailed monitoring showed ineffectiveness of this method.

This paper pertains to the next phase of remediation at this site in which the passive method of permanganate remediation was used for DNAPL source zone remediation. This method was applied in combination with detailed depth-discrete monitoring to establish the pre-treatment conditions for design of the injections and for remediation progress tracking and post-treatment assessment. The permanganate injections accomplished near complete source zone destruction of both TCE and TCA and monitoring indicates that complete destruction can be expected with minimal addition of permanganate and effort.

SITE DESCRIPTION AND BACKGROUND

The site is underlain by 85 ft of fine and medium-grained sand resting on fossiliferous limestone. The sand has a near-shore marine origin and is nearly homogeneous, with hydraulic conductivity slightly greater than 10^{-2} cm/s. The upper 50 ft are nearly devoid of carbonate minerals and at greater depth, gravel-size limestone fragments occur with increasing size and frequency down to the top of competent bedrock at 90 ft bgs. The carbonate mineral content ranges from 0.3 to greater than 2% expressed as weight percent inorganic carbon.

Detailed site characterization was done in February 2000 to facilitate the design of the permanganate solution injections for remediation of the DNAPL source zone. Two continuous cores were collected from ground surface to direct-push refusal depth of 75 ft bgs. The cores were obtained using the piston coring technique described by Starr and Ingleton (1992) and Zapico et al. (1987). Detailed sampling of these cores for DNAPL detection using the Sudan IV dye method and quantitative VOC analyses by gas chromatography showed no DNAPL occurrences and highest TCE values at half TCE solubility. Also, detailed depth discrete groundwater sampling was done using multi-level monitoring systems (bundle wells) similar to those described by Cherry et al. (1983). The highest TCE value measured in the bundle wells prior to permanganate treatment was 625,500 ug/L and the highest TCE value found previously by Geoprobe sampling was 940,000 ug/L. These values are only slightly below the aqueous solubility for pure-phase TCE (1,100,000 to 1,400,000 ug/L). Concentrations of TCA were an order of magnitude below TCE.

The persistence of high TCE concentrations beneath the TCE release area and the occurrence of highest TCE values deep in the sand aquifer (55-65 ft bgs) indicate that the TCE contamination is caused by DNAPL, however the DNAPL is probably distributed sparsely as small globules that constitute extremely low residual saturations. Figure 1 illustrates our conceptual model for the TCE contamination and also shows typical pre-treatment TCE results obtained from two bundle wells. DNAPL occurs in the source zone as dispersed globules representing the vertical trail of downward DNAPL migration. The DNAPL descended vertically until it entered a thin (8 in) coarse sand layer at 57 ft bgs. The larger permeability of the coarse sands likely caused the DNAPL to spread laterally with minimal DNAPL penetrating below this zone. All of the highest TCE and TCA concentrations found prior to permanganate treatment occurred within a near circular area with a radius of 10-15 ft. We refer to this area as the DNAPL source zone (Figure 2a). A

zone of much lower TCE and TCA concentrations occurring beyond the source zone is the plume (Figure 2a). The horizontal gradient is slight, mainly stabilized by a locally controlled canal network and, therefore, the plume is small. The goal of the permanganate remediation is to oxidize the TCE mass in the DNAPL source zone so that the source for the plume no longer exists, allowing the plume to attenuate by natural processes.

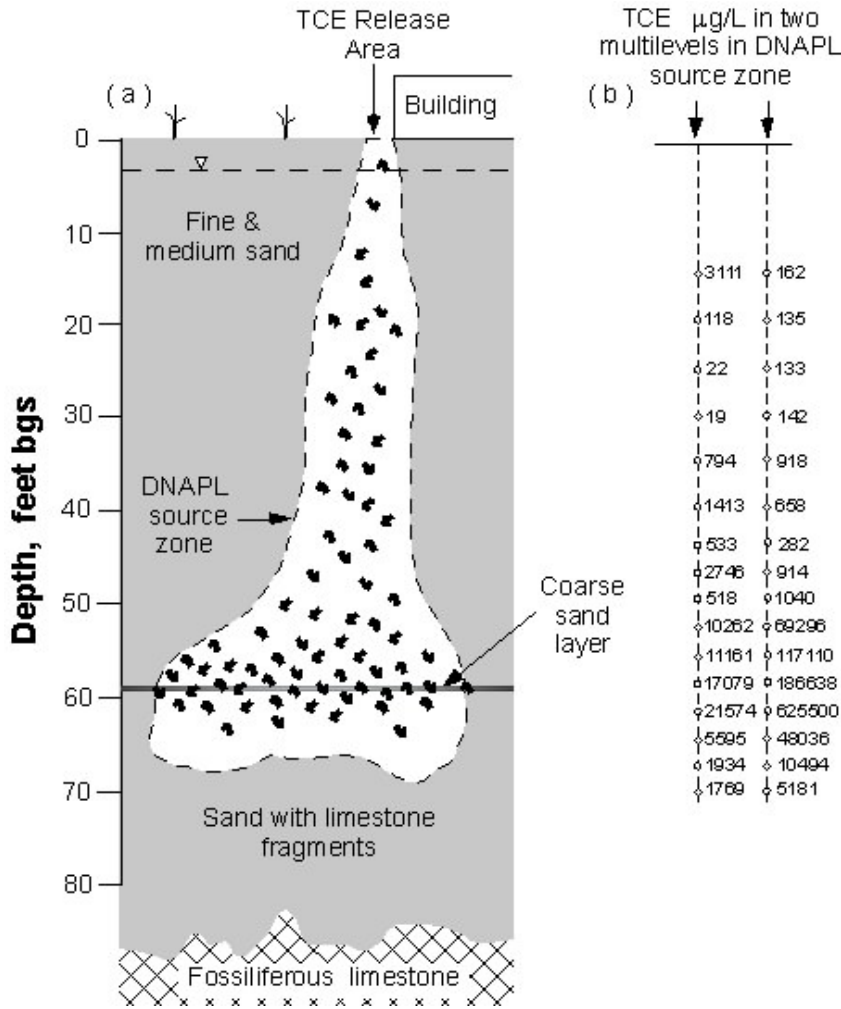


FIGURE 1. Nature of the DNAPL source zone: a) geology and conceptualization of DNAPL occurrence, and b) TCE concentrations in two multilevel systems in the source zone prior to KMnO_4 treatment.

PASSIVE APPROACH FOR KMnO_4 TREATMENT

Our remediation approach used at the Broward County site is aimed at effective destruction of the TCE mass in the DNAPL source zone by KMnO_4 injections while minimizing the displacement of groundwater with high TCE concentrations away from the source zone into the surrounding plume. These dual objectives were pursued through injection episodes in which many discrete zones of near-saturation KMnO_4 solution were created at multiple depths in direct-push holes in the targeted zone (i.e. in the DNAPL source zone). At each injection point, a small volume of KMnO_4 solution is injected

laterally to form an initial local zone (i.e. disc or ellipsoid). Stacked discs with vertical gaps in between are created in each hole using a short-screen well-point (7.6 cm length and 3.8 cm diameter) driven with a direct push rig. The time taken to create several discs per hole in several locations is referred to as an injection episode. At the end of an injection episode, the pressure pulses in the aquifer quickly dissipate. However, density-driven advection combined with fingering and diffusion causes the KMnO_4 solution to spread, which achieves the coverage in the targeted volume. In essence the dense, permanganate solution sweeps through the source zone following each injection episode to cause destruction of TCE mass. A period of time is allowed after each injection episode for the redistribution and concurrent KMnO_4 consumption as TCE is oxidized.

In the DNAPL source zone at the site the injection point attached to drill rods was driven to 60 ft bgs using the model SD-2 direct push rig manufactured by Precision Sampling Inc. The injection tool and system used at the site was developed previously by Nelson et al. (2000, 2001) and used at the Borden, Ontario research site. The remediation of the Broward County site was done using the inject-and-leave approach in three episodes, all in 2000. In the three episodes, a total of 2,791 pounds (1,266 Kg) of KMnO_4 dissolved in 9,166 gallons of water (34,703 liters) at a concentration of 40 g/L was injected into a total of 21 holes. The first episode took place during March 31 to April 10 at 6 locations, the second during June 1 to 7 at 8 locations and the third during September 29 to October 4 at 7 locations. Each episode was followed by two sampling events of the detailed network of multilevel systems for measurement of KMnO_4 , VOC's and chloride concentrations for tracking remediation progress.

RESULTS

The effectiveness of the KMnO_4 treatment was demonstrated based on a before-and-after comparison of TCE and TCA concentrations in the detailed network of multi-level systems and conventional wells. Figure 2a shows that, before KMnO_4 treatment, all seven of the monitoring locations situated inside the 10,000 ug/L contour had TCE values above 16,000 ug/L and as high as 625,500 ug/L. When the comprehensive post-treatment monitoring occurred three months after the last injection episode, only two of these seven locations showed high values, but at concentrations less than 35,000 ug/L (Figure 2b). Figure 2a also shows two locations just outside of the 10,000 ug/L contour that had moderately high TCE values (3,560 and 7,650 ug/L) before treatment. After KMnO_4 treatment, TCE values at these two locations were below 50 ug/L. Of the five inside the initial 10,000 ug/L contour area that declined below 10,000 ug/L after treatment, three dropped below 150 ug/L and the other two dropped to 1,300 and 670 ug/L. Therefore, this plan view comparison of the maximum before-and-after TCE values at monitoring locations shows clearly that the volume of aquifer with high TCE values diminished greatly after KMnO_4 treatment.

Figure 3 shows the large decline in TCE contamination in cross sectional view through the middle of the KMnO_4 treatment zone three months after the last injection. Refer to Figure 1 for the cross section location. The cross sectional area above 100 ug/L declined markedly to 10% of the before treatment area and the area above 10,000 ug/L declined to 3% of the before treatment area. Evidence for the TCE destruction is also established by the number of sampling points above specified concentrations shown on the cross section. Figure 3 shows that 20 sampling points had TCE in the 100 to 1,000

ug/L range before treatment; only four had such values after. Before treatment, 10 sampling points had TCE values above 10,000 ug/L but after, only two were above 10,000 ug/L. Other vertical sections positioned across the former source area displayed similar large decreases in areas and number of sampling points above specified values. Measurements of the carbon isotope ($^{13/12}\text{C}$) ratio of TCE in groundwater before and after KMnO_4 treatment provided confirmation of TCE mass destruction. Large increases in ^{13}C relative to ^{12}C attributable only to oxidation were observed in the treatment zone (Hunkeler et al., 2002 this volume).

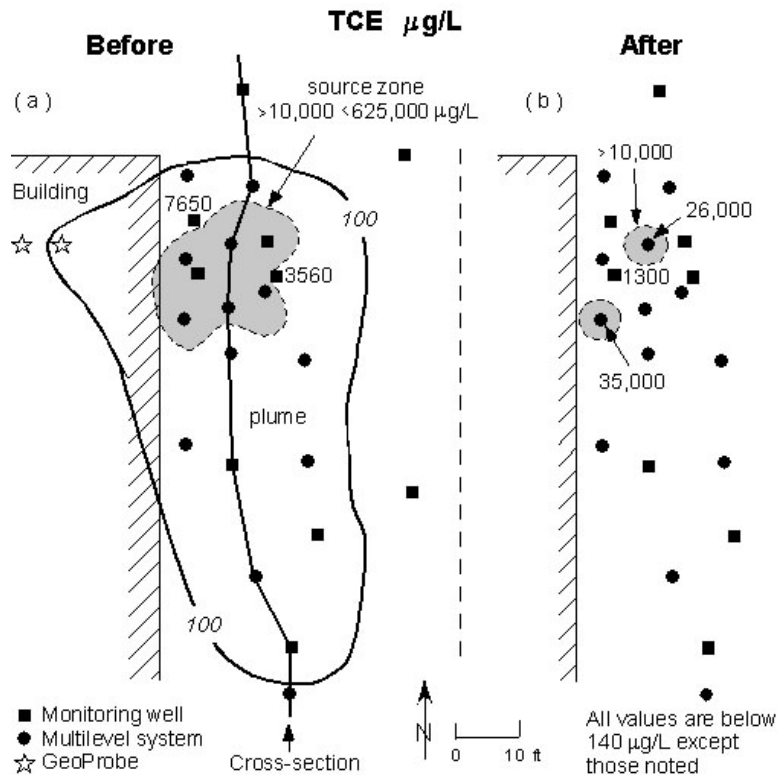


FIGURE 2. Plan view of maximum TCE concentrations found at each monitoring location: a) prior to KMnO_4 injections and b) 3 months after.

An issue that must be resolved when assessing treatment effectiveness is the role of displacement of contaminated water away from the injection points. Depending on sampling locations observed, post-injection declines might reflect the displacement of contaminated water rather than actual TCE mass destruction. The before-and-after monitoring results at the site are not attributable to displacement because monitoring at all locations in the plume declined after the injections. If contaminated water had been displaced from the source zone into the plume, increases in TCE at one or more plume locations would be expected. Negligible displacement was ensured given the design of the injections. Another concern inherent in remediation performance assessment is the potential for rebound of contaminant concentrations in the treated zone as a result of persistent residual DNAPL dissolution. The comprehensive post-injection sampling described above was done three months after the last injection. Additional sampling of

selected multilevel points was done three months later. These sampling events comprised several points in each of eight bundle wells within the former source area. Three of the bundle wells showed no increase, and in the fourth, one point at 60 feet bgs increased from 34,500 to 50,400 $\mu\text{g/L}$. This small increase is consistent with the temporal variability expected from slight groundwater gradient changes causing shifts of the position of the highest concentration zone. The expected rebound would be much larger if appreciable DNAPL mass remained in this zone.

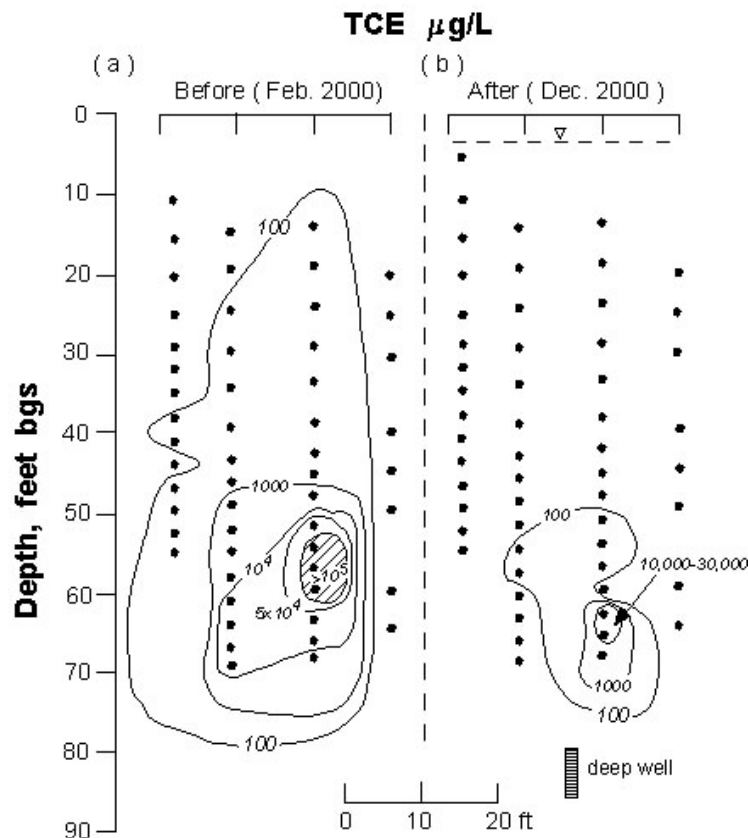


FIGURE 3. Comparison of TCE concentrations one month before and three months after KMnO_4 treatment observed along cross section through DNAPL source zone.

DISCUSSION

Success of the passive method involving episodic injections of small volumes of dense KMnO_4 solution at multiple discrete depths depends on post-injection spreading and sinking of the solution. Density-driven advection combined with fingering and diffusion must cause invasion of the KMnO_4 between injection points. Evidence of this invasion derives from the large decrease in volume of the TCE contaminated zone, described above, and from comprehensive sampling of the bundle wells for KMnO_4 at various times following each injection episode. As expected, immediately after each injection episode, KMnO_4 appeared in only a few sampling points because the volume input at each injection point was small. At later sampling times, nearly all sampling points in the target zone (i.e. inside the initial 10,000 $\mu\text{g/L}$ contour) showed KMnO_4 on one or more occasions. These occurrences were only temporary because the KMnO_4 is

continually moving, mixing and being consumed by oxidation of TCE and reaction with natural aquifer components.

The distribution of monitoring points (wells and multilevels) that existed prior to the KMnO_4 injection and during the comprehensive post-treatment sampling left uncertainty about the maximum depth of initial TCE occurrence and deep TCE treatment. Therefore, near the end of this study a deep monitoring well was installed using rotosonic core drilling. This hole was drilled at the location where deepest TCE would most likely be found if present. Figure 3 shows this well situated in the depth range of 81.3 to 86.3 ft bgs, which is directly below the zone of highest TCE in the 55-65 ft depth zone. This well showed no significant TCE (12 ug/L). Resampling in February 2002 confirmed the absence of TCE in this well (< 1 ug/L). These results indicate that the TCE source zone did not extend to this depth or that the sinking of KMnO_4 below the deepest injection depth (60 ft bgs) destroyed any deep TCE.

The oxidation of TCE results in release of chloride ions (Cl^-) from the TCE to the groundwater. The stoichiometry for this oxidation reaction specifies that for each mole of TCE oxidized, three moles of Cl^- are produced. The pre-injection Cl^- values in the source zone ranged from 20 to 60 mg/L. The maximum post-treatment Cl^- values were in the range of 150-260 mg/L in the zone where the pre-treatment TCE values were generally between 100-300 mg/L. The stoichiometric view for Cl^- production presented above considered only the dissolved-phase TCE in the source zone. We believe that DNAPL residual also existed prior to treatment in the source zone, as dispersed globules spaced sufficiently far apart to prevent TCE concentrations from approaching TCE solubility even at the small spatial scale used for groundwater monitoring. KMnO_4 treatment oxidized dissolved phase TCE and as the dissolved phase TCE was destroyed, it was replenished by DNAPL dissolution. Therefore, one should expect that Cl^- would accumulate in the treatment zone to cause a concentration rise above the concentrations expected when only the initial aqueous TCE distribution is considered. No such Cl^- accumulation is indicated by the post-treatment Cl^- distribution. However, the KMnO_4 treatment system at the Broward site is an open system, with an outlet at the bottom. Density-driven sinking of the KMnO_4 solution after each injection episode must cause downward transport of Cl^- by the sinking KMnO_4 solution. Therefore, some of the Cl^- was probably transported below the maximum depth of Cl^- monitoring (i.e. below 70 ft bgs).

The three episodes of KMnO_4 injection caused a large reduction in the volume of groundwater with TCE concentrations above 100 ug/L and above 10,000 ug/L. These results indicate that it is reasonable to expect that an additional injection episode will bring the destruction of the DNAPL source zone to completion. The selection of three injection episodes for the initial phase of this project was arbitrary. The total initial TCE mass in the source was unknown and therefore there was no basis for specifying the number of injections and total mass needed to achieve complete remediation. It was intended that three injection episodes would be sufficient to establish a trend that would serve as a basis for judging prospects for complete remediation. The trend from the three injections indicates that very little DNAPL remains in the source zone and that it exists in a very small volume, exemplified by the small areas within the >10,000 ug/L contour (Figures 2a and 3b). Although not expected, the KMnO_4 treatments reduced the concentrations and volume of TCA contaminated aquifer similar to the TCE reductions.

CONCLUSIONS

Significant progress towards complete remediation was achieved by injecting small volumes of near-saturation KMnO_4 solution at several depths in each of 6 to 8 holes during each of three episodes. These injections created an initial condition of many small, stacked KMnO_4 zones with large vertical gaps in between. Only 8% of the total pore volume in the lower half of the aquifer (high TCE concentration zone) was invaded by KMnO_4 solution immediately after each injection episode. However, during the few weeks following each injection episode, these many small KMnO_4 zones spread out and descended under the influence of density combined with fingering and diffusion to achieve complete coverage within the source zone. Use of this episodic, stacked-injection approach resulted in no observable displacement of high-concentration TCE water outward from the source zone into the surrounding plume. The post-treatment monitoring using an exceptionally detailed three-dimensional network of depth-discrete samplers showed the combined effect of the three permanganate injection episodes caused a 90% reduction in the aquifer volume where TCE in groundwater is above 100 ug/L, and an even greater reduction of the volume above 10,000 ug/L. Therefore, the passive approach achieved high-percentage remediation with minimal engineering effort that also minimized displacement.

ACKNOWLEDGMENTS

The main crew from the University of Waterloo that conducted the field work included Matthew Nelson and Colin Meldrum, who also performed most of the data compilation and display; and Robert Ingleton and Paul Johnson. The VOC analyses were done by Maria Gorecka. The project benefited from the planning advice of William Pence and Robert Osar. Joseph Ghiold coordinated on-site activities and provided logistical support and Sun Belt Precision Products, Inc. supplied project funding.

REFERENCES

- Cherry, J.A., R.W. Gillham, E.G. Anderson, and P.E. Johnson. 1983. "Hydrogeological Studies of a Sand Aquifer at an Abandoned Landfill, 2: Groundwater Monitoring Devices". *J. Hydrology*. 63:31-49.
- Hunkeler, D., R. Aravena, B.L. Parker and J.A. Cherry. 2002. "Monitoring *In Situ* Oxidation of TCE by Permanganate Using Carbon Isotopes". *In Remediation of Recalcitrant Compounds* (this volume), Monterey, CA, May 20-23.
- Nelson, M.D., B.L. Parker, J.A. Cherry and T.A. Al. 2000. "Passive destruction of PCE DNAPL by Potassium Permanganate in a Sandy Aquifer". *In Remediation of Recalcitrant Compounds*, Monterey, CA, May 22-25, pp.135-143.
- Nelson, M.D., B.L. Parker, T.A. Al, J.A. Cherry and D. Loomer. 2001. "Geochemical Reactions Resulting from *In Situ* Oxidation of PCE DNAPL by KMnO_4 in a Sandy Aquifer". *Environ. Sci. Technol.* 35(6):1266-1275.
- Starr, R.C. and R.A. Ingleton. 1992. "A New Method for Collecting Core Samples Without a Drilling Rig". *Ground Water Monitoring Review* 12(1):91-95.
- Zapico, M.M., S. Vales, and J.A. Cherry. 1987. "A Wireline Piston Core Barrel for Sampling Cohesionless Sand and Gravel Below the Water Table". *Ground Water Monitoring Review* 7:74-84.