Demonstration of ISCO Treatment of a DNAPL Source Zone at Launch Complex 34 in Cape Canaveral Air Station

Final Innovative Technology Evaluation Report

Prepared for

The Interagency DNAPL Consortium:

U.S. Department of Energy
U.S. Environmental Protection Agency
U.S. Department of Defense
National Aeronautics and Space Administration

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October 17, 2002

Notice

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Acknowledgments

The Battelle staff who worked on this project include Arun Gavaskar (Project Manager), Woong-Sang Yoon, Eric Drescher, Joel Sminchak, Bruce Buxton, Steve Naber, Jim Hicks, Neeraj Gupta, Bruce Sass, Chris Perry, Lydia Cumming, Sandy Anderson, Sumedha de Silva, Thomas Wilk, and Loretta Bahn.

Battelle would like to acknowledge the resources and technical support provided by several members of the Interagency DNAPL Consortium, the Technical Advisory Group, and several other organizations and government contractors:

- Skip Chamberlain (DOE), Tom Holdsworth (U.S. EPA), Charles Reeter (NFESC), and Jackie Quinn (NASA) for mobilizing the resources that made this demonstration possible. These individuals participated actively in the demonstration and provided guidance through weekly conference calls.
- Stan Lynn and others from TetraTech EM, Inc., for providing significant logistical and field support.
- Laymon Gray from Florida State University for coordinating the site preparations and technology vendors' field activities.
- Steve Antonioli from MSE Technology Applications, Inc., for coordinating vendor selection and subcontracting, Technical Advisory Group participation, and tracking of technology application costs.
- Tom Early from ORNL and Jeff Douthitt from GeoConsultants, Inc., for providing technical and administrative guidance.
- Paul DeVane from the Air Force Research Laboratory for providing resources and guidance during the early stages of the demonstration.
- The members of the Technical Advisory Group for their technical guidance. The members of this group were Dr. Robert Siegrist, Colorado School of Mines; Kent Udell, University of California at Berkeley; Terry Hazen, Lawrence Berkeley National Laboratory; Lorne Everett, IT Corporation; and A. Lynn Wood, R.S. Kerr Environmental Research Center.
- Janice Imrich, Jennifer Kauffman, and Emily Charoglu from EnviroIssues, Inc., for coordinating the weekly conference calls, Visitor's Day, and other demonstration-related events.
- The Interstate Technology Regulatory Council (ITRC) for their review support.
- Dr. D.H. Luu, DHL Analytical Services, Inc., and John Reynolds, STL Environmental Services, Inc., for their laboratory analysis support.
- Wendy Leonard and others from IT Corporation for their cooperation during the demonstration.

Executive Summary

Dense, nonaqueous-phase liquid (DNAPL) contaminants are a challenge to characterize and remediate at many sites where such contaminants have entered the subsurface due to past use or disposal practices. Chlorinated solvents, comprised of chlorinated volatile organic compounds (CVOCs), such as trichloroethylene (TCE) and perchloroethylene (PCE), are common DNAPL contaminants at sites where operations, such as aircraft maintenance, dry cleaning, metal finishing, and electronics manufacturing have historically occurred. In the past, because of the difficulty in identifying the DNAPL source zone, most remediation efforts focused on controlling the migration of the dissolved CVOC plume. In recent years, many site owners have had success in locating DNAPL sources. DNAPL source remediation may be beneficial because once the source has been significantly mitigated, the strength and duration of the resulting plume can potentially be lowered in the long term, and sometimes in the short term as well.

The Interagency DNAPL Consortium

The Interagency DNAPL Consortium (IDC) was formally established in 1999 by the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (U.S. EPA), Department of Defense (DoD), and National Aeronautics and Space Administration as a vehicle for marshalling the resources required to test innovative technologies that promise technical and economic advantages in DNAPL remediation. The IDC is advised by a Technical Advisory Group comprised of experts drawn from academia, industry, and government. The IDC and other supporting organizations facilitate technology transfer to site owners/managers though dissemination of the demonstration plans and results, presentations at public forums, a website, and visitor days at the site.

Demonstration Site and Technology

In 1998, after preliminary site characterization conducted by Westinghouse Savannah River Company indicated the presence of a sizable DNAPL source at Launch Complex 34 in Cape Canaveral, Florida, the IDC selected this site for demonstrating three DNAPL remediation technologies. The surficial aquifer at this site lies approximately between 5 to 45 ft bgs. This aquifer can be subdivided into three stratigraphic units — the Upper Sand Unit, the Middle Fine-Grained Unit, and the Lower Sand Unit. Although the Middle Fine-Grained Unit is a conspicuous hydraulic barrier, a Lower Clay Unit underlying the surficial aquifer is considered to be the aquitard that prevents downward migration of the DNAPL source. The Lower Clay Unit appears to be pervasive throughout the demonstration area, although it is only 1.5 to 3 ft thick. The hydraulic gradient in the surficial aquifer is relatively flat. The native aquifer is anaerobic and neutral in pH. Also the aquifer contains relatively high levels of chloride and total dissolved solids (TDS).

The source zone was divided into three test plots, 75 ft × 50 ft each in size, for testing three technologies — in situ chemical oxidation (ISCO), resistive heating, and steam injection. About 15 ft of each plot was under the Engineering Support Building. ISCO and resistive heating were tested concurrently between September 1999 and April/June 2000 in the two outer plots, separated by about 80 ft. Steam injection was subsequently tested in the middle plot, beginning June 2001. The IDC contracted MSE Technology Applications, Inc., to conduct vendor selection and subcontracting for the three technology demonstrations, and to track costs for each demonstration. IT Corporation was the vendor selected for implementing ISCO (using potassium permanganate) at Launch Complex 34. Potassium permanganate was selected due to the fact that the oxidation reaction with permanganate is relatively pH insensitive and proceeds acceptably under alkaline conditions. The reaction is not subject to inhibition by free-radical scavengers like carbonates, both of which (i.e., high pH and radical scavengers) are a challenge for other oxidants, such as Fenton's reagent. In addition, it is a strong oxidant, relatively easy to handle, commonly available and inexpensive, does not generate strong exothermic reactions in the aquifer, and persists long enough in the environment to enable efficient distribution in the aquifer.

Performance Assessment

The IDC contracted Battelle in 1998 to plan and conduct the technical and economic performance assessment of the three technologies. The EPA Superfund Innovative Technology Evaluation (SITE) Program and its contractor TetraTech EM, Inc., provided Quality Assurance (QA) oversight and field support for the performance assessment. Before the ISCO field application, Battelle prepared a Quality Assurance Project Plan (QAPP) or test plan that was reviewed by all the project stakeholders. This report describes the results of the performance assessment of the ISCO technology. The objectives of the performance assessment were to:

- Estimate the TCE/DNAPL mass removal
- Evaluate changes in aquifer quality
- Evaluate the fate of the TCE/DNAPL removed from the ISCO plot
- Verify ISCO operating requirements and costs.

Estimating the TCE/DNAPL mass removal due to the ISCO application was the primary objective of the demonstration in terms of resources expended for planning, data gathering, and interpretation; the other three were secondary, but important, objectives.

In February 1999, Battelle conducted the preliminary characterization of the DNAPL source region on the north side of the Engineering Support Building. This characterization provided preliminary DNAPL mass estimates and aquifer data to support the vendor's design of the technology application. It also provided data on the spatial variability of the TCE/DNAPL that supported the design of a more detailed characterization of each test plot before the demonstration. In June 1999, a detailed predemonstration characterization of the ISCO plot was conducted to initiate the performance assessment of the ISCO technology. From September 1999 to April 2000, when the ISCO field application was conducted, Battelle collected subsurface data to monitor the progress of the demonstration; the vendor collected additional data to aid in the operation of the technology. In May 2000, the postdemonstration assessment of the ISCO plot was conducted, followed by an extended monitoring event in February 2001.

TCE/DNAPL Mass Removal

Detailed soil sampling was used as the main tool for determining TCE/DNAPL mass removal. The spatial distribution data from the preliminary characterization were used to determine a statistically significant number and location of soil samples required to obtain good coverage of the ISCO plot. A systematic unaligned sampling scheme was used to conduct pre- and postdemonstration soil coring at 12 locations in a 4 × 3 grid in the test plot. Continuous soil samples were collected at every 2-ft vertical interval in each core, resulting in nearly 300 soil samples in the ISCO plot during each event. A vertical section (approximately 200 g of wet soil) from each 2-ft interval was collected and extracted with methanol in the field; the methanol extract was sent to an off-site laboratory for analysis. In this manner, the entire soil column was analyzed from ground surface to aquitard, at each coring location. Evaluation of this extraction method with Launch Complex 34 soil showed between 84 and 113% recovery (92% average) of the spiked surrogate compound (trichloroethane).

The TCE concentrations (mg/kg of dry soil) obtained by this method were considered “total TCE.” Total TCE includes TCE in the dissolved and adsorbed phases, as well as in the free phase (DNAPL). The portion of the total TCE that exceeded a threshold concentration of 300 mg/kg was considered “DNAPL.” This threshold was calculated based on properties of the TCE and the subsurface media at Launch Complex 34, and is determined as the maximum TCE concentration in the dissolved and adsorbed phases; any TCE concentration exceeding this threshold would be DNAPL.

The results of the TCE/DNAPL mass removal evaluation by soil sampling show the following:

- Linear interpolation of TCE concentrations between sampled points indicated that there was 6,122 kg of total TCE in the ISCO plot before the demonstration; approximately 5,039 kg of this TCE mass was DNAPL. Approximately 77% of the total TCE mass and 76% of the DNAPL mass was removed from the plot due to the ISCO application. This predicted removal is less than the 90% DNAPL removal target proposed at the beginning of the demonstration, but is still a significant achievement for the technology.
- A statistical evaluation of the pre- and postdemonstration TCE concentrations confirmed these results. Kriging, a geostatistical tool that takes the spatial variability of the TCE distribution into account, indicated that between 6,217 and 9,182 kg of total TCE was present in the test plot before the demonstration. Kriging of the pre- and postdemonstration TCE data indicated that between 62 and 84% of the total TCE was removed from the test plot by the technology application. When the predemonstration and extended monitoring event TCE mass estimates were compared, kriging indicated that between 49 and 68% of the TCE was removed from the plot. The extended monitoring event was conducted nine months after the end of the oxidant injections. The slightly lower removal estimates during the extended monitoring event are due to an isolated DNAPL pocket found on the north end of the test plot. These statistics are significant at the 80% confidence level specified before the demonstration. In summary, it can be said that at least half the initial TCE mass in the test plot was removed by the ISCO treatment.
- The highest TCE/DNAPL mass removal was obtained in the Upper Sand Unit, followed by the Lower Sand Unit. The Middle Fine-Grained Unit showed the least removal. This shows that the oxidant distribution was most effective in the coarser soils. The level of TCE/DNAPL removal was not as high under the building as outside it, indicating that these regions could not be efficiently accessed from outside the building. The general radius of influence of the potassium permanganate appeared to be less than 15 ft around the injection points, although preferential flowpaths sometimes transported the oxidant to more distant locations.

Changes in Aquifer Quality

Application of the ISCO technology caused the following short-term changes in the treated aquifer:

- Dissolved TCE levels declined sharply in several monitoring wells in the ISCO plot, with some wells showing postdemonstration concentrations of less than 5 µg/L, the federal drinking water standard. Achievement of the State of Florida groundwater target cleanup level of 3 µg/L could not be determined because excessive permanganate in several of the postdemonstration groundwater samples caused analytical interference and required dilution. In some wells within the ISCO plot, TCE levels declined, but stayed above 5 µg/L. In one of the shallow wells, TCE levels rose through the demonstration, indicating that local heterogeneities (limited oxidant distribution) or redistribution of groundwater flow due to partial DNAPL removal may have affected dissolved TCE levels. *cis*-1,2-DCE levels in all monitoring wells declined to below 70 µg/L. Vinyl chloride levels in some wells declined to less than 1 µg/L, the State of Florida target; in some wells, higher TCE levels elevated the detection limits of vinyl chloride. This indicated that ISCO considerably improved groundwater quality in the short term. There are some signs of a rebound in TCE and *cis*-1,2-DCE concentrations in the test plot during the extended monitoring that was conducted nine months after the end of the injections. Although TCE and *cis*-1,2-DCE levels rebounded to some extent in the nine months following the demonstration, they were still considerably below the predemonstration levels in most wells. In any case, DNAPL mass removal is expected to lead to eventual and earlier disappearance of the plume over the long term. There is also the possibility that even in the medium term, as normal groundwater flow is reestablished, a weakened plume may be generated and the resulting CVOC levels may be amenable to natural attenuation.
- Groundwater pH and dissolved oxygen levels remained stable, but oxidation-reduction potential (ORP), chloride, alkalinity, and TDS levels rose following the demonstration. TDS levels were above the secondary drinking water standard of 500 mg/L both before and after the demonstration, classifying the aquifer as brackish. Dissolved manganese levels rose above the 50 µg/L secondary drinking water standard; the dissolved manganese is expected to be mostly Mn^{7+}, while there still is excess permanganate in the plot. More manganese dioxide solids and Mn^{2+}, a reduced form of dissolved manganese, may be generated as the oxidant is depleted and the aquifer reverts to reducing conditions. The reduced manganese can cause discoloration of water when it exceeds 50 µg/L. Downgradient concentrations of manganese may have to be monitored over the next few years. However, manganese levels dropped considerably with distance from the test plot.
- Biological oxidation demand and total organic carbon (TOC) levels in the groundwater generally increased. TOC in soil remained relatively constant through the demonstration. These parameters were expected to decrease following oxidation. Dissolved iron levels remained relatively constant, and sulfate levels increased. The anomalous behavior of these parameters indicates that the oxidant-contaminant-aquifer reactions are complex and may result in a wider variety of byproducts.
- The postdemonstration groundwater levels of three trace metals — chromium, nickel, and thallium — showed a short-term increase above State of Florida standards. These metals are present in the aquifer at levels that are too high to be explained solely by their presence in the industrial-grade permanganate injected. Possible sources for some of these metals could be the native aquifer solids or the stainless steel monitoring wells in the plot; although stainless steel

is relatively resistant to oxidation, high levels of oxidant and chloride could have caused corrosion. Nine months after the end of the oxidant injections, the levels of these metals in the test plot were still elevated. The elevated levels of these trace metals are expected to subside over time, as flow is re-established. The levels of these metals decline significantly as the water reaches the monitoring wells surrounding the plot, probably due to adsorption on the aquifer solids and on the newly generated manganese dioxide.

- Slug tests conducted in the ISCO plot before and after the demonstration did not indicate any noticeable changes in the hydraulic conductivity of the aquifer; any manganese dioxide accumulation in the aquifer did not appear to have affected its hydraulic properties. Also, it is possible that the porosity loss due to formation of manganese dioxide solids is offset by the dissolution of native calcium carbonate solids in the aquifer.

Fate of TCE/DNAPL Removed

The TCE/DNAPL removed from the plot could have taken several pathways, including destruction by oxidation, migration to surrounding aquifer, or migration to vadose zone/atmosphere.

- The sharp rise in chloride levels in all three stratigraphic units is the strongest indicator that destruction by oxidation contributed significantly to TCE/DNAPL mass removal in the plot. The rise in chloride levels was conspicuous, despite the relatively high level of native chloride in the groundwater and despite dilution from the hydrant water used to make up the permanganate solution.
- The large increase in aquifer alkalinity, a sign of carbon dioxide generation, is a strong indicator of oxidation in the aquifer, although not of TCE alone. Native organic matter may also account for some of the oxidant consumption and carbon dioxide generation. One research need for this technology is determining the possible generation and potential toxicity of any organic byproducts of incomplete oxidation of TCE and native organic matter.
- Some DNAPL movement occurred in the saturated zone after the start of the ISCO and resistive heating demonstrations. However, because the DNAPL appeared in monitoring wells between the two test plots, it is difficult to attribute the cause of the DNAPL movement to one of the two technologies. If the strong hydraulic gradient created by the oxidant injection caused DNAPL to migrate, the DNAPL would have to have been present in mobile, and not residual, form. A limited number of additional soil cores collected around the ISCO plot did not show any signs of DNAPL accumulation. Monitoring of the vadose zone soil and surface atmosphere did not indicate any TCE/DNAPL migration in the upward direction, as could have happened had exothermic reactions taken place in the aquifer. Monitoring was conducted below the Lower Clay Unit only after the demonstration because of NASA’s initial concerns over breaching the aquitard. The three semi-confined aquifer wells were installed after the demonstration. The one well below the aquitard in the ISCO plot did not show soil or groundwater TCE levels reflective of DNAPL. None of the data indicate that downward migration of DNAPL was a significant pathway for the TCE in the test plot.
- Surface emission tests before, during, and after the demonstration did not show any elevated levels of TCE emanating from the ISCO plot. Unlike other strong oxidants, permanganate does not generate exothermic reactions that could cause VOCs to vaporize and escape to the vadose zone and atmosphere. The

top portion of the soil cores in the vadose zone did not show any elevated TCE concentrations either.

Verifying Operating Requirements

The vendor injected a total of 842,985 gal of permanganate solution (or 66,956 kg of solid potassium permanganate) in three injection cycles over an 8-month period. In the first injection cycle, the vendor injected the oxidant (1 to 2% solution of industrial-grade potassium permanganate from Carus® Chemical Company, Inc.) through 11 more-or-less equally spaced locations. At each location, the vendor advanced a specially designed injection tip in 2-ft intervals, using a Geoprobe®. The amount of permanganate injected at each location and depth was based on prior knowledge of the TCE/DNAPL distribution from the site characterization.

The injection pressure, flowrate, and period of injection were used to control the radius of influence of the permanganate around the injection point. The vendor estimates that 10 to 12 ft or less radius of influence was achieved at some injection points. However, local heterogeneities, DNAPL content, and native organic matter content limited oxidant distribution at some points, as indicated by the varying injection flowrates achieved. For example, whereas one injection point would permit 2 to 3 gpm of flow, another point only one horizontal foot away would permit less than 0.1 gpm of flow. Both groundwater and soil samples indicated (visually and analytically) that oxidant distribution varied in different parts of the plot. The portion of the aquifer underneath the building also appeared to have received insufficient oxidant; the plot extended 15 ft inside the building, whereas all injections were conducted outside.

Both the vendor and Battelle conducted additional monitoring in the periods between each injection cycle. During the second and third injection cycles, the vendor focused on only those portions of the plot that the interim monitoring showed had not received sufficient oxidant during the previous cycle.

Use of heavy equipment and handling of a strong oxidant were the primary hazards during the operation. The operators donned Level D protection at most times, except when a respirator had to be worn in order for the operator to protect against spray and dust generated while handling the dry potassium permanganate oxidant. A solution consisting of vinegar and hydrogen peroxide was kept on site to neutralize any exposure to potassium permanganate solution due to spills or hose leaks. The permanganate delivery system was automated so that it would shut off if any excessive pressure (clogging) or loss of pressure (leaks) was experienced in the system.

Economics

The vendor incurred a total cost of approximately $1 million for the field application of ISCO process. This includes the design, procurement, mobilization/demobilization, oxidant injection, and process monitoring. The vendor estimated that approximately 15% of this cost was incurred due to the fact that this was a technology demonstration, not a full-scale clean-up treatment. In addition, NASA incurred site preparation costs of $2,800. No aboveground wastes were generated from the injections. Waste disposal costs were minimal and were limited to nonhazardous solid waste disposal of materials generated during mobilization and operation.

A comparison of the cost of ISCO treatment of the DNAPL source the size of the ISCO plot and an equivalent (2 gpm) pump-and-treat system for plume control over the next 30 years was conducted to evaluate the long-term economic impact of the technology. The ISCO application cost was found to be less than the present value (PV) of a 30-year pump-and-treat application. This comparison assumes that natural attenuation would be sufficient to address any residual source. Also, in the absence of source treatment, the plume emanating from this relatively large DNAPL source may be expected to last much more than 30 years. ISCO and natural attenuation require none of the aboveground structures, recurring operational costs, and maintenance that pump-and-treat systems require. Anecdotal evidence indicates that, at many sites, pump-and-treat systems are operational only about 50% of the time. The impact of this downtime and the associated maintenance costs should also be considered. In general, the economics favor DNAPL source treatment, and ISCO (non-extraction mode) in particular, over a pump-and-treat system at this site.

Site characterization costs were not included in the cost comparison because a good design of a source treatment or plume control remedial action is assumed to require approximately the same degree of characterization. The site characterization conducted by Battelle in February 1999 is typical of the characterization effort that may be required for delineating a 75-ft × 50-ft × 45-ft DNAPL source; the cost of this effort was $255,000, which included a work plan, 12 continuous soil cores to 45 ft bgs, installation of 36 monitoring wells, field sampling, laboratory analysis of samples, field parameter measurements, hydraulic testing, and data analysis and report.

Summary of Conclusions and Recommendations

As described above, the following conclusions were drawn from the ISCO demonstration:

- At least half (49% to 84%) of the initial total TCE mass and possibly 76% of the DNAPL mass in the source zone were removed by ISCO.
- Much of this removal can be attributed to destruction of TCE by oxidation, as indicated by the chloride buildup in the plot. The sharp increase in carbon dioxide and, consequently, alkalinity levels in the groundwater, is another sign of considerable oxidation of TCE and natural organic matter occurring in the aquifer.
- Dissolved TCE levels declined considerably in most parts of the test plot in the short term, immediately following the demonstration. The federal drinking water standard for TCE (5 µg/L) was met in several monitoring wells during postdemonstration monitoring. Achievement of the lower State of Florida standard (3 µg/L) could not be determined due to analytical interference from the permanganate. Postdemonstration sampling indicated that *cis*-1,2-DCE and vinyl chloride levels in the many parts of the plot declined considerably as well. Some rebound in concentrations is evident in the extended monitoring event conducted nine months after the demonstration, after some re-equilibration occurred between the remaining DNAPL and dissolved TCE concentrations. However, the rebounded levels of these contaminants were still considerably below the predemonstration levels.
- It is possible to achieve a relatively good distribution of permanganate oxidant in sandy soils. Distribution of oxidant is more difficult in finer-grained soils. A radius of influence of 10 to 12 ft around the injection point was achieved at several locations. However, at some locations, resistance to oxidant flow was considerable, and the radius of influence was much smaller. Local geologic heterogeneities and native organic matter content of the aquifer may limit oxidant distribution in some regions. These factors may have also limited the reach of the oxidant under the building, from the injection points located outside.

- Elevated levels of some trace metals, such as chromium, nickel, and thallium, may occur in the short term. The source of these trace metals is partly the industrial-grade permanganate used and partly the native aquifer solids or stainless steel monitoring wells. Levels of dissolved manganese, a species subject to secondary drinking water standards, may be elevated in the short term as well. The concentrations of the trace metals and other dissolved species were found to mitigate quickly with distance from the treatment area. Elevated levels of even potassium ion, a relatively conservative species, subsided by the time the groundwater moved about 80 to 100 ft from the plot. This indicates that permanganate oxidation, even in an injection-only mode, can be applied at many sites at locations that are relatively close to receptors or property boundaries.
- Some DNAPL appeared in monitoring wells located between the two test plots, where ISCO and resistive heating technologies were being applied concurrently. It is difficult to attribute the DNAPL migration to one of the two technologies. The strong hydraulic gradient generated by the oxidant injection is unlikely to cause DNAPL migration, unless some DNAPL is already present in mobile form. When permanganate is used as the oxidant, there are no strong exothermic reactions involved and the potential for migration of DNAPL to the vadose zone or atmosphere is minimal.
- The cost of the ISCO application was approximately $1 million, including the design, oxidant purchase, equipment procurement and installation, operation, and limited monitoring costs. The vendor estimated that approximately 15% of these costs were for the demonstration specific rather than a full-scale. A comparison of the DNAPL source treatment with ISCO cost with the life cycle cost of an equivalent pump-and-treat system at the site showed that the ISCO treatment was more economical in the long term.

Based on the lessons learned during the demonstration, the following recommendations can be made for future applications:

- It is imperative to delineate the boundaries of the DNAPL source zone. A treatment such as oxidation also requires knowledge of the distribution of the DNAPL in the source region. The ISCO treatment can be better targeted and injections can be arranged suitably to mitigate any potential for DNAPL migration. A combination of monitoring well clusters with discrete screened intervals and strategically located continuous soil cores are a good way of delineating the source, in preparation for remedial design and treatment.
- If the DNAPL source boundaries can be identified with a fair degree of confidence, an injection-only scheme should be applied in such a way that the oxidant is first injected around the perimeter of the source, and then applied progressively to inner regions. This will minimize the potential for DNAPL migration. Alternatively, extraction wells can be used for better hydraulic control, but this will involve additional costs for aboveground treatment and reinjection/disposal of extracted fluids.
- For the portion of a DNAPL source that is under a building, the oxidant can be more effectively distributed by locating injection points inside the building (in this demonstration, this was not performed). This may create administrative difficulties if the building is in use, but will lead to more effective source removal. Alternatively, angled injection points or injection-extraction schemes with injection at one end of the building and extraction at another end could be considered.
- The native hydraulic gradient at this site is relatively flat, but the high injection pressures that were used here and that were required to achieve a reasonable radius of influence indicate that the native groundwater flow is not likely to play a significant role in oxidant distribution on the localized scale of most DNAPL

zones. For schemes that rely on lower injection pressures, injection points would have to be much more closely spaced and injections would have to start much further upgradient to take advantage of the natural gradient and obtain good coverage of the plot.

- One way of lowering oxidant injection pressures, if desirable at a site, may be to inject lower concentrations of oxidant for a longer period of time. This will mitigate the potential for elevated trace metal levels in the groundwater during the application, but may lead to higher operational costs.
- Sodium permanganate, which is commercially available as a concentrated solution, may be used to ease the difficulties associated with the handling of a solid oxidant (potassium permanganate).
- Additional research is required to elucidate the geochemistry of the oxidant-aquifer-contaminant interactions, particularly the effects of the oxidant on native organic matter and the effects of excessive chloride generation on underground structures, such as monitoring wells or buildings. Additional research also is required to evaluate further rebound of dissolved CVOC concentrations in the long term and to evaluate the survival and regrowth of microbial populations in the plot. These factors are important for natural attenuation of any residual contamination following ISCO treatment.

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Acronyms and Abbreviations

3-D	three-dimensional
ACL	alternative concentration limits
AFRL	Air Force Research Laboratory
ARAR	applicable or relevant and appropriate requirement
bgs	below ground surface
BOD	biological oxygen demand
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CES	Current Environmental Solutions
CFU	colony forming units
CMT	Core Management Team
CVOC	chlorinated volatile organic compound
CWA	Clean Water Act
DCE	dichloroethylene
DNAPL	dense, nonaqueous-phase liquid
DO	dissolved oxygen
DoD	(U.S.) Department of Defense
DOE	(U.S.) Department of Energy
EM50	Environmental Management 50 (Program)
FDEP	(State of) Florida Department of Environmental Protection
f_{oc}	fraction organic carbon
FSU	Florida State University
gpm	gallon(s) per minute
HDPE	high-density polyethylene
HSWA	Hazardous and Solid Waste Amendments
IDC	Interagency DNAPL Consortium
ISCO	in situ chemical oxidation
ITRC	Interstate Technology Regulatory Council
K_{oc}	organic carbon partitioning coefficient
LCS	laboratory control spikes
LCSD	laboratory control spike duplicates
LRPCD	Land Remediation and Pollution Control Division

MCL	maximum contaminant level
MS	matrix spikes
MSD	matrix spike duplicates
msl	mean sea level
MSE	MSE Technology Applications, Inc.
MTBE	methyl-*tert*-butyl ether
mV	millivolts
MYA	million years ago
NA	not applicable/not available
N/A	not analyzed
NAAQS	National Ambient Air Quality Standards
NASA	National Aeronautics and Space Administration
ND	not detected
NFESC	Naval Facilities Engineering Service Center
NPDES	National Pollutant Discharge Elimination System
O&M	operation and maintenance
ORD	Office of Research and Development
ORNL	Oak Ridge National Laboratory
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
PID	photoionization detector
POTW	publicly owned treatment works
ppb	parts per billion
psig	pounds per square inch gage
PV	present value
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RI/FS	Remedial Investigation/Feasibility Study
RPD	relative percent difference
RSKERC	R.S. Kerr Environmental Research Center (of the U.S. EPA)
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SIP	State Implementation Plan
SITE	Superfund Innovative Technology Evaluation (Program)
STL	STL Environmental Services, Inc.
TCA	trichloroethane
TCE	trichloroethylene
TDS	total dissolved solids
TOC	total organic carbon
UIC	Underground Injection Control (permit)
U.S. EPA	United States Environmental Protection Agency
VOA	volatile organic analysis
WSRC	Westinghouse Savannah River Company

1. Introduction

This section introduces the project demonstration of in situ chemical oxidation (ISCO) technology for remediation of a dense, nonaqueous-phase liquid (DNAPL) source zone at Launch Complex 34, Cape Canaveral Air Station, FL. The section also summarizes the structure of this report.

1.1 Project Background

The goal of the project is to evaluate the technical and cost performances of ISCO technology for remediation of DNAPL source zones. The chlorinated volatile organic compound (CVOC) trichloroethylene (TCE) is present in the aquifer as a DNAPL source at Launch Complex 34. Smaller amounts of dissolved *cis*-1,2-dichloroethylene (*cis*-1,2-DCE) and vinyl chloride also are present in the groundwater. The field demonstration of ISCO technology started at Launch Complex 34 in September 1999 and ended in April 2000. Performance assessment activities were conducted before, during, and after the field demonstration.

1.1.1 The Interagency DNAPL Consortium

The ISCO demonstration is part of a larger demonstration of three different DNAPL remediation technologies being conducted at Launch Complex 34 with the combined resources of several U.S. government agencies. The government agencies participating in this effort have formed the Interagency DNAPL Consortium (IDC). The IDC is composed primarily of the following agencies, which are providing most of the funding for the demonstration:

- U.S. Department of Energy (DOE), Environmental Management 50 (EM50) Program
- U.S. Environmental Protection Agency (U.S. EPA), Superfund Innovative Technology Evaluation (SITE) Program
- U.S. Department of Defense (DoD), Naval Facilities Engineering Service Center (NFESC)
- National Aeronautics and Space Administration (NASA).

In the initial stages of the project, until January 2000, the Air Force Research Laboratory (AFRL) was the DoD representative on this consortium and provided significant funding. NFESC replaced AFRL in March 2000. In addition, the following organizations are participating in the demonstration by reviewing project plans and data documents, funding specific tasks, and/or promoting technology transfer:

- Patrick Air Force Base
- U.S. EPA Technology Innovation Office and U.S. EPA R.S. Kerr Environmental Research Center (RSKERC)
- Interstate Technology Regulatory Council (ITRC).

Key representatives of the various agencies constituting the IDC formed a Core Management Team (CMT), which guided the progress of the demonstration. An independent Technical Advisory Group was formed to advise the Core Management Team on the technical aspects of the site characterization and selection, remediation technology selection and demonstration, and performance assessment of the technologies. The Technical Advisory Group consisted of experts drawn from industry, academia, and government.

The IDC contracted MSE Technology Applications, Inc. (MSE), to conduct technology vendor selection, procure the services of the three selected technology vendors, and conduct the cost evaluation of the three technologies. The IT Corporation is the selected vendor for implementing the ISCO technology at Launch Complex 34. Current Environmental Solutions and Integrated Water Resources, Inc., are the vendors for the resistive heating and steam injection technologies, respectively. In addition, the IDC also contracted Westinghouse Savannah River Company (WSRC) to conduct the preliminary site characterization for site selection, and Florida State University (FSU) to coordinate site preparation and other field arrangements for the demonstration. Figure 1-1 summarizes the project organization for the IDC demonstration.

1.1.2 Performance Assessment

The IDC contracted Battelle to plan and conduct the detailed site characterization and an independent performance assessment for the demonstration of the three technologies. U.S. EPA and its contractor, TetraTech EM, Inc., provided quality assurance (QA) oversight and field support for the performance assessment activities. Before the field demonstration, Battelle prepared a Quality Assurance Project Plan (QAPP) that was reviewed by all the project stakeholders. This QAPP was based on the general guidelines provided by the U.S. EPA's SITE Program for test plan preparation, quality assurance, and data analysis (Battelle, 1999d). Once the demonstration started, Battelle prepared six interim reports (Battelle 1999e, and f; Battelle 2000a, b, c, and d) for the IDC.

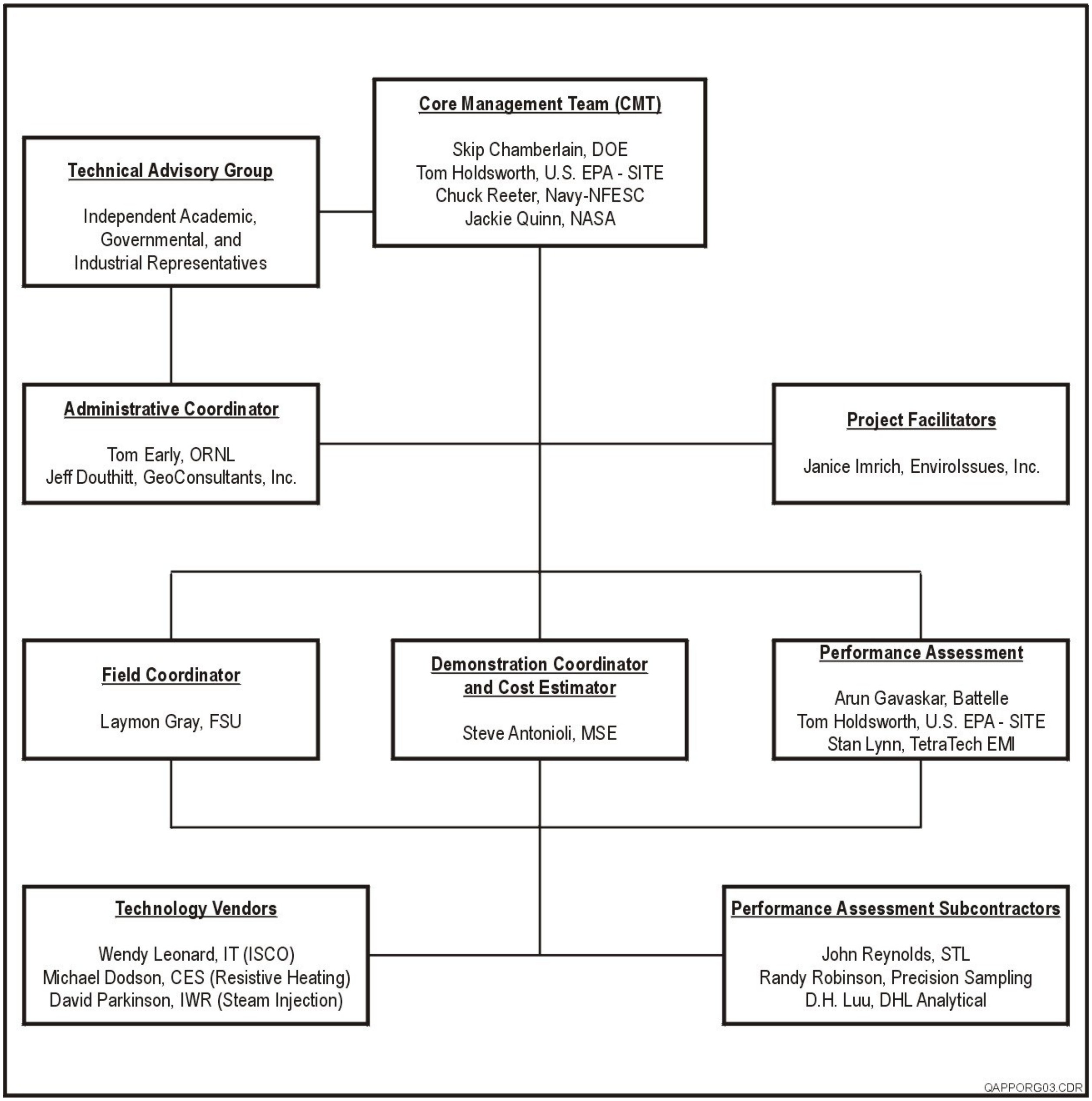


Figure 1-1. Project Organization for the IDC Demonstration at Launch Complex 34

1.1.3 *The SITE Program*

The performance assessment planning, field implementation, and data analysis and reporting for the ISCO demonstration followed the general guidance provided by the U.S. EPA’s SITE Program. The SITE Program was established by U.S. EPA's Office of Solid Waste and Emergency Response and the Office of Research and Development (ORD) in response to the 1986 Superfund Amendments and Reauthorization Act, which recognized a need for an "Alternative or Innovative Treatment Technology Research and Demonstration Program." ORD’s National Risk Management Research Laboratory in the Land Remediation and Pollution Control Division (LRPCD), headquartered in Cincinnati, OH, administers the SITE Program. The SITE Program encourages the development and implementation of (1) innovative treatment technologies for hazardous waste site remediation, and (2) innovative monitoring and measurement tools.

In the SITE Program, a field demonstration is used to gather engineering and cost data on the innovative technology so that potential users can assess the technology's applicability to a particular site. Data collected during the field demonstration are used to assess the performance of the technology, the potential need for pre- and postprocessing of the waste, applicable types of wastes and waste matrices, potential operating problems, and approximate capital and operating costs.

U.S. EPA provides guidelines on the preparation of an Innovative Technology Evaluation Report at the end of the field demonstration. These reports evaluate all available information on the technology and analyze its overall applicability to other site characteristics, waste types, and waste matrices. Testing procedures, performance and cost data, and quality assurance and quality standards also are presented. This IDC report on the ISCO technology demonstration at Launch Complex 34 is based on these general guidelines.

1.2 The DNAPL Problem

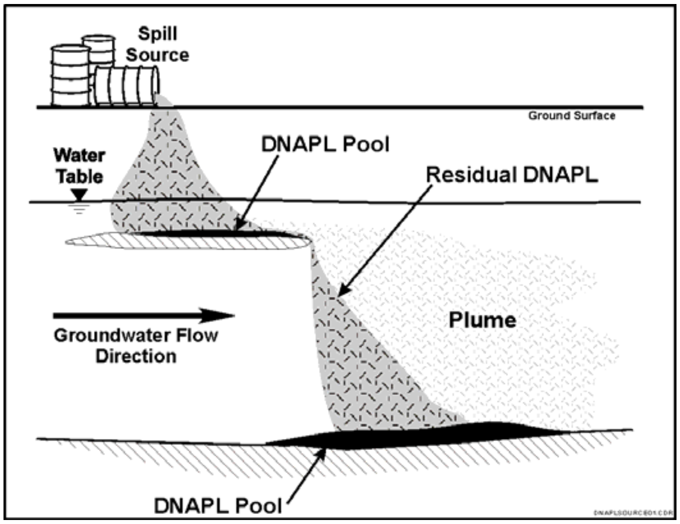


Figure 1-2. Simplified Depiction of the Formation of a DNAPL Source Zone in the Subsurface

Figure 1-2 illustrates the formation of a DNAPL source at a chlorinated solvent release site. When solvent is released into the ground due to previous use or disposal practices, it travels downward through the vadose zone to the water table. Because many chlorinated solvents are denser than water, the solvent continues its downward migration through the saturated zone (assuming sufficient volume of solvent is involved) until it encounters a low-permeability layer or aquitard, on which it may form a pool. During its downward migration, the solvent leaves a trace of residual solvent in the soil pores. Many chlorinated solvents are only sparingly soluble in water; therefore, they can persist as a separate phase for several years (or decades). This free-phase solvent is called DNAPL.

DNAPL in pools often can be mobilized towards extraction wells when a strong hydraulic gradient is imposed; this solvent is called mobile DNAPL. Residual DNAPL can be DNAPL that can be trapped in pores and cannot be mobilized towards extraction wells, regardless of how strong the applied gradient. DNAPL pools may dissolve in the groundwater flow over time, leaving behind residual DNAPL. At most sites, DNAPL pools are rare, as DNAPL is often present in residual form.

As long as DNAPL is present in the aquifer, a plume of dissolved solvent is generated. DNAPL therefore constitutes a secondary source that keeps replenishing the plume long after the primary source (leaking aboveground or buried drums, drain pipes, vadose zone soil, etc.) has been removed. Because DNAPL persists for many decades or centuries, the resulting plume also persists for many years. As recently as five years ago, DNAPL sources were difficult to find and most remedial approaches focused on plume treatment or plume control. In recent years, many chlorinated solvent-contaminated sites have been successful in identifying DNAPL sources, or at least identifying enough indicators of DNAPL. The focus is now shifting from plume control to DNAPL source removal or treatment.

Pump-and-treat systems have been the conventional treatment approach at DNAPL sites and these systems have proved useful as an interim remedy to control the progress of the *plume* beyond a property boundary or other compliance point. However, pump-and-treat systems are not economical for *DNAPL* remediation. Pools of DNAPL, which can be pumped and treated above ground, are rare. Residual DNAPL is immobile and does not migrate towards extraction wells. As with plume control, the effectiveness and cost of DNAPL remediation with pump and treat is governed by the time (decades) required for slow dissolution of the DNAPL source in the groundwater flow. An innovative approach is required to address the DNAPL problem.

1.3 The ISCO Technology

Figure 1-3 illustrates the in situ application of a chemical oxidant for remediation of a DNAPL source zone. This innovative technology is based on the ability of strong oxidants to react with and destroy several types of DNAPL contaminants. Common chemicals with high oxidation potential that have been used to treat DNAPL zones are Fenton's reagent and potassium permanganate (Watts et al., 1990; Vella et al., 1990; Gates et al., 1995; Siegrist et al., 2001). Notably, the DNAPL constituents most susceptible to oxidation by potassium permanganate are Cl-alkenes. Treatment of CVOCs with oxidants has been used historically for drinking water and wastewater treatment, but the in situ use of these oxidants for DNAPL source treatment is relatively new. Equation 1-1 illustrates how a common contaminant, TCE, would react with (and be destroyed by) potassium permanganate.

$$\begin{gathered} 2KMnO_4 + C_2HCl_3 \rightarrow \\ 2CO_2 + 2MnO_2\,(s) + 2K^+ + H^+ + 3Cl^- \end{gathered} \qquad (1\text{-}1)$$

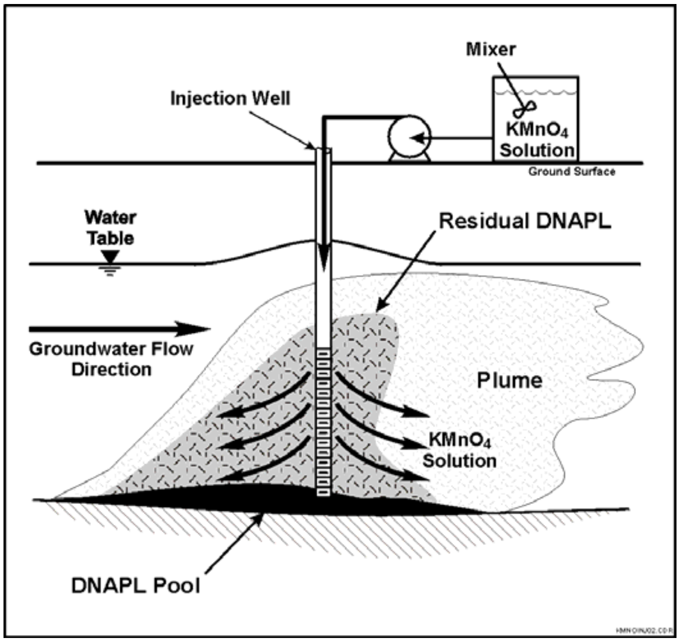


Figure 1-3. In Situ Chemical Oxidation of a DNAPL Source Zone

TCE is oxidized to potentially nontoxic byproducts, such as carbon dioxide, manganese dioxide (solid), and chloride. In the absence of other organic matter, the reaction is second order and the rate is governed by the concentrations of both TCE and MnO_4^- ion.

In an aquifer setting, permanganate also reacts with other reduced species, including native organic matter. The natural organic matter in an aquifer competes with the contaminant for consuming the oxidant. Therefore, the amount of oxidant required to sweep an aquifer depends on the characteristics of both the contaminants and the aquifer. Also, geologic heterogeneities may limit the degree of contact achievable between the oxidant and the contaminant. In this respect, a longer-lived oxidant, such as permanganate, has some advantage over a short-lived oxidant, such as the hydroxyl free radical created from Fenton's reagent. Because permanganate does not degrade as quickly as the hydroxyl free radical, it can potentially sweep longer distances around the injection point and persist long enough to diffuse slowly into more isolated pores. In addition, $KMnO_4$ oxidation is a redox reaction that is relatively effective over a wide pH range, thus making it suitable for the alkaline subsurface conditions in the Launch Complex 34 aquifer. Therefore, potassium permanganate was selected as the oxidant in the IDC demonstration.

When permanganate is applied in an injection-only mode, as was done in this demonstration, extraction of the injected fluids and their subsequent treatment and disposal/reinjection is not required. Therefore, ISCO has a potential advantage over technologies that rely on enhanced mobilization, capture, and aboveground treatment of DNAPL contaminants. One concern with in situ application of permanganate has been related to the generation of manganese dioxide, a solid that could build up in the aquifer and potentially cause plugging of pores. Another concern has been the spread of dissolved manganese (Mn^{2+}), a reduced species that is generated from manganese (Mn^{4+}) dioxide, if and when the oxidative environment reverts to a reducing environment. Dissolved manganese is subject to a secondary (nonhealth-based) drinking water standard. A third concern relates to the potential for release of regulated metals from the aquifer formation under strong oxidizing conditions. These concerns were evaluated during the demonstration.

1.4 The Demonstration Site

Launch Complex 34, the site selected for this demonstration, is located at Cape Canaveral Air Station, FL (see Figure 1-4). Launch Complex 34 was used as a launch site for Saturn rockets from 1960 to 1968. Historical

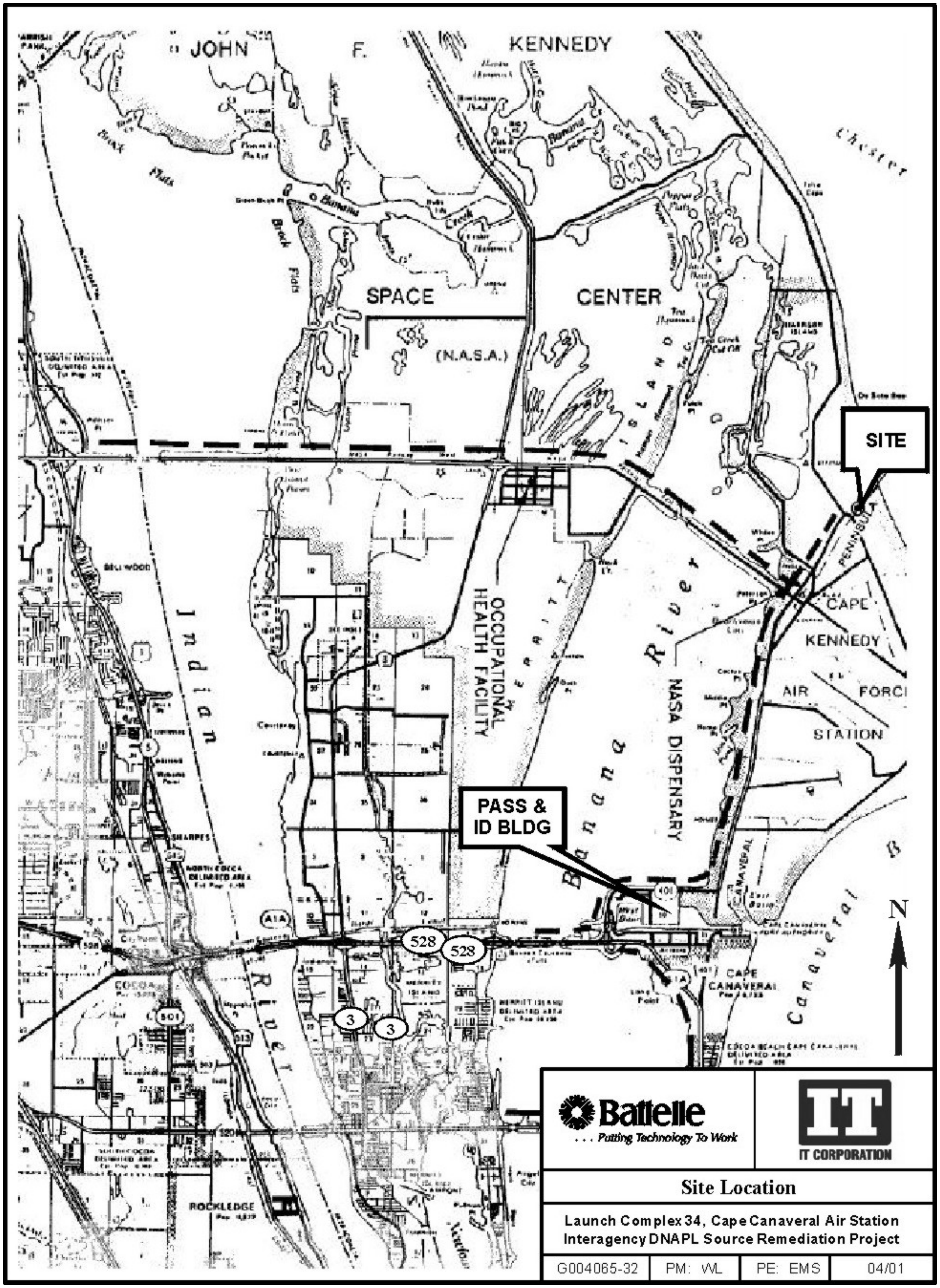


Figure 1-4. Demonstration Site Location

records and worker accounts suggest that rocket engines were cleaned on the launch pad with chlorinated organic solvents such as TCE. Other rocket parts were cleaned on racks at the western portion of the Engineering Support Building and inside the building. Some of the solvents ran off to the surface or discharged into drainage pits. The site was abandoned in 1968 and since that time much of the site has been overgrown by vegetation, although several on-site buildings remain operational.

Preliminary site characterization efforts suggested that approximately 20,600 kg (Battelle, 1999a) to 40,000 kg (Eddy-Dilek et al., 1998) of solvent could be present in the subsurface near the Engineering Support Building at Launch Complex 34. Figure 1-5 is a map of the Launch Complex 34 site at Cape Canaveral that shows the target DNAPL source area, located in the northern vicinity of the Engineering Support Building. The DNAPL source zone was large enough that the IDC and the Technical Advisory Group could assign three separate test plots encompassing different parts of this source zone. Figure 1-5 also shows the layout of the three test plots along the northern edge of the Engineering Support Building at Launch Complex 34. The ISCO plot is the easternmost of these plots. Figure 1-6 is a photograph looking southward towards the three test plots and the Engineering Support Building. All three test plots lie partly under the Engineering Support Building in order to encompass the portion of the DNAPL source under the building.

1.5 Technology Evaluation Report Structure

The ISCO technology evaluation report starts with an introduction to the project organization, the DNAPL problem, the technology demonstrated, and the demonstration site (Section 1). The rest of the report is organized as follows:

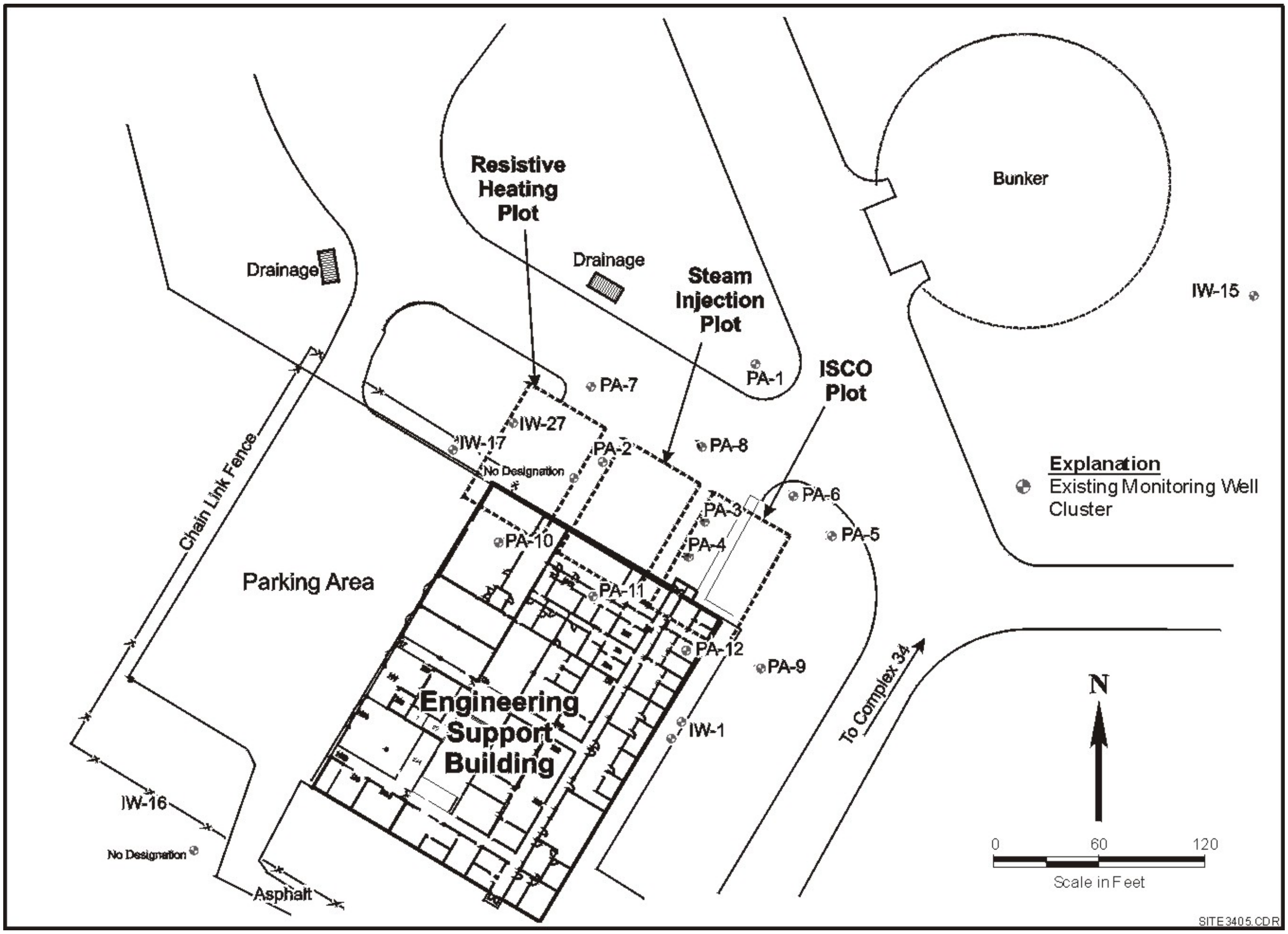


Figure 1-5. Location Map of Launch Complex 34 Site at Cape Canaveral Air Station

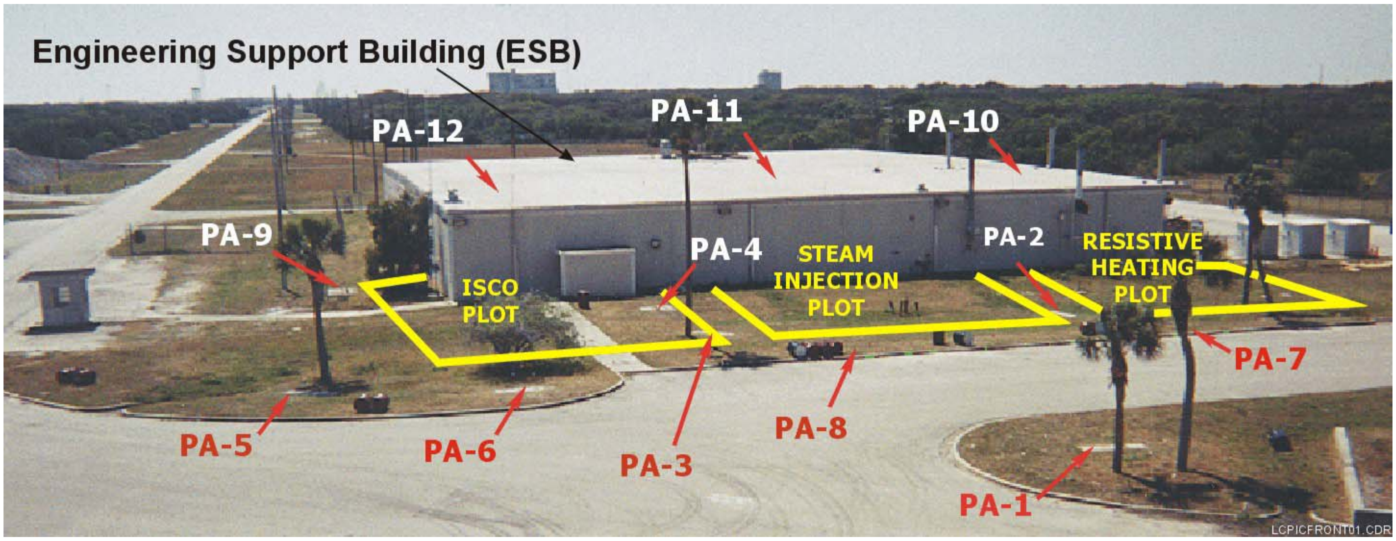


Figure 1-6. View Looking South towards Launch Complex 34, the Engineering Support Building, and the Three Test Plots

- Site Characterization (Section 2)
- Technology Operation (Section 3)
- Performance Assessment Methodology (Section 4)
- Performance Assessment Results and Conclusions (Section 5)
- Quality Assurance (Section 6)
- Economic Analysis (Section 7)
- Technology Applications Analysis (Section 8)
- References (Section 9).

Supporting data and other information are presented in the appendices to the report. The appendices are organized as follows:

- Performance Assessment Methods (Appendix A)
- Hydrogeologic Measurements (Appendix B)
- CVOC Measurements (Appendix C)
- Inorganic and Other Aquifer Parameters (Appendix D)
- Microbiological Assessment (Appendix E)
- Surface Emissions Testing (Appendix F)
- Quality Assurance/Quality Control (QA/QC) Information (Appendix G)
- Economic Analysis Information (Appendix H)
- Technical Information for $KMnO_4$ Used for the ISCO Demonstration (Appendix I).

2. Site Characterization

This section provides a summary of the hydrogeology and chemistry of the site based on the data compilation report (Battelle, 1999a), the additional site characterization report (Battelle, 1999b), and the predemonstration characterization report (Battelle, 1999c).

2.1 Hydrogeology of the Site

A surficial aquifer and a semi-confined aquifer comprise the major aquifers in the Launch Complex 34 area, as described in Table 2-1. The surficial aquifer extends from the water table to approximately 45 ft below ground surface (bgs) in the Launch Complex 34 area. A clay semi-confining unit separates the surficial aquifer from the underlying confined aquifer.

Figures 2-1 and 2-2 are geologic cross sections, one along the northwest-southeast (NW-SE) direction across the middle of the three test plots and the other along the southwest-northeast (SW-NE) direction across the middle of the ISCO plot. As seen in these figures, the surficial aquifer is subclassified as having an Upper Sand Unit, a Middle Fine-Grained Unit, and a Lower Sand Unit. The Upper Sand Unit extends from ground surface to approximately 20 to 26 ft bgs and consists of unconsolidated, gray fine sand and shell fragments. The Middle Fine-Grained Unit is a layer of gray, fine-grained silty/clayey sand that exists between about 26 and 36 ft bgs. In general, this unit contains soil that is finer-grained than the Upper Sand Unit and Lower Sand Unit, and varies in thickness from about 10 to 15 ft. The Middle Fine-Grained Unit is thicker in the northern portions of the test plots and appears to become thinner in the southern and western portions of the test area (under the Engineering Support Building and in the resistive heating plot). Below the Middle Fine-Grained Unit is the Lower Sand Unit, which consists of gray fine to medium-sized sand and shell fragments. The unit contains isolated fine-grained lenses of silt and/or clay. Figure 2-2 shows a stratigraphic cross section through the demonstration area. The lithologies of thin, very coarse, shell zones were encountered in several units. These zones probably are important as reservoirs for DNAPL.

A 1.5- to 3-ft-thick semi-confining layer exists at approximately 45 ft bgs in the Launch Complex 34 area. The layer consists of greenish-gray sandy clay. The semi-confining unit (i.e., the Lower Clay Unit) was encountered in all borings across the Launch Complex 34 site, and it appears to be a pervasive unit. However, the clay unit is fairly thin (around 1.5 ft thick) in some areas, especially under the resistive heating plot. Site characterization data (Battelle, 1999a and b; Eddy-Dilek et al., 1998) suggest that the surfaces of the Middle Fine-Grained Unit and the Lower Clay Unit are somewhat uneven (see Figures 2-3 to 2-5). The Lower Clay Unit slopes downward toward the southern part of all three test plots and toward the center plot and the building (Battelle, 2001).

Table 2-1. Local Hydrostratigraphy at the Launch Complex 34 Site

Hydrostratigraphic Unit		Thickness (ft)	Sediment Description	Aquifer Unit Description
Surficial Aquifer	Upper Sand Unit	20-26	Gray fine sand and shell fragments	Unconfined, direct recharge from surface
	Middle Fine-Grained Unit	10-15	Gray, fine-grained silty/clayey sand	Low-permeability, semi-confining layer
	Lower Sand Unit	15-20	Gray fine to medium-sized sand and shell fragments	Semi-confined
Lower Clay Unit (Semi-Confining Unit)		1.5-3	Greenish-gray sandy clay	Thin low-permeability semi-confining unit
Semi-Confined Aquifer		>40	Gray fine to medium-sized sand, clay, and shell fragments	Semi-confined, brackish

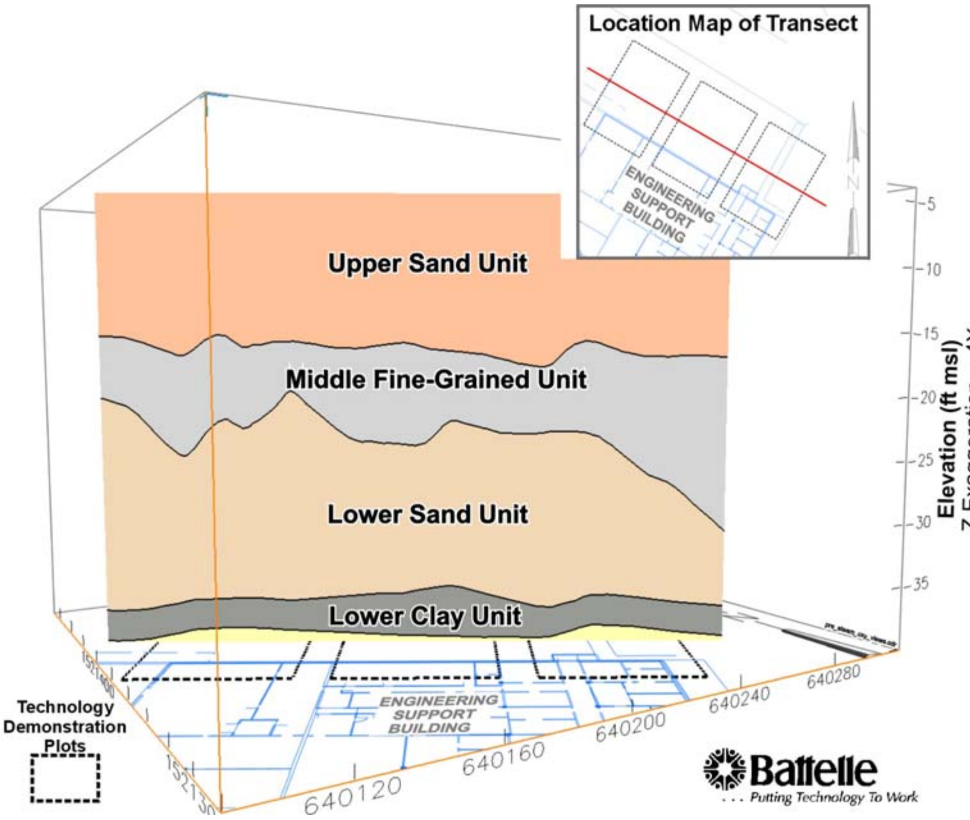


Figure 2-1. NW-SE Geologic Cross Section through the Three Test Plots

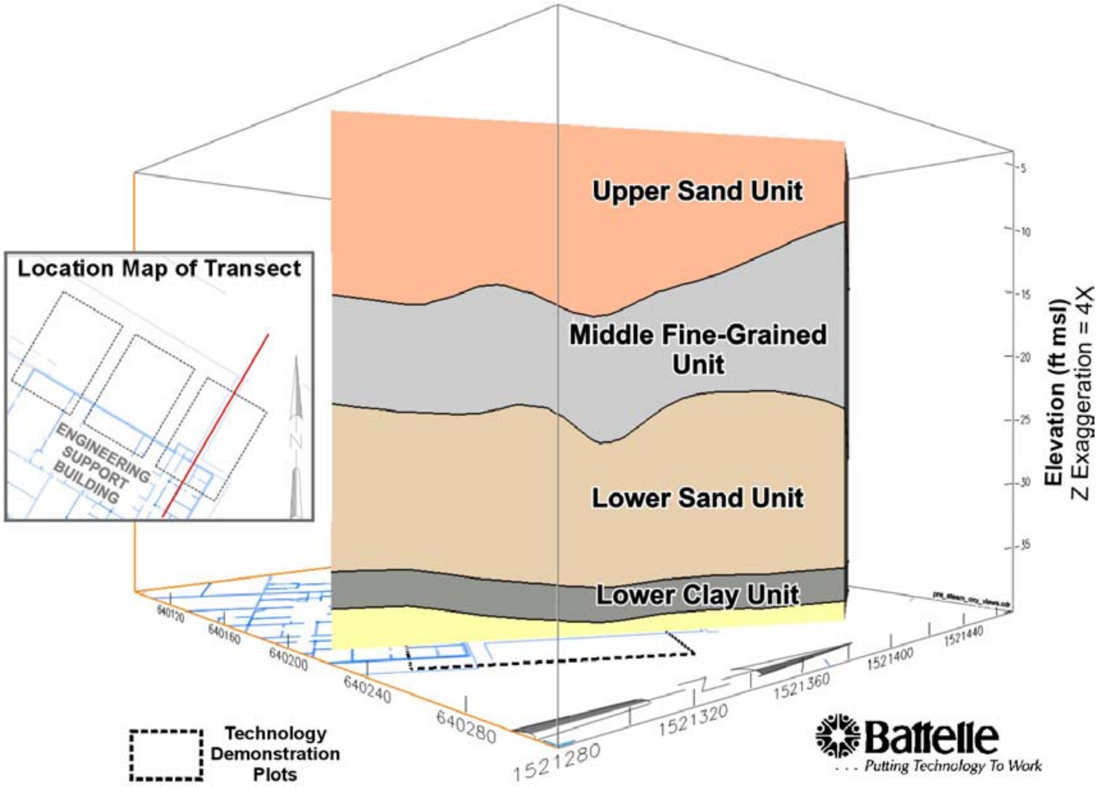


Figure 2-2. SW-NE Geologic Cross Section through ISCO Plot

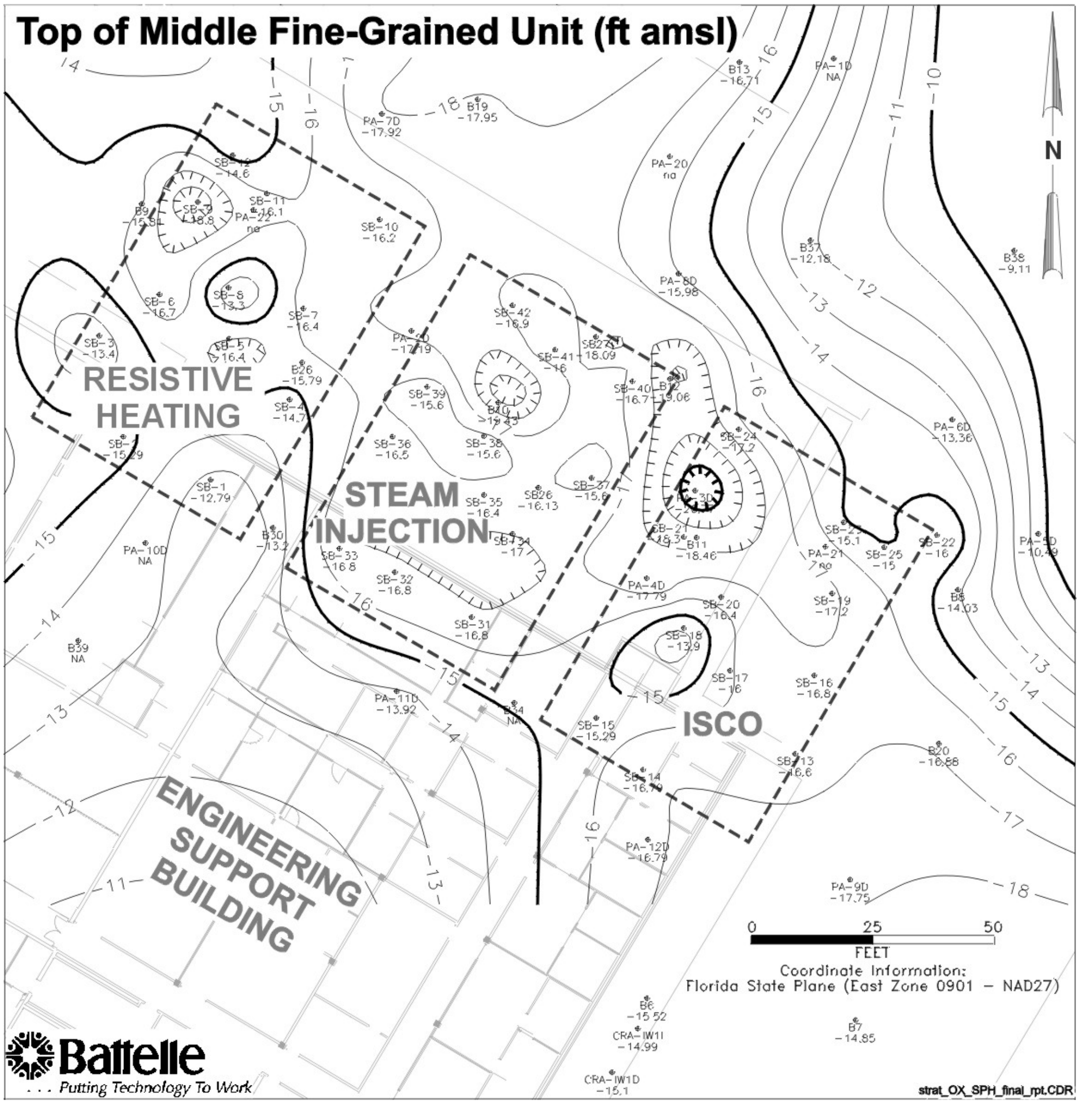


Figure 2-3. Topography of Top of Middle Fine-Grained Unit

The semi-confined aquifer underlies the Lower Clay Unit. The aquifer consists of gray fine to medium-sized sand, clay, and shell fragments during the investigation to the aquifer below the Lower Clay Unit (Battelle 2001). Water levels from wells in the aquifer were measured at approximately 4 to 5 ft bgs. Few cores were advanced below the semi-confined aquifer. The thickness of the semi-confined aquifer is between 40 ft and 120 ft.

Water-level surveys were performed in the surficial aquifer in May 1997, December 1997, June 1998, October 1998, and March 1999. Water table elevations in the surficial aquifer were between about 1 and 5 ft mean sea level (msl). In general, the surveys suggest that water levels form a radial pattern with highest elevations near the Engineering Support Building. Figure 2-6 shows a water-table map of June 1998. The gradient and flow directions vary over time at the site. Table 2-2 summarizes the hydraulic gradients and their directions near the Engineering Support Building. The gradient ranged from 0.00009 to 0.0007 ft/ft. The flow direction varied from north-northeast to south-southwest.

Predemonstration water-level measurements in all three surficial aquifer zones — Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit — indicate a relatively flat hydraulic gradient in the localized setting of the three test plots, as seen in Figures 2-7 to 2-9 (Battelle, 1999c). On a regional scale, mounding of water levels near the Engineering Support Building generates a radial gradient; the regional gradient across the test plots is weak and appears to be toward the northeast (see Figure 2-6). Probable discharge points for the aquifer include wetland areas, the Atlantic Ocean, and/or the

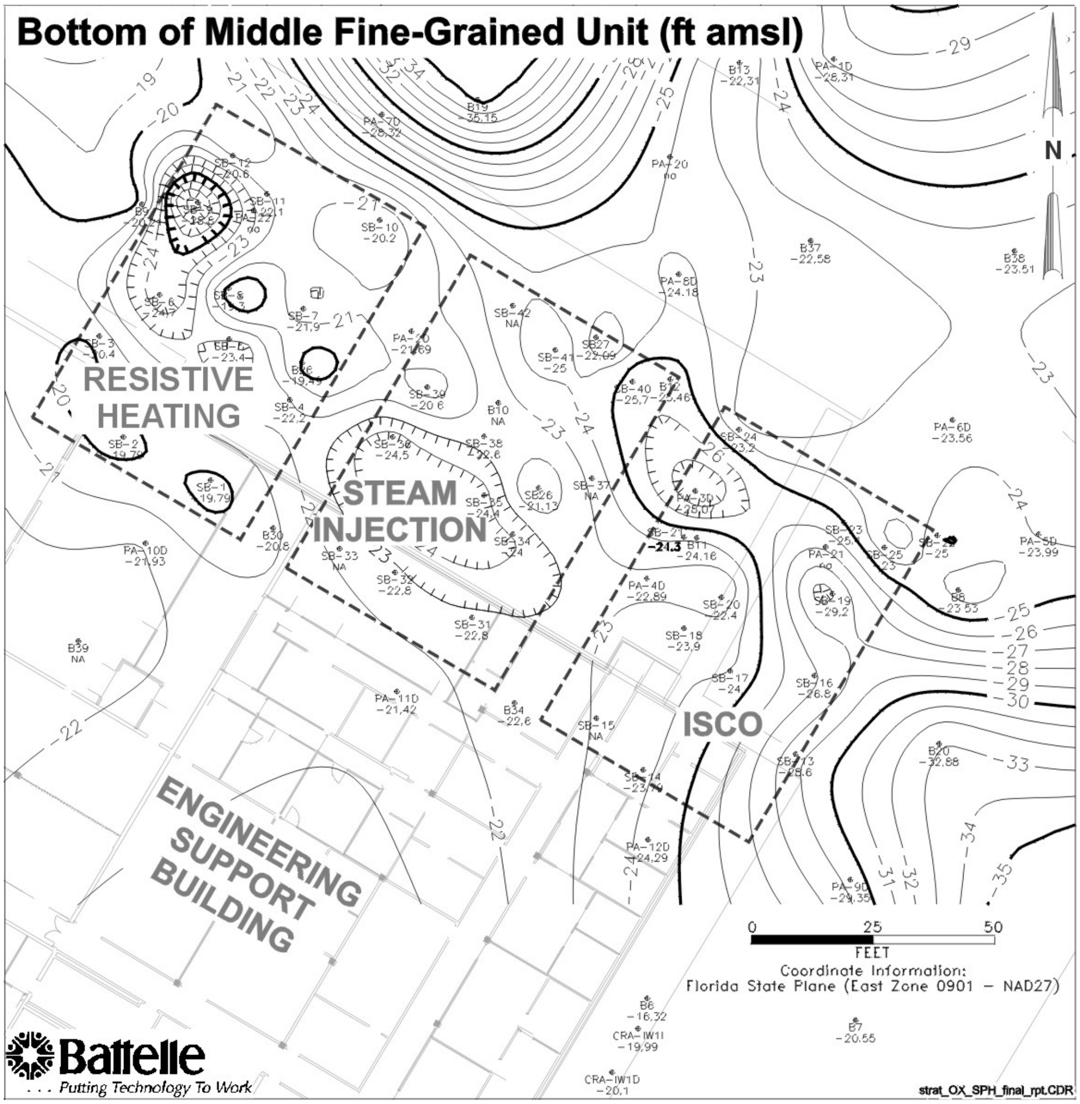


Figure 2-4. Topography of Bottom of Middle Fine-Grained Unit

Banana River. Water levels from wells screened in the Lower Sand Unit usually are slightly higher than the water levels from the Upper Sand Unit and/or the Middle Fine-Grained Unit. The flow system may be influenced by local recharge events, resulting in the variation in the gradients. Recharge to the surficial aquifer is from infiltration of precipitation through surface soils to the aquifer.

In general, predemonstration slug tests show that the Upper Sand Unit is more permeable than the underlying units, with hydraulic conductivity ranging from 4.0 to 5.1 ft/day in the shallow wells at the site (Battelle, 1999c). The hydraulic conductivity of the Middle Fine-Grained Unit ranges from 1.4 to 6.4 ft/day in the intermediate wells; measured conductivities probably are higher than the actual conductivity of the unit because the well screens include portions of the Upper Sand Unit. The hydraulic conductivity of the Lower Sand Unit ranged from 1.3 to 2.3 ft/day. Porosity averaged 0.26 in the Upper Sand Unit, 0.34 in the Middle Fine-Grained Unit, 0.29 in the Lower Sand Unit, and 0.44 in the Lower Clay Unit. The bulk density of the aquifer materials averaged 1.59 g/cm^3 (Battelle, 1999b). Groundwater temperatures ranged from 22.4 to 25.7°C during a March 1999 survey.

Water level surveys in the semi-confined aquifer were performed in December 1997, June 1998, and October 1998. Water table elevations were measured at approximately 1 to 5 ft msl, and formed a pattern similar to the pattern formed by surficial aquifer water levels. Groundwater elevations in the semi-confined aquifer are above the semi-confining unit. The gradient in the semi-confined

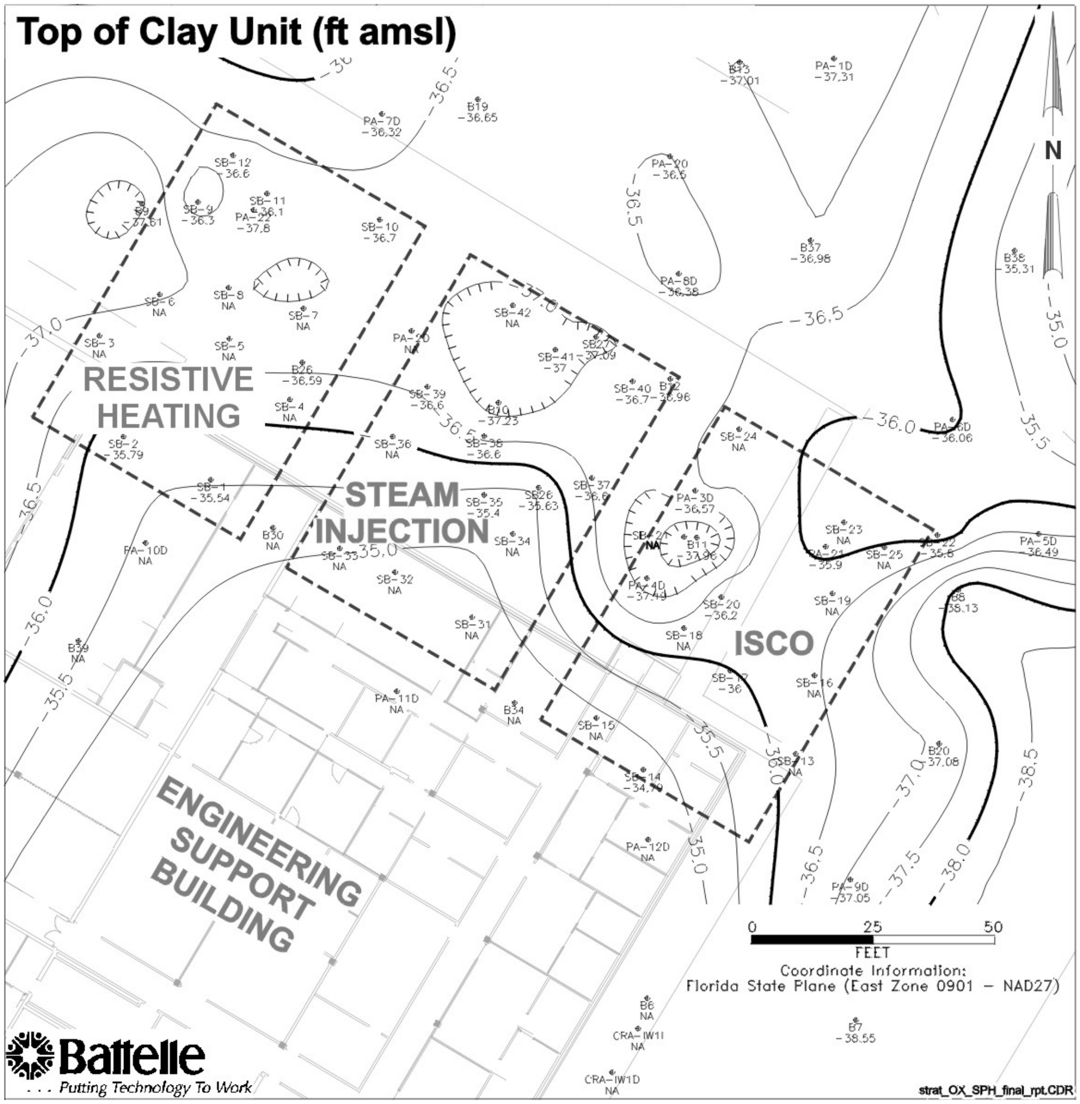


Figure 2-5. Topography of Top of Lower Clay Unit

aquifer is positioned in a similar direction to the surficial aquifer. The flow direction varies from east to south-southwest. In general, water levels in the aquifer below the Lower Clay Unit are higher than those in the surficial aquifer, suggesting an upward vertical gradient. Recharge to the aquifer may occur by downward leakage from overlying aquifers or from direct infiltration inland where the aquifer is unconfined. Schmalzer and Hinkle (1990) suggest that saltwater intrusion may occur in intermediate aquifers such as the semi-confined aquifer.

Other notable hydrologic influences at the site include drainage and recharge. Paved areas, vegetation, and topography affect drainage in the area. No streams exist in the site area. Engineered drainage at the site consists of ditches that lead to the Atlantic Ocean or swampy areas. Permeable soils exist from the ground surface to the water table and drainage is excellent. Water infiltrates directly to the water table.

2.2 Surface Water Bodies at the Site

The major surface water body in the area is the Atlantic Ocean, located to the east of Launch Complex 34. To determine the effects of surface water bodies on the groundwater system, water levels were monitored in 12 piezometers over 50 hours for a tidal influence study during Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) activities (G&E Engineering, Inc., 1996). All the piezometers used in the study were screened in the surficial aquifer. No detectable effects from the tidal cycles were measured, suggesting that the surficial aquifer and the Atlantic Ocean are not well connected hydraulically. However, the Atlantic Ocean

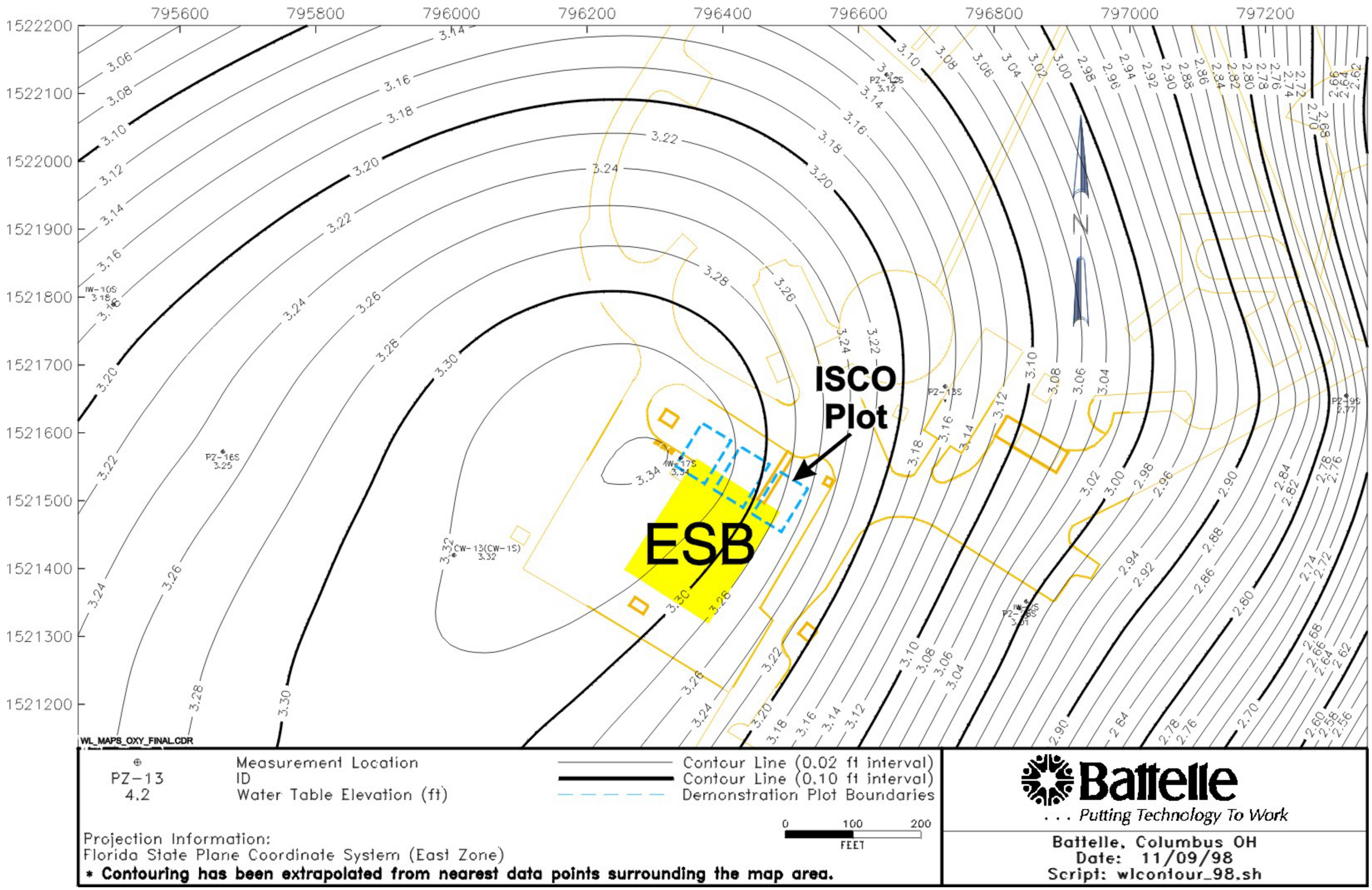


Figure 2-6. Water Table Elevation Map for Surficial Aquifer from June 1998

Table 2-2. Hydraulic Gradients and Directions in the Surficial and Semi-Confined Aquifers

Hydrostratigraphic Unit	Sampling Date	Hydraulic Gradient	Gradient Direction
Surficial Aquifer	May 1997	0.00009	SW
	December 1997	0.0001	SSW
	June 1998	0.0006	WNW
	October 1998	0.0007	NNE
	March 1999	undefined	undefined
Semi-Confined Aquifer	December 1997	0.0008	S
	June 1998	0.0005	E
	October 1998	0.00005	SSW

and the Banana River seem to act as hydraulic barriers or sinks, as groundwater likely flows toward these surface water bodies and discharges into them.

2.3 TCE/DNAPL Contamination in the ISCO Plot and Vicinity

Figures 2-10 to 2-12 show representative predemonstration distributions of TCE, the primary contaminant at Launch Complex 34, in the shallow, intermediate, and deep wells, installed during the site characterization, to correspond with the hydrostratigraphic units: Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit (Battelle, 1999c), respectively. No free-phase solvent was observed in any of the wells during the predemonstration sampling; however, groundwater analysis in many wells shows TCE at levels near or above its solubility, indicating the presence of DNAPL at the site. Lower levels of *cis*-1,2-DCE and vinyl chloride are also present in the aquifer, indicating some historical natural attenuation of TCE. Groundwater sampling indicates that the highest levels of TCE are in the Lower Sand Unit (deep wells) and closer to the Engineering Support Building.

Figures 2-13 to 2-15 show representative predemonstration horizontal distributions of TCE in soil from the Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit, respectively (Battelle, 1999c). TCE levels are highest in the Lower Sand Unit and concentrations indicative of DNAPL extend under the building. As seen in the vertical cross section in Figure 2-16, much of the DNAPL is present in the Middle Fine-Grained Unit and the Lower Sand Unit.

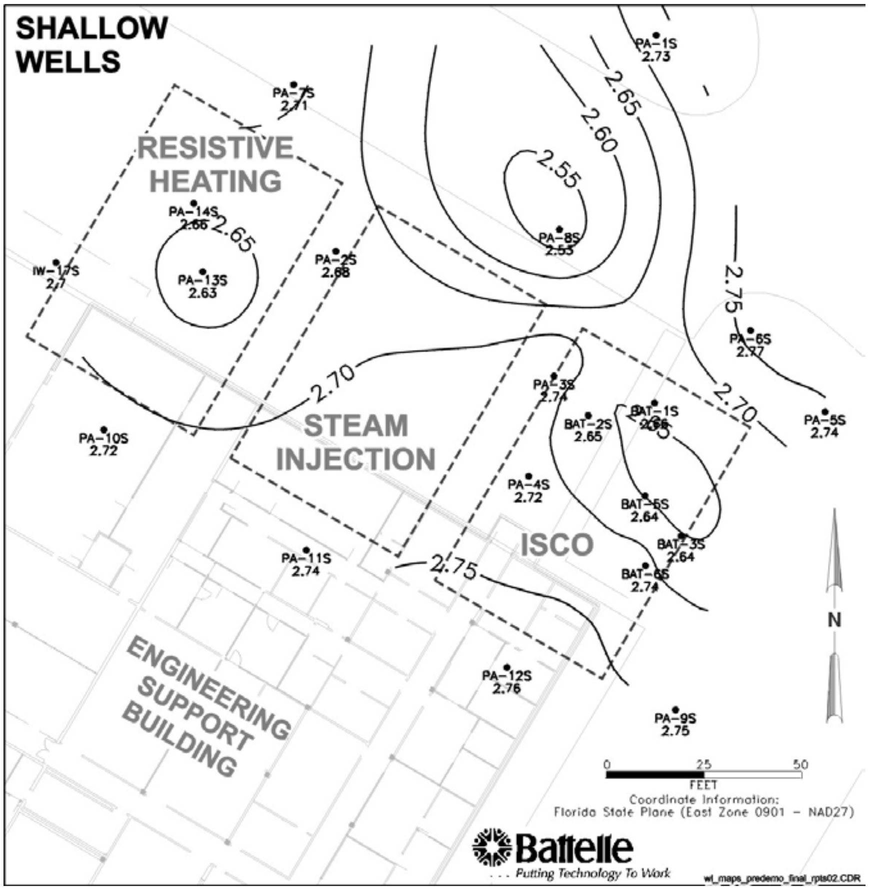


Figure 2-7. Predemonstration Water Levels (as Elevations msl) in Shallow Wells at Launch Complex 34 (September 1999)

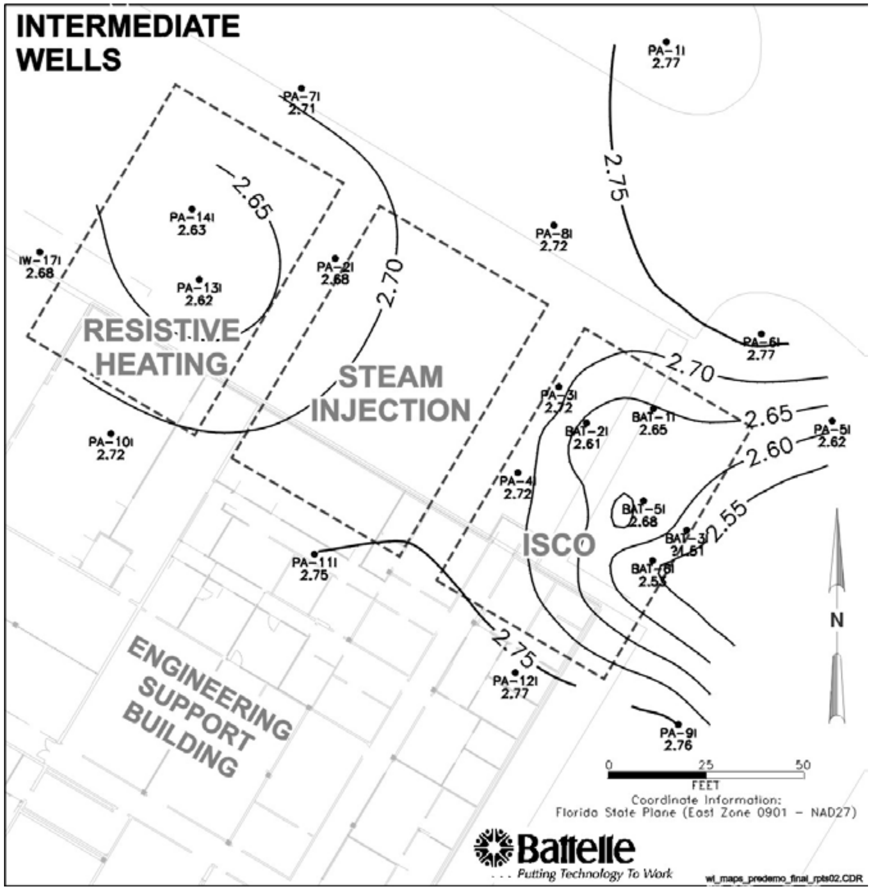


Figure 2-8. Predemonstration Water Levels (as Elevations msl) in Intermediate Wells at Launch Complex 34 (September 1999)

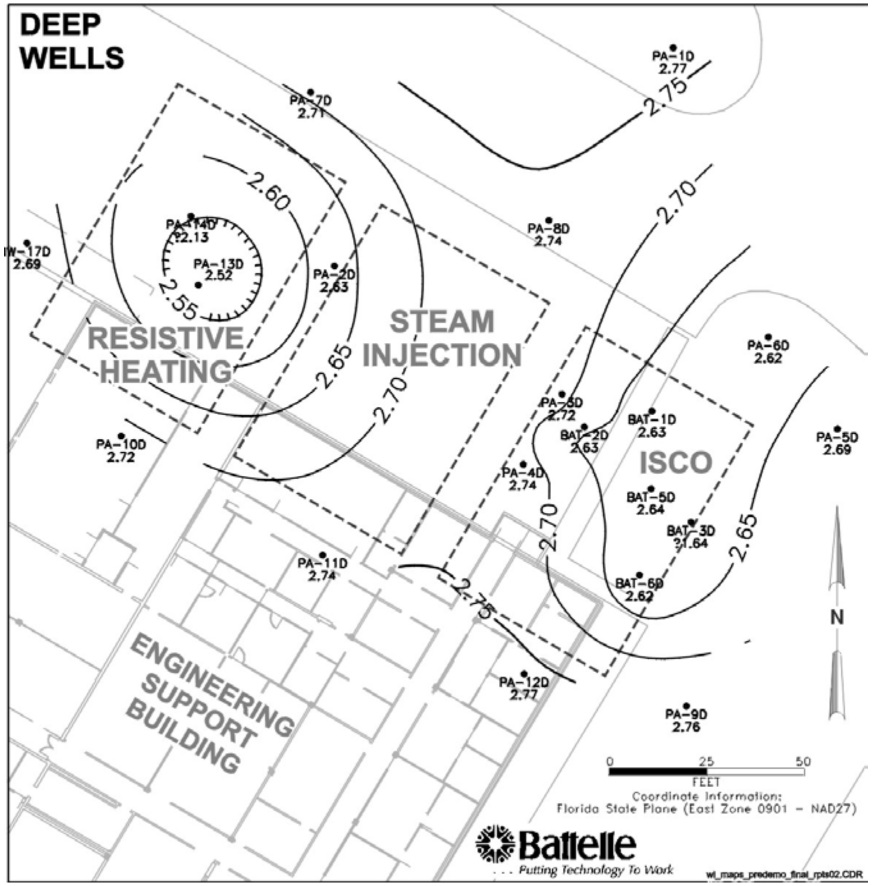


Figure 2-9. Predemonstration Water Levels (as Elevations msl) in Deep Wells at Launch Complex 34 (September 1999)

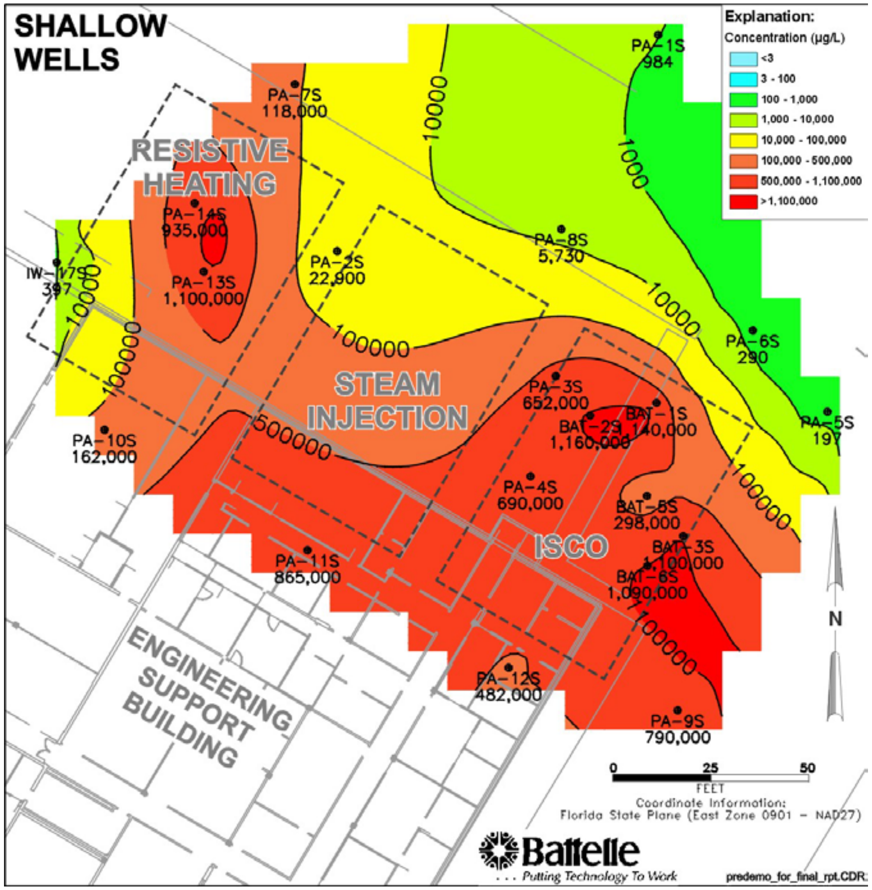


Figure 2-10. Predemonstration Dissolved TCE Concentrations (µg/L) in Shallow Wells at Launch Complex 34 (September 1999)

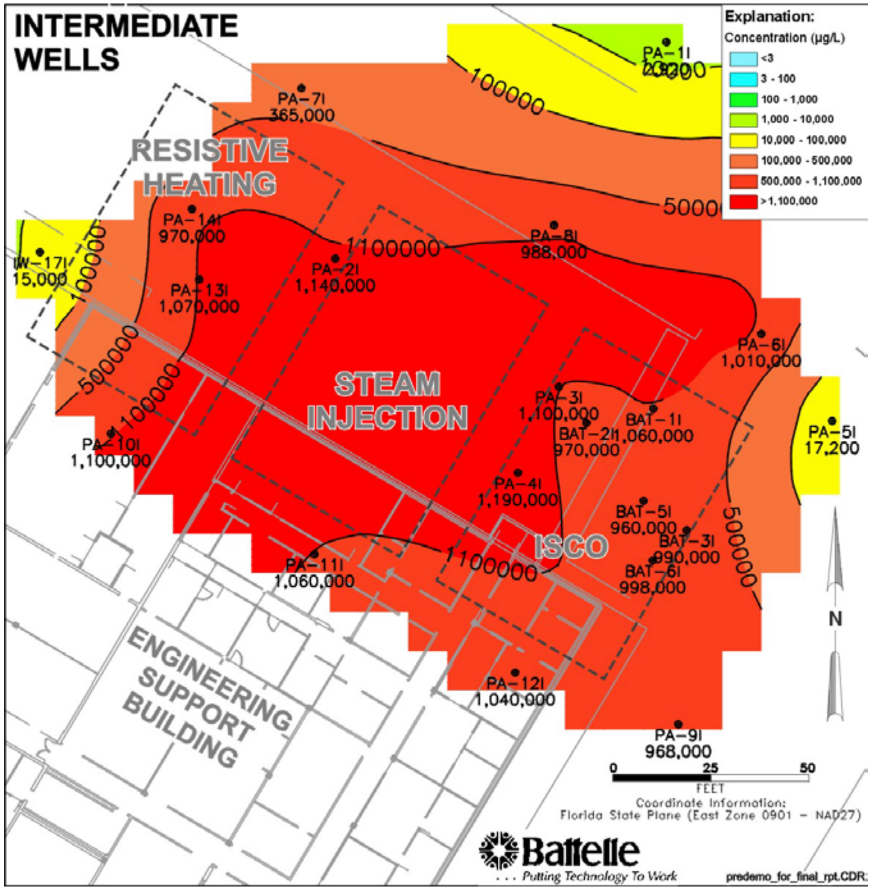


Figure 2-11. Predemonstration Dissolved TCE Concentrations (µg/L) in Intermediate Wells at Launch Complex 34 (September 1999)

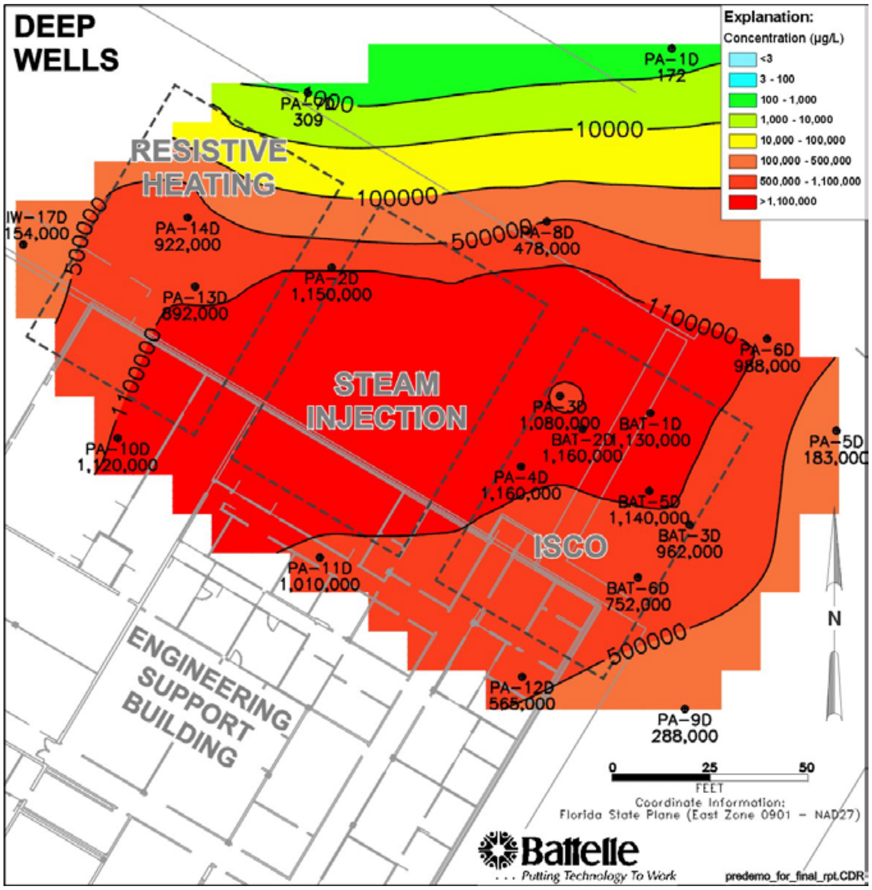


Figure 2-12. Predemonstration Dissolved TCE Concentrations (µg/L) in Deep Wells at Launch Complex 34 (September 1999)

The predemonstration soil sampling indicated that between 6,217 and 9,182 kg of TCE was present in the ISCO plot before the demonstration (see Section 5.1.3). Approximately 5,039 kg of this TCE may occur as DNAPL, based on a threshold TCE concentration of about 300 mg/kg in the soil (see Section 5.1.2). This threshold is determined as the maximum TCE concentration in the dissolved and adsorbed phases in the Launch Complex 34 soil; it was calculated based on properties of the TCE and the subsurface media (the porosity, organic matter content of the soil, etc.) as follows:

$$C_{sat} = \frac{C_{water}\,(K_d \rho_b + n)}{\rho_b} \qquad (2\text{-}1)$$

where C_{sat} = maximum TCE concentration in the dissolved and adsorbed phases (mg/kg)
C_{water} = TCE solubility (mg/L) = 1,100
ρ_b = bulk density of soil (g/cm^3) = 1.59
n = porosity (unitless) = 0.3
K_d = partitioning coefficient of TCE in soil [(mg/kg)/(mg/L)], equal to ($f_{oc} \cdot K_{oc}$)
f_{oc} = fraction organic carbon (unitless)
K_{oc} = organic carbon partition coefficient [(mg/kg)/(mg/L)].

TCE with concentrations below the threshold value of 300 mg/kg was considered dissolved phase; at or above this threshold, the TCE was considered to be DNAPL. The 300-mg/kg figure is a conservative estimate and takes into account the minor variability in the aquifer characteristics, such as porosity, bulk density, and organic carbon content. The native organic carbon content of the Launch Complex 34 soil is relatively low and the threshold TCE concentration is driven by the solubility of TCE in the porewater.

In Figures 2-13 to 2-16, the colors yellow to red indicate presence of DNAPL. As described in Section 4.1.1, contouring software from EarthVision™ was used to divide the plot into isoconcentration shells. A total TCE mass was obtained from multiplying the TCE concentration in each shell by: (1) the volume of the shell; and (2) the

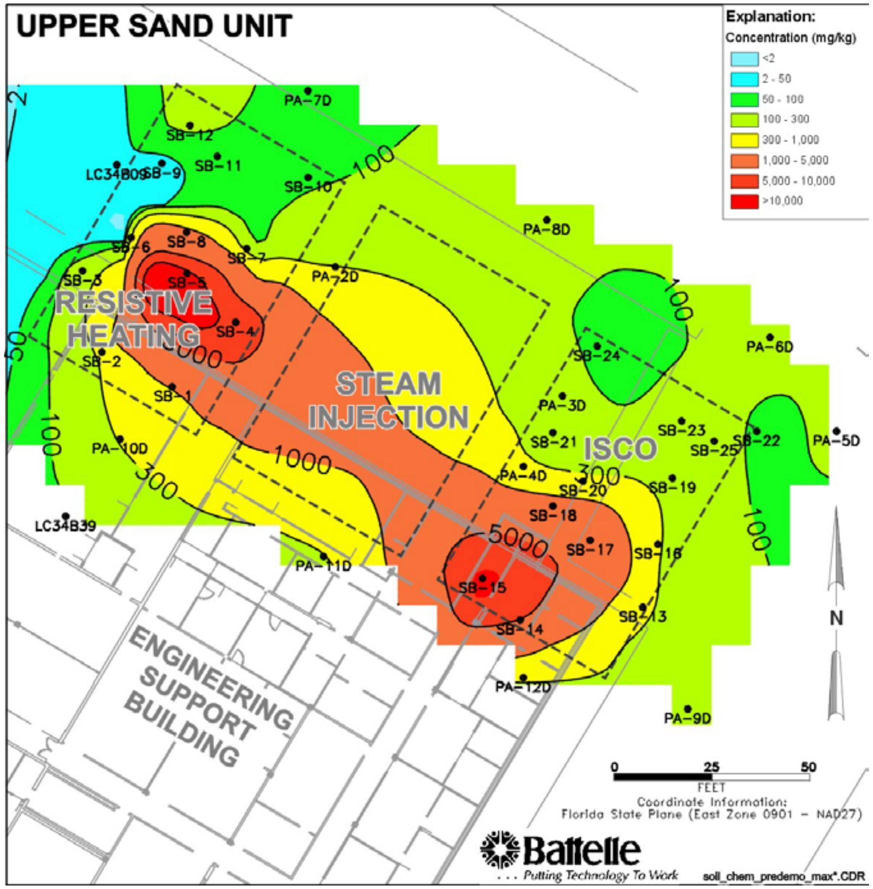


Figure 2-13. Predemonstration TCE Concentrations (mg/kg) in the Upper Sand Unit [-15±2.5 ft msl] Soil at Launch Complex 34 (September 1999)

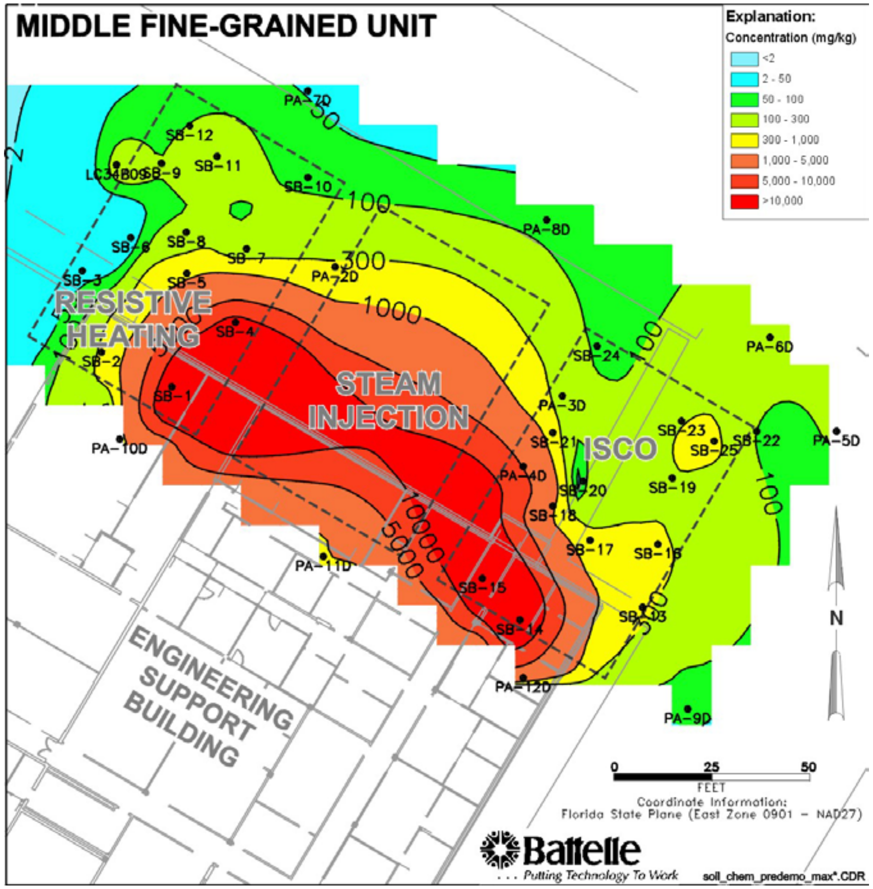


Figure 2-14. Predemonstration TCE Concentrations (mg/kg) in the Middle Fine-Grained Unit [-20±2.5 ft msl] Soil at Launch Complex 34 (September 1999)

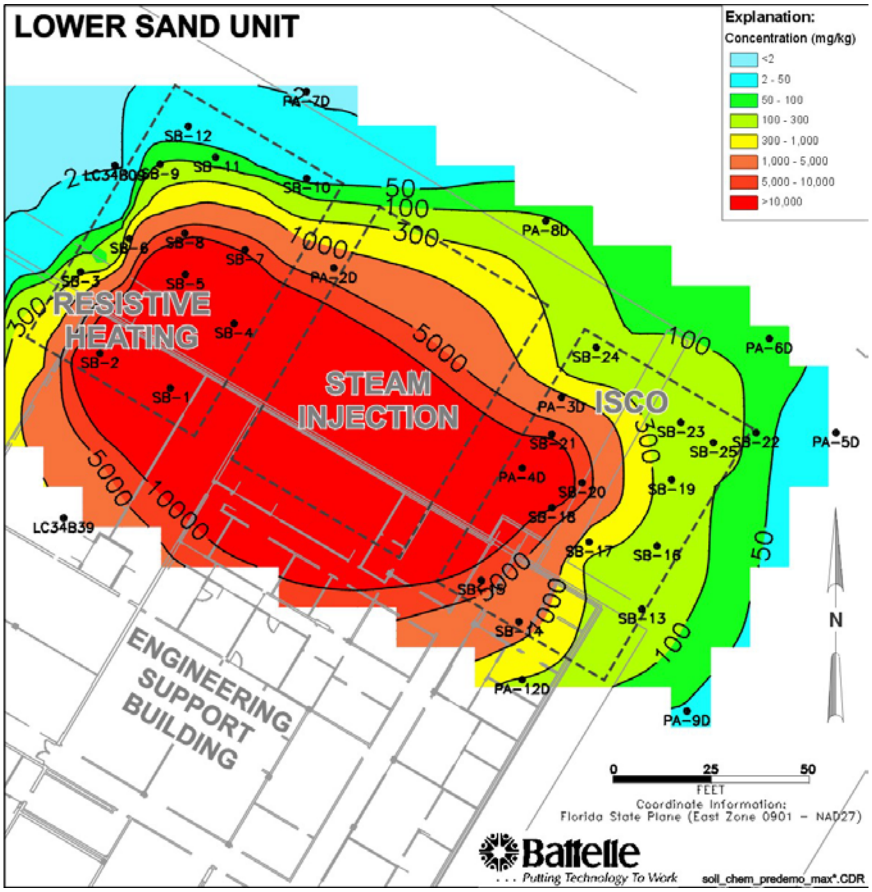


Figure 2-15. Predemonstration TCE Concentrations (mg/kg) in the Lower Sand Unit Unit [–35 ±2.5 ft msl] Soil at Launch Complex 34 (September 1999)

bulk density of the soil. To determine the DNAPL mass in the plot, the TCE mass in the shells containing concentrations greater than 300 mg/kg was used. Section 5.1 contains a more detailed description of the TCE/DNAPL mass estimation procedures for the ISCO plot.

2.4 Aquifer Quality/Geochemistry

Appendix A.3 lists the various aquifer parameters measured and the standard methods used to analyze them. Appendix D contains the results of the predemonstration groundwater analysis. Predemonstration groundwater field parameters were measured in several wells in the demonstration area in August 1999 (Battelle, 1999c). The pH was relatively constant with depth, and ranged from 7.0 to 7.6. Measured dissolved oxygen (DO) levels were mostly less than 1 mg/L in deep wells, indicating that the aquifer was anaerobic. Oxidation-reduction potential (ORP) from all the sampled wells ranged from –165 to –22 millivolts (mV). Total organic carbon (TOC) concentrations in soil samples ranged from 0.9 to 1.7% dry weight basis; some of this TOC might be attributed to DNAPL, as the samples were collected from the DNAPL source region.

Inorganic groundwater parameters were tested in August 1999 in selected wells to determine the predemonstration quality of the groundwater in the target area (Battelle, 1999c). Inorganic parameters of the groundwater in the surficial aquifer at Launch Complex 34 are summarized as follows:

- Total dissolved solids (TDS) concentrations increased sharply with depth, suggesting that the water becomes more brackish with depth. The TDS levels ranged from 387 to 1,550 mg/L. Chloride concentrations ranged from 38 to 752 mg/L and increased sharply with depth, indicating some salt-water intrusion in the deeper layers. These high levels of chloride made a chloride mass balance difficult during the performance assessment.
- Alkalinity levels ranged from 204 to 323 mg/L and showed little trend with depth or distance.

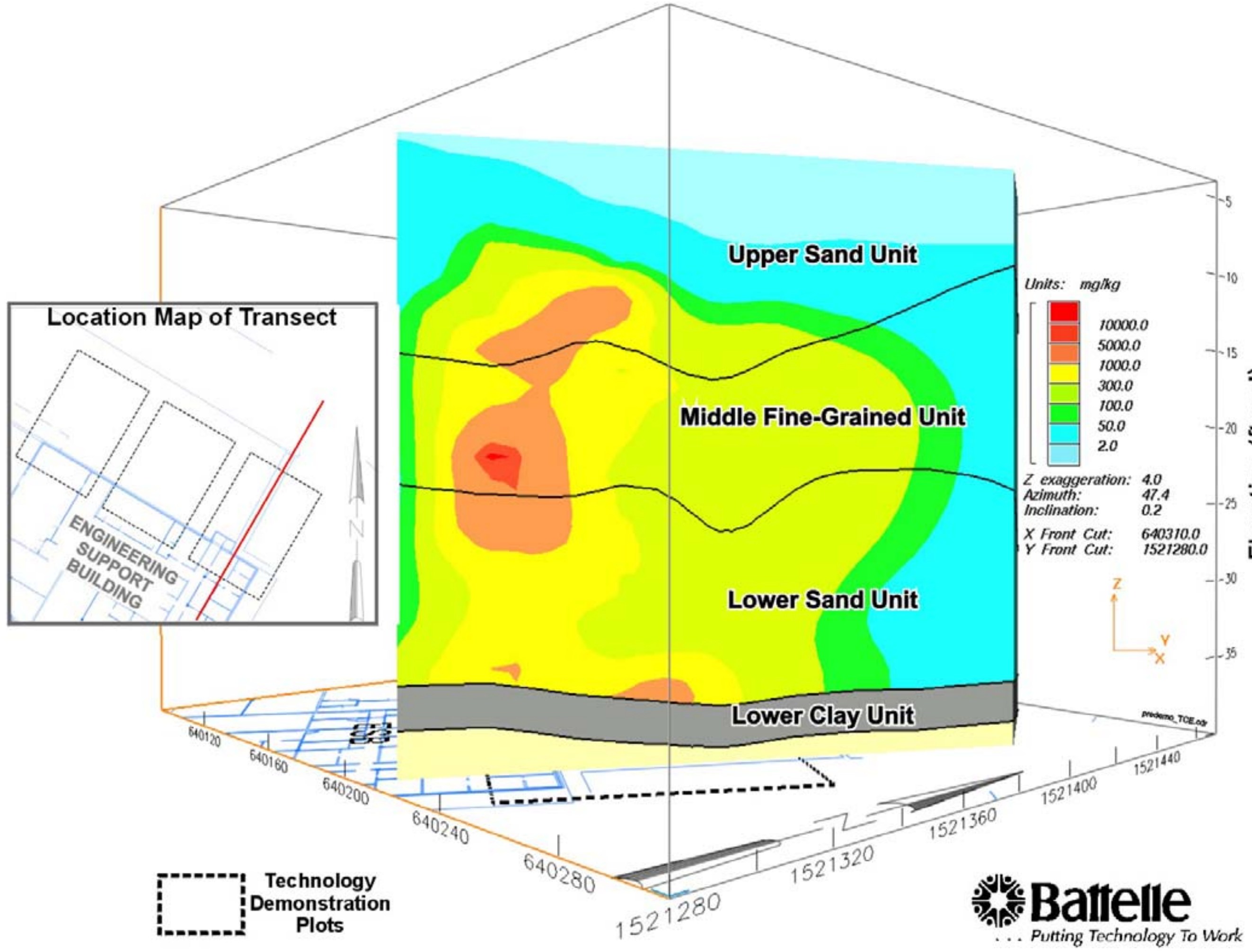


Figure 2-16. Vertical Cross Section through ISCO Plot Showing TCE Soil Concentrations (mg/kg) in the Subsurface

- Iron concentrations ranged from <0.05 to 2.5 mg/L in the groundwater, and manganese concentrations ranged from <0.015 to 1.1 mg/L with little vertical or lateral trend.
- Calcium concentrations ranged from 41 to 88 mg/L and magnesium concentrations ranged from 53 to 84 mg/L.
- Sulfate concentrations were between 29 and 138 mg/L and showed no discernable trends. Nitrate concentrations were below detection.

2.5 Aquifer Microbiology

A separate exploratory microbiological study was conducted in the predemonstration, postdemonstration, and one-year after the demonstration in the ISCO plot under a Work Plan prepared by Battelle and Lawrence Berkeley National Laboratory (Hazen et al., 2000). The approach and results of this study are presented in Appendix E.

3. Technology Operation

This section describes how ISCO technology was implemented at Launch Complex 34.

3.1 ISCO Concept

In an in situ application (see Figure 1-3 and Section 1.3), a chemical oxidant is injected in the subsurface, where it contacts target contaminants and oxidizes them. The main advantage of this technology is that, in many cases, target contaminants can be oxidized to potentially nontoxic products in the ground itself. The benefits of chemical oxidation have been known in the drinking water and wastewater treatment industry for many years. ISCO technology has emerged as a promising option for in situ treatment of contaminated aquifers, especially DNAPL source zones. The oxidant used during the demonstration at Launch Complex 34 was industrial-grade potassium permanganate. The stoichiometric reaction of permanganate with TCE, the primary contaminant at the site, is shown in Equation 3-1.

$$\begin{gathered} 2KMnO_4 + C_2HCl_3 \rightarrow \\ 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^- \end{gathered} \qquad (3\text{-}1)$$

3.2 Regulatory Requirements

Prior to the injection of chemical oxidants such as $KMnO_4$ into the subsurface, an Underground Injection Control (UIC) permit is required, as the potassium permanganate injection may generate byproducts that temporarily exceed drinking water standards. Elevated levels of trace metals were expected in the treated aquifer, given the fact that these metals were present as minor components in the industrial-grade potassium permanganate. For the permanganate demonstration at Launch Complex 34, a variance was obtained from the State of Florida Department of Environmental Protection.

3.3 Application of ISCO Technology at Launch Complex 34

In the IDC demonstration, potassium permanganate was used for in situ oxidation of a DNAPL source zone consisting primarily of TCE. Lesser amounts of *cis*-1,2-DCE are also present in the aquifer at Launch Complex 34. For the purpose of the demonstration, the relatively large source zone was divided into three test plots for three different technology applications. The 75-ft × 50-ft test plot assigned to the ISCO technology is shown in Figure 3-1 and is referred to as the ISCO plot. The ISCO and resistive heating technology demonstrations were conducted concurrently in the two outer plots, which are separated by about 80 ft. The steam injection demonstration will be conducted later.

In their final report (IT Corporation, 2000) on the IDC demonstration, the vendor provided a detailed description of their ISCO equipment, injection methodology, and process measurements. A summary description of the ISCO process implemented by the vendor at Launch Complex 34 follows in this section. Table 3-1 includes a chronology of events constituting the ISCO demonstration and an inventory of the volume of 1 to 2% potassium permanganate solution injected and the mass of $KMnO_4$ consumed. The industrial-grade $KMnO_4$ contains less than 1% of minor impurities (see Appendix I).

The field application of the technology was conducted over a period of 8 months from September 8, 1999 to April 17, 2000. The vendor conducted the field application relatively efficiently, without significant downtime. Because the field system did not involve any complex equipment, maintenance requirements were minimal. This period includes an unexpected interruption from September 13 to 20 due to hurricanes. Other than the hurricanes, the main interruptions were the time intervals between the three series of oxidant injections; these time intervals were used by the vendor to monitor the effectiveness of the oxidant distribution within the plot and by Battelle and the vendor to monitor the degree of interim TCE removal from the plot. The vendor used these breaks to plan each successive series of oxidant injections.

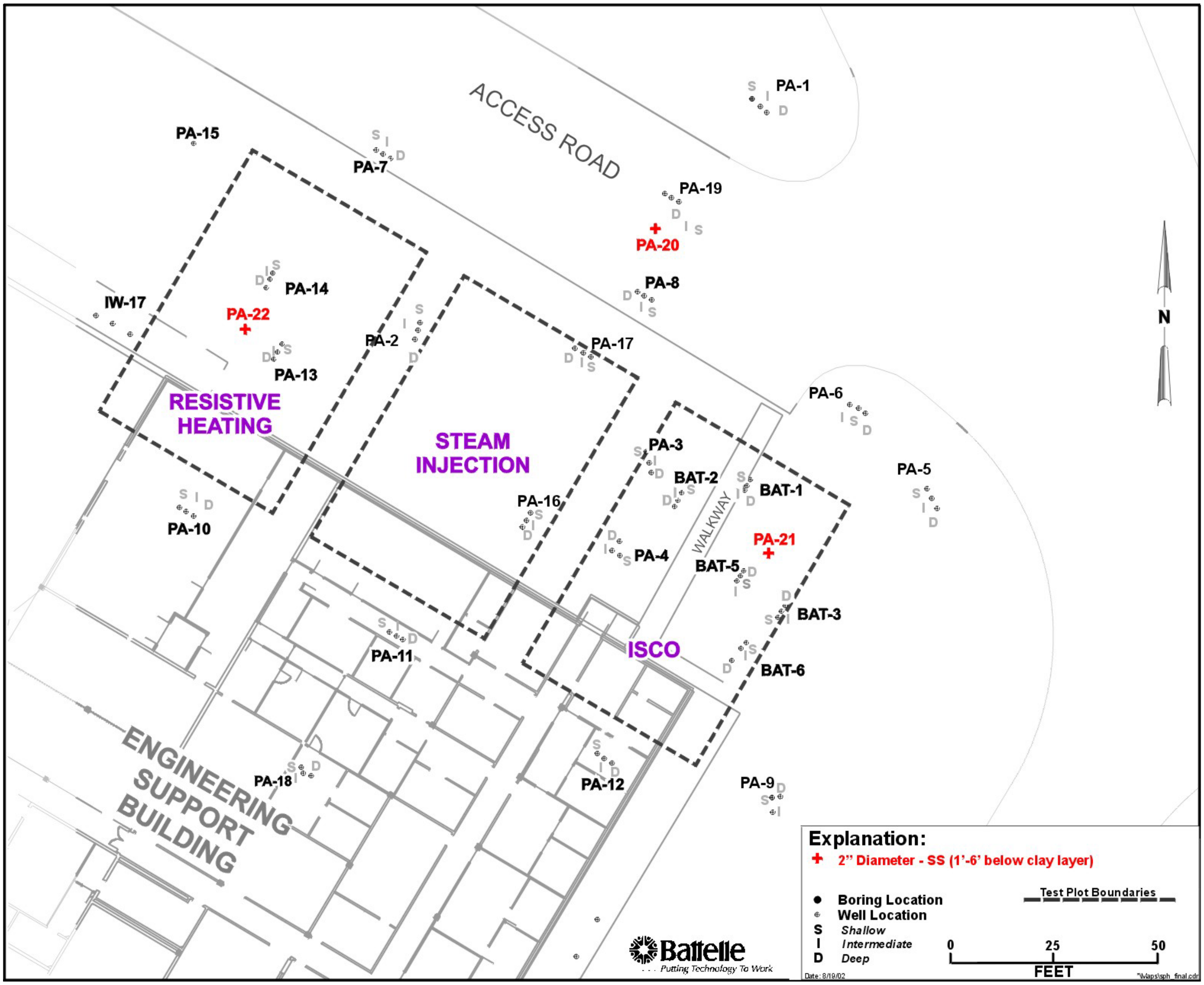


Figure 3-1. The ISCO Plot and Monitoring Well Layout for Performance Assessment

3.3.1 ISCO Equipment and Setup

Figure 3-2 shows a schematic of the aboveground oxidant handling system installed in and around the ISCO plot. Starting with solid potassium permanganate delivered to the site by Carus Chemical Company, Inc. (Carus), the vendor prepared and injected a 1.4 to 2% permanganate solution in the plot. The permanganate injection concentration used was the highest that the vendor projected they could use without causing trace metal levels to increase significantly in the aquifer. Carus also designed and supplied a continuous mix and automated feed system for the demonstration. The feed system consisted of a portable dry bulk hopper to store and feed solid permanganate to the mixer, where hydrant water was added to make the desired injection solution. A single delivery consisted of 45,000 lb of free-flowing–grade permanganate that was transferred to the hopper by a solids blower (see Appendix I). (The permanganate was manufactured in July 1998 by Carus, and delivered from Carus' lot No. 20.) An auger screw conveyor transferred the permanganate from the hopper to the mixing tank. This system was automated to provide the desired flowrate and permanganate concentration, as well as to shut down if a pressure loss (pipe leak) or pressure spike (clogging) was detected in the injection lines. Figure 3-3 is a photograph of the aboveground oxidant handling system installed at Launch Complex 34.

The solution in the mixing tank was transferred to the injection well manifold using a high-pressure dual chemical feed pump. To handle the strong oxidant, the pump

Table 3-1. ISCO Technology Demonstration Schedule

Start Date	End Date	No. of Days	Events/Injection Stage	Volume of $KMnO_4$ solution injected (gal)	Mass of $KMnO_4$ injected (kg)[(a)]	Comments
June 18, 1998	–	–	Solicitation received from IDC	–	–	Final cost proposal for design submitted by IT on 7/13/98.
August 20, 1998	Oct 20, 1998	60	Design/modeling/treatability tests	–	–	Design report submitted on 10/20/98. Cost proposal for installation and operation submitted on 3/10/99.
March 11, 1999	April 8, 1999	28	IDC approval to proceed with final design and installation	–	–	Final design/construction report submitted on 6/24/99.
August 2, 1999	Sept 5, 1999	34	Mobilization to site and setup	–	–	
April 1, 1999	June 25, 1999	90	Test Plan/QAPP	–	–	
June 21, 1999	July 17, 1999	27	Predemonstration characterization of plot	–	–	
August 12,1999	August 14, 1999	3	Tracer Test ($KMnO_4$ with Sodium Fluoride)	8,980	1,401	
Sept 8, 1999	Sept 27, 1999	8	First injection (Phase 1) in Upper Sand Unit	85,793	6,059	Standby for hurricane from 9/13/99 through 9/20/99.
Sept 28, 1999	Oct 12, 1999	9	First injection (Phase 1) in Middle Fine-Grained Unit	93,228	8,484	Equipment downtime on 10/4-5/99 and 10/8/99.
Oct 12, 1999	Oct 29, 1999	15	First injection (Phase 1) in Lower Sand Unit	125,742	13,904	
			Break			Evaluate results of first injection
Nov 17, 1999	Nov 24, 1999	8	Second injection (Phase 2) in Upper Sand Unit	65,892	4,923	
Nov 22, 1999	Nov 24, 1999	3	Second injection (Phase 2) in Middle Fine-Grained Unit	21,591	1,348	
–	–	–	Second injection (Phase 2) in Lower Sand Unit	–	–	No injection in Lower Sand Unit
			Break			Evaluate results of second injection
March 30, 2000	April 7, 2000	8	Third injection (Phase 3) in Upper Sand Unit	43,665	3,372	
April 6, 2000	April 17, 2000	8	Third injection (Phase 3) in Middle Fine-Grained Unit	59,421	4,589	Equipment downtime from 4/11/00 to 4/12/00.
March 20, 2000	April 17, 2000	22	Third injection (Phase 3) in Lower Sand Unit	347,653	24,277	
May 8, 2000	May 30, 2000	22	Postdemonstration characterization of plot	–	–	
			Break			Evaluate postdemonstration characterization results
February 1, 2001	February 28, 2001	28	Extended monitoring of plot	–	–	

(a) This is the mass of the industrial-grade potassium permanganate (containing less than 1% minor impurities) that was used.

was made from 316 stainless steel with Teflon® seals and was rated for pumping 80 pounds per square inch gage (psig) of water at 10 to 40 gallons per minute (gpm). Before reaching the injection manifold, the permanganate solution was passed through a 1,500-lb high-pressure sand filter to remove any particulates. Expected particulate matter in the permanganate solution included the 1% sand present in the technical-grade (free flow) potassium permanganate (to improve its flow characteristics), partially dissolved potassium permanganate, and any MnO_2 precipitates formed during the mixing of permanganate solids with reduced species in the hydrant water.

The vendor used polyvinyl chloride (PVC) pressure hoses with dry-disconnect quick-connect fittings to transport the oxidant solution. A grating box was placed under the premanifold and manifold piping for secondary containment in case of leaks or spills. Oxidant flow was metered to 11 individual drive stems through the injection manifold. The vendor avoided using rubber hoses, galvanized steel piping, or other materials incompatible with the strong oxidant. High-density polyethylene (HDPE) tanks, PVC pipes and hoses, stainless steel appurtenances, and polyvinylidene fluoride (PVDF) or Teflon® gaskets were used. Figure 3-4 is a photograph of the oxidant injection manifold.

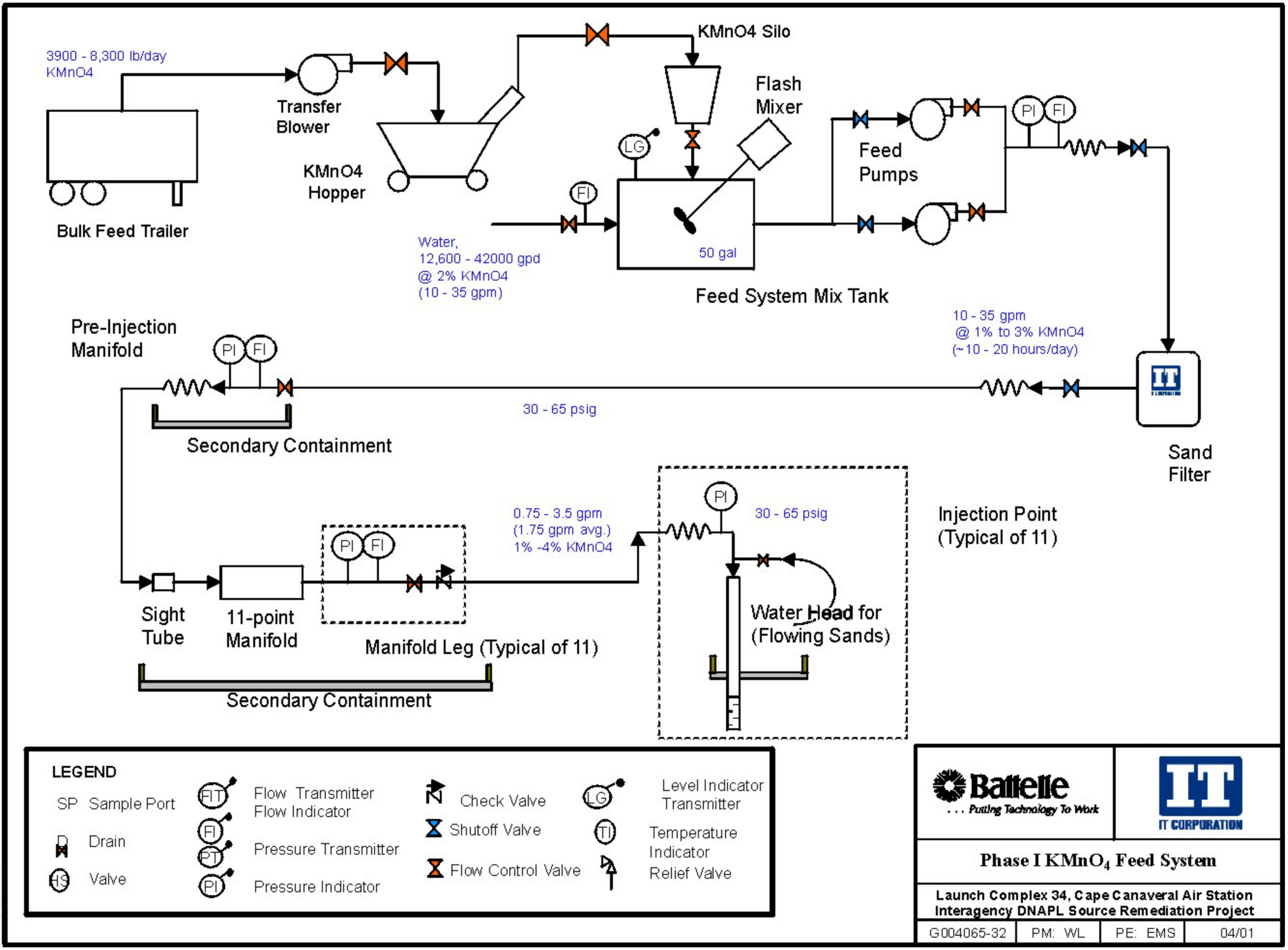


Figure 3-2. Aboveground Oxidant Handling System Installed at Launch Complex 34

Figure 3-3. ISCO Setup at Launch Complex 34 Showing Permanganate Storage Hopper and Mixer

Figure 3-4. Oxidant Preinjection Manifold

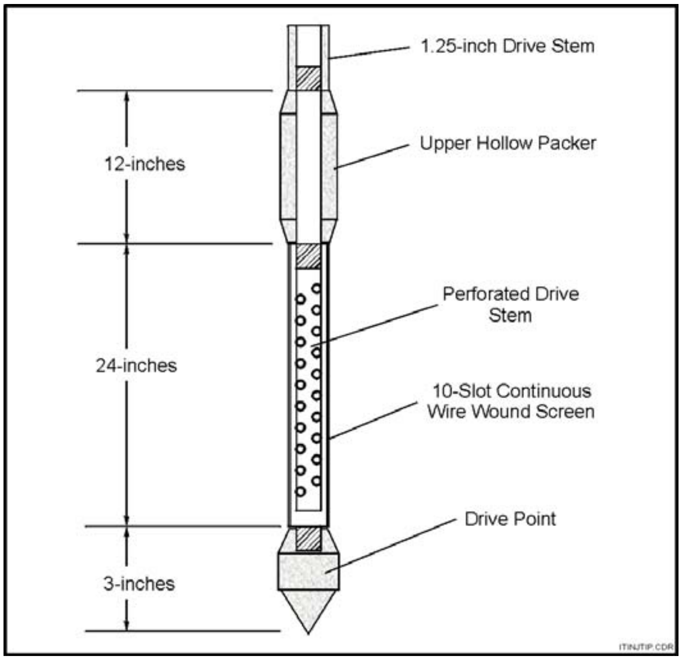


Figure 3-5. Schematic of the ISCO Injection Tip Used by the Vendor (Source: IT Corporation, 2000)

The vendor designed a custom injection tip (see Figure 3-5) that was used at the end of a direct-push drive rod for delivery of the oxidant to the aquifer. A separate downhole drive rod and injection tip were used at each of the 11 injection points used in the first injection (Phase 1). A single direct-push rig was used to advance all 11 injection points to the first injection interval at 15 ft bgs. Oxidant was injected from all 11 points simultaneously. The rig then was used to advance each injection tip and casing 2 ft at a time, stopping at each interval to inject oxidant. The two wider-diameter sections above and below the perforated drive stem and 10-slot wire-wound screen served as packers during the injection and prevented smearing across the borehole walls, thus minimizing fouling of the screen. A shorter screen allowed the vendor to focus injections into the desired low- or high-permeability strata encountered at different depths; longer screens would have caused the injected oxidant to preferentially enter the high-permeability strata.

3.3.2 ISCO Field Operation

Before full deployment of their injection strategy, the vendor conducted a tracer test at an injection point (IP-1, see Figure 3-6) of the ISCO plot to evaluate the injection flowrate and radius of influence in the entire hydrostratigraphic units and finalize the treatment design. The tracer used was a combination of 1.4 to 2% potassium permanganate solution and 2 mg/L of pharmaceutical-grade sodium fluoride. The sodium fluoride concentration was targeted to stay below the primary drinking water standard of 2 µg/L. The potassium permanganate was used as a reactive tracer to determine permanganate consumption and retardation characteristics of the aquifer; the fluoride was used as a nonreactive, nonadsorptive tracer to evaluate the radius of influence and hydraulic flow characteristics in the aquifer. The vendor gained the following important information from the tracer test:

- The sustainable injection flowrate in this aquifer ranges from 2.6 to 5.0 gpm.
- The aquifer is anisotropic with preferential flow to the north and south. Fluoride tracer was detected 26 ft north and south, but only 18 ft east and west from the injection point.

The vendor conducted the ISCO plot treatment in three phases. The chronology of the oxidation field activities is given in Table 3-1. As shown in Figure 3-6, Phase 1 (first injection cycle) consisted of 11 more-or-less equally spaced injection locations. At each location, the oxidant was injected sequentially with every 2-ft depth interval.

The amount of permanganate injected at each location and depth was based on prior knowledge of the TCE/DNAPL distribution in the plot gained from the predemonstration characterization. The vendor injected higher amounts of permanganate at depths known to contain higher concentrations of DNAPL. The injection pressure and flowrate were used to control the radius of influence, which was also a determinant of the time period of injection at a given depth. Permanganate measurements in various multilevel wells installed throughout the plot were used to verify the radius of influence. For this purpose, the vendor installed the multilevel wells (MP-#) shown in Figure 3-6. In addition to the vendor's wells (such as MP #), Battelle installed monitoring wells BAT-1 to BAT-6 and PA-4 cluster wells for an independent performance assessment of the technology.

For approximately one month after Phase 1 injections, the vendor monitored the plot with a combination of groundwater and soil sampling to evaluate the effectiveness of the oxidation at different points in the plot. During this time, the vendor identified regions of the plot that appeared to have received less than the desired dose of oxidant, as indicated either by persistently higher levels of TCE or lower levels of permanganate. The distinctive discoloration of groundwater and soil exposed to different levels of permanganate was an obvious indicator of the efficiency of oxidant distribution in a given region. Phase 2 injections (second injection cycle) were directed towards regions of residual contamination in the Upper Sand Unit and Middle Fine-Grained Unit.

After another break, during which the vendor monitored the plot to evaluate the effectiveness of Phase 2 injections, Phase 3 injections (third injection cycle) were conducted to polish off the remaining CVOCs in all three units (Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit). During the break after Phase 2, the vendor modified the equipment and injection scheme as follows, to improve the mass throughput of oxidant into the aquifer:

- The 45,000-lb hopper was replaced by 3,300-lb "Cycle Bin" skidded containers from Carus. A forklift was rented to switch cycle bins as each bin was emptied. This change eliminated the moisture condensation and hardening of permanganate solids experienced in the larger hopper.
- To eliminate the pressure drop and fouling in the sand filter, this filter was replaced by a 21,000-gal steel "frac" tank with an epoxy liner. This tank provided flow equalization, storage, and sufficient area for settling of solids from the solution.
- An injection pump was added to convey the oxidant solution from the frac tank to the injection manifold. These changes improved the overall flow from 23 gpm to 40 gpm and increased the mass throughput of oxidant to the aquifer.
- Nine more injection tips were added to the 11 previous injection tips to obtain better coverage of the plot.
- The maximum $KMnO_4$ concentration was reduced from 3% (the maximum allowed to fulfill regulatory requirements on trace metals) to 2% to allow for better dissolution in the volume available in the mixing tank. This change eliminated fouling problems due to persistence of undissolved permanganate particles.

The vendor's measurements show that average injection flow rates varied from 0 to 5.4 gpm at individual injection locations, using average injection pressures from 20 to 41 psig (IT Corporation, 2000); the flow variation was due to the variable resistance to flow in different parts of the plot. For example, the southwest corner of the plot (under the Engineering Support Building) permitted very

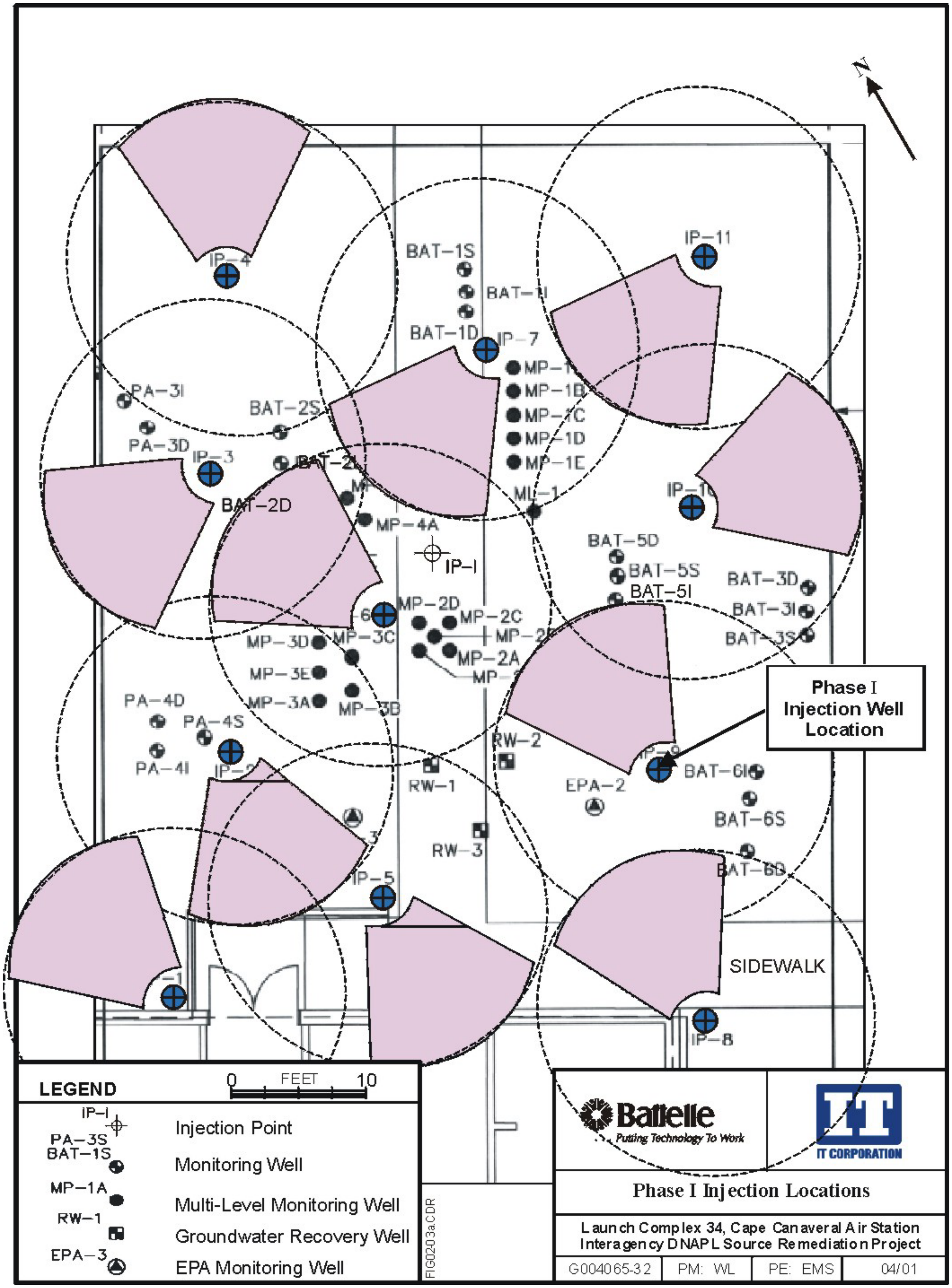


Figure 3-6. Phase 1 Injection Locations and Radii of Influence of the Injected Oxidant

little or no flow; this part of the plot also had the highest DNAPL mass. On the other hand, other regions of high-DNAPL mass in the plot were more conducive to flow.

The vendor estimates that hydraulic displacement from several injection points exceeded 30 ft. However, the radius of permanganate distribution around each injection point was probably less than 10 ft, and varied based on the hydraulic conductivity and TCE/organic matter content of the surrounding aquifer. Such variations were unpredictable, with instances where an injection point would permit only 0 to 0.1 gpm of flow within one horizontal foot of a point that permitted 2 to 3 gpm. Permanganate was injected for durations of up to 4 days at each given injection point. Between 8 to 20 points were injected simultaneously. Between oxidant injections, water was kept flowing through the injection tips to maintain sufficient static head to prevent fine sands and silt from fouling the tips.

During the treatment, the vendor injected a total of 842,985 gal of permanganate solution into the ISCO plot aquifer (see Table 3-1), which corresponds to 66,956 kg (150,653 lb) of $KMnO_4$ mass. On average, the oxidant loading equates to 2.5 kg of $KMnO_4$ per kilogram of soil in the test plot. Not all of the injected permanganate stayed in the test plot; some may have migrated to the surrounding aquifer. The vendor initially based the desired oxidant loading on the results of treatability tests, and the amount and distribution of TCE in the test plot. However, as the treatment progressed, the vendor adjusted the amount of oxidant injected at each location and at each depth based on field indicators, such as visual observation and analysis of groundwater from neighboring monitoring wells.

The hydrant water used for preparing the solution contained 3.8 mg/L of TOC, which adds up to 27 lb of TOC that could have consumed approximately 107 lb of permanganate (assuming a 4:1 potassium permanganate-to-TOC ratio). Approximately 22 drums or 9,300 lb of sludge was generated during the filtration of the injected liquid. After accounting for the sand (about 1,500 lb or 1% by weight of the potassium permanganate stock) that was present in the delivered solid potassium permanganate and some amount of MnO_2 generated, the vendor estimates that most of these solids were undissolved permanganate. This indicates that the mixing tank (50 gal) may have been sized too small. The permanganate supplier indicated that one option in the future to reduce the level of undissolved solids would be to use sodium permanganate, which is available as a solution, instead of solid potassium permanganate (Lowe et al., 2002).

3.4 Health and Safety Issues

Use of heavy equipment (hopper, GeoProbe®, mixer, pumps, and forklift) and a strong oxidant (potassium permanganate) were the main hazards encountered during the demonstration. The vendor's personnel wore Level D personal protective equipment during the demonstration. Steel-toed shoes and hard hats were worn when dealing with heavy equipment. Safety glasses were worn when dealing with the oxidant. Sometimes, operators wore Tyvek® suits when handling the oxidant injection apparatus. A solution consisting of vinegar, hydrogen peroxide, and water was kept handy in a spray bottle and used for neutralizing any oxidant spills on the ground or on clothing. This solution was used whenever a hose burst or oxidant surged up into a monitoring well vault adjacent to an injection point.

The vendor reported an incidental airborne release of $KMnO_4$ while filling the silo with dry permanganate. The release abated when the hatch was sealed tighter. Fugitive dust from the cycle bin feeder in the equipment enclosure had to be abated periodically by spraying the enclosure with the neutralizing solution while wearing respiratory protection. The only incident that caused a slight concern occurred during demobilization, when the hopper used for storage of potassium permanganate solids toppled over as the permanganate supplier was dismounting it and loading it on a truck. There were no injuries during the demonstration.

4. Performance Assessment Methodology

Battelle, in conjunction with the U.S. EPA SITE Program and TetraTech EM, Inc., conducted an independent performance assessment of the ISCO demonstration at Launch Complex 34 (see Figure 4-1). The objectives and methodology for the performance assessment were outlined in a QAPP prepared before the field demonstration and reviewed by all stakeholders (Battelle, 1999d). The objectives of the performance assessment were:

- Estimating the TCE/DNAPL mass removal
- Evaluating changes in aquifer quality due to the treatment
- Evaluating the fate of TCE/DNAPL removed from the ISCO plot
- Verifying ISCO operating requirements and costs.

The first objective, estimating the TCE/DNAPL mass removal percentage, was the primary objective. The rest were secondary objectives in terms of demonstration focus and resources expended. Table 4-1 summarizes the four objectives of the performance assessment and the methodologies used to achieve them.

Figure 4-1. Sampling for Performance Assessment at Launch Complex 34

4.1 Estimating TCE/DNAPL Mass Removal

The primary objective of the performance assessment was to estimate the mass removal of total TCE and DNAPL. Total TCE includes both dissolved- and free-phase TCE present in the aquifer soil matrix. DNAPL refers to free-phase TCE only and is defined by the threshold TCE concentration of 300 mg/kg described in Section 2.3. The method used for estimating TCE/DNAPL mass removal was soil sampling in the ISCO plot before and after the demonstration.

At the outset of the demonstration, the Technical Advisory Group, formed by a group of independent academic, government, and industrial representatives, proposed 90% DNAPL mass removal as a target for the three remedial technologies being demonstrated. This target represented an aggressive treatment goal for the technology vendors. Soil sampling was the method selected in the QAPP for determining percent TCE/DNAPL removal at this site. Previous soil coring, sampling, and analysis at Launch Complex 34 (Battelle, 1999b; Eddy-Dilek, 1998) had shown that this was a viable technique for identifying the boundaries of the DNAPL source zone and estimating the DNAPL mass. The advantage of soil sampling was that relatively intensive horizontal and vertical coverage of the ISCO plot, as well as of the dissolved-phase TCE and DNAPL distribution, could be achieved with a reasonable number of soil samples and without DNAPL access being limited to preferential flowpaths in the aquifer. Soil sampling was conducted before (predemonstration event), immediately after (postdemonstration event), and nine months after (extended monitoring event) the ISCO application.

Although the primary focus of the performance assessment was on TCE, *cis*-1,2-DCE and vinyl chloride, contaminants that could be oxidized by permanganate also were measured in the soil samples; however, high TCE

Table 4-1. Summary of Performance Assessment Objectives and Associated Measurements

Objective	Measurements	Sampling Locations[(a)]
Estimating TCE/ DNAPL mass removal	CVOCs in soil; once before and twice after treatment	12 horizontal locations, every 2-ft depth interval
Evaluating changes in aquifer quality	CVOCs in groundwater; before, during, and after treatment	Primarily well clusters BAT-2 and BAT-5; other plot wells (BAT-1, BAT-3, BAT-6, and PA-4) sampled to guide oxidant injections
	Field parameters in groundwater; before, during, and after treatment	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)] for verifying spread
	Inorganic parameters in groundwater (cations, anions, including alkalinity); before and after treatment	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)] for verifying spread
	Trace metals in groundwater; before, during, and after treatment	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)] for verifying spread
	TOC in soil; before and after treatment	Two locations, three depths inside plot
	TDS and BOD; before and after treatment	Primarily well clusters BAT-2 and BAT-5
	Hydraulic conductivity; before and after treatment	BAT-5S, BAT-6S, BAT-3I, BAT-5I, BAT-6I, BAT-3D, and BAT-6D
Evaluating fate of TCE/DNAPL	Chloride in groundwater	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)]
	Alkalinity in groundwater	Primarily well clusters BAT-2 and BAT-5
	Hydraulic gradients	All wells
	Potassium ion in groundwater	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)]
	Potassium permanganate in groundwater	Primarily well clusters BAT-2 and BAT-5; perimeter wells[(b)]
	Surface emissions; primarily during oxidant injection	Three locations inside plot; 3 background locations
Verifying operating requirements and cost	Field observations; tracking materials consumption and costs	Field observations by vendor and Battelle; materials consumption and costs reported by vendor to MSE

(a) Monitoring well locations inside and outside the ISCO plot are shown in Figure 3-1. Soil coring locations are shown in Figures 4-2 (predemonstration) and 4-3 (postdemonstration).

(b) Perimeter wells are PA-3, PA-5, PA-9, and PA-12. Distant wells PA-1, PA-8, and PA-11, as well as other wells in the vicinity, were sampled for various parameters, based on ongoing data acquisition and interpretation during the demonstration.

levels often masked the other two compounds and made their detection difficult.

The statistical basis for determining the number of soil coring locations and number of soil samples required to be collected in the ISCO plot is described in Appendix A.1. Based on the horizontal and vertical variability observed in the TCE concentrations in soil cores collected during preliminary site characterization in February 1999, a systematic unaligned sampling approach was used to divide the plot into a 4 × 3 grid and collect one soil core in each grid cell for a total of 12 soil cores (soil cores SB-13 to SB-24 shown in Figure 4-2). The resulting 12 cores provided good spatial coverage of the 75-ft × 50-ft ISCO plot and included two cores inside the Engineering Support Building. For each soil core, the entire soil column from ground surface to aquitard (approximately 45 ft bgs) was sampled and analyzed in 2-ft sections. Sets of 12 cores each were similarly collected after the demonstration (SB-213 to SB-224) and nine months after the demonstration (SB-313 to SB-324 in corresponding locations), as shown in Figure 4-3. Each sampling event, therefore, consisted of nearly 300 soil samples (12 cores, 23 two-foot intervals per core, plus duplicates). The thicker dashed lines in Figures 4-2 and 4-3 represent the predemonstration DNAPL source boundary. This boundary includes all the soil coring locations where at least one of the soil samples (depth intervals) showed TCE levels above 300 mg/kg.

Soil coring, sampling, and extraction methods are described in Appendix A.2 and summarized in this section. Figures 4-4 and 4-5 show the outdoor and indoor rigs used for soil coring outside and inside the Engineering Support Building. A direct-push rig with a 2-inch diameter, 4-ft-long sample barrel was used for coring. As soon as the sample barrel was retrieved, the 2-ft section of core was split vertically and approximately one-quarter of the core (approximately 200 g of wet soil) was deposited into a predetermined volume (250 mL) of methanol for extraction in the field. The methanol extract was transferred into 20-mL volatile organic analysis (VOA) vials, which were shipped to a certified laboratory for analysis. The sampling and extraction technique used at this site provided better coverage of a heterogeneously distributed contaminant distribution as compared to the more conventional method of collecting and analyzing small soil samples at discrete depths, because

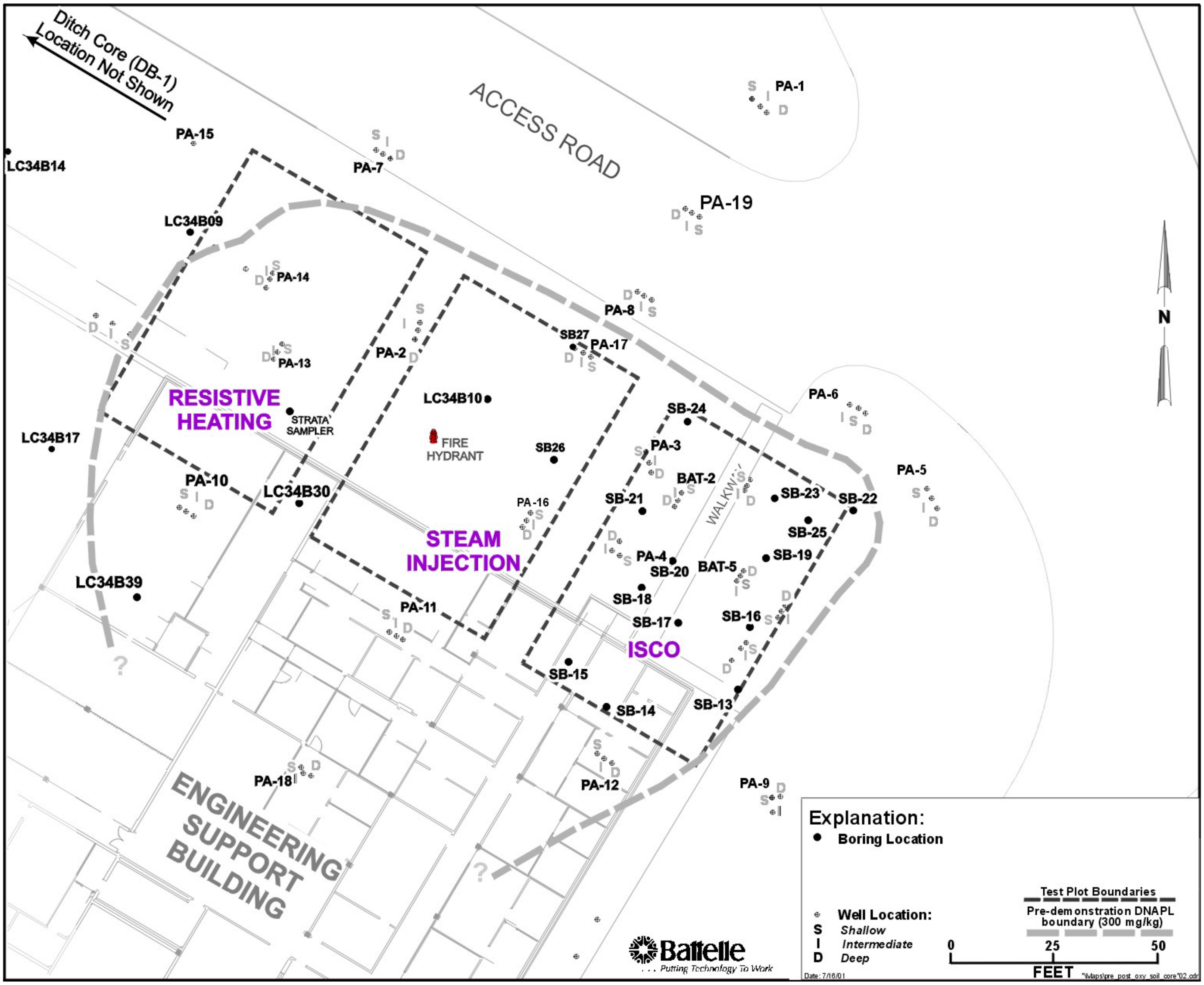


Figure 4-2. Predemonstration Soil Coring Locations (SB-13 to SB-24) in ISCO Plot (June 1999)

the entire vertical depth of the soil column at the coring location could be analyzed. Preliminary site characterization had showed that the vertical variability of the TCE distribution was greater than the horizontal variability, and this sampling and extraction method allowed continuous vertical coverage of the soil column. The efficiency of TCE recovery by this method (modified EPA Method 5035; see Appendix A.2) was evaluated through a series of tests conducted for the demonstration (see Appendix G). In these tests, a surrogate compound (trichloroethane [TCA]) was spiked into soil cores from the Launch Complex 34 aquifer, extracted, and analyzed. Replicate extractions and analysis of a spiked surrogate (TCA) indicated a CVOC recovery efficiency between 84 and 113% (with an average recovery of 92%), which was considered sufficiently accurate for the demonstration.

Two data evaluation methods were used for estimating TCE/DNAPL mass removal in the ISCO plot: linear interpolation or contouring, and kriging. The spatial variability or spread of the TCE distribution in a DNAPL source zone typically is high, the reason being that small pockets of residual solvent may be distributed unevenly across the source region. The two methods address this spatial variability in different ways, and therefore the resulting mass removal estimates differ slightly. Because it is impractical to sample every single point in the ISCO plot and obtain a true TCE mass estimate for the plot, both methods basically address the practical difficulty of estimating the TCE concentrations at unsampled points by interpolating (estimating) between sampled points. The objective in both methods is to use the information from a limited sample set to make an inference about the entire population (the entire plot or a stratigraphic unit).

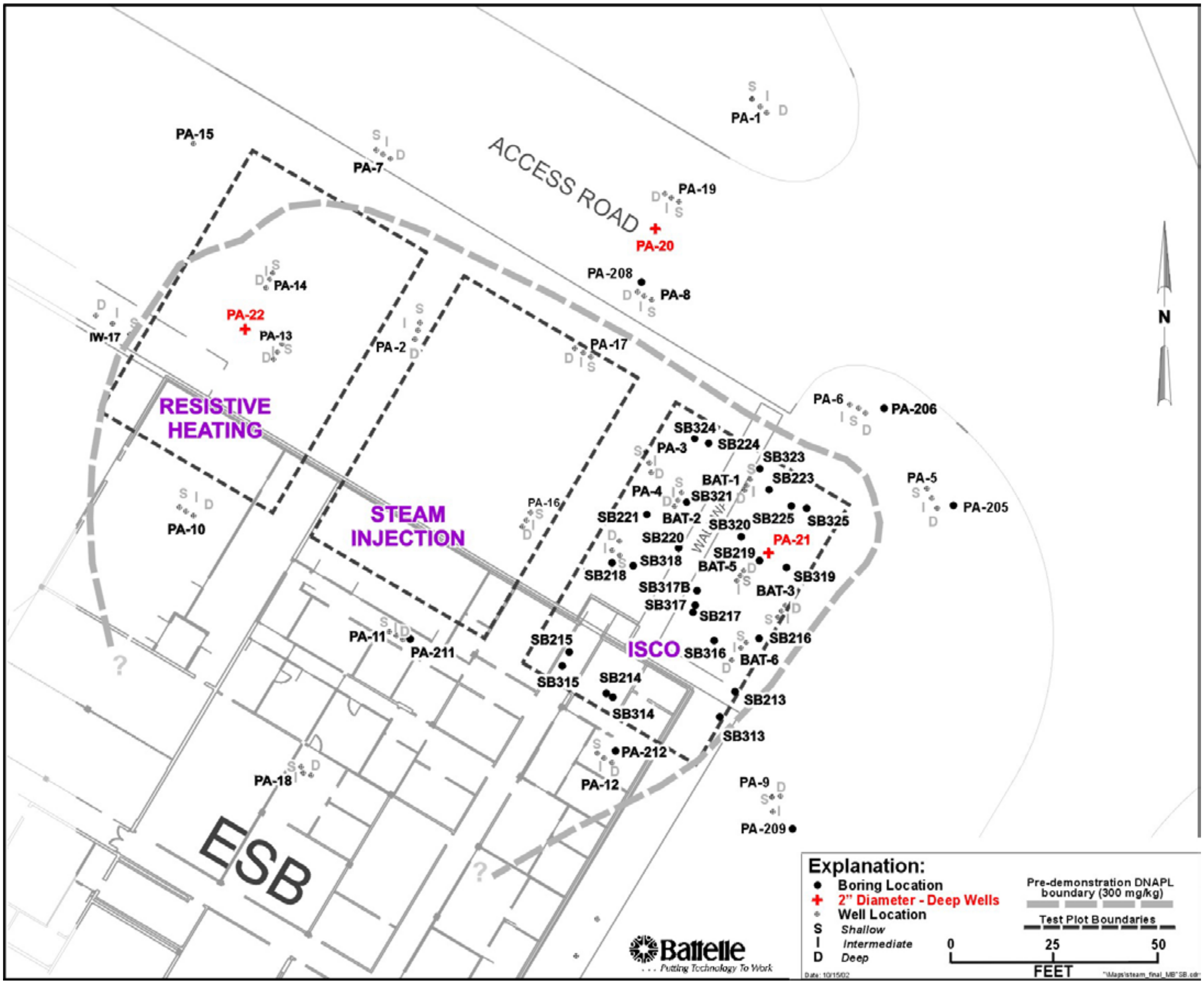


Figure 4-3. Postdemonstration Soil Coring Locations SB-213 to SB-224 in the Test Plot (May 2000) (the corresponding extended monitoring soil coring locations are similarly numbered SB-313 to SB-324 [February 2001])

4.1.1 Linear Interpolation

Linear interpolation is the more straightforward and intuitive method for estimating TCE concentration or mass in the entire plot, based on a limited number of sampled points. TCE concentrations are assumed to be linearly distributed between sampled points. A software program, such as EarthVision™, has an edge over manual calculations in that it is easier to conduct the linear interpolation in three dimensions. In contouring, the only way to address the spatial variability of the TCE distribution is to collect as large a number of samples as is practical so that good coverage of the plot is obtained; the higher the sampling density, the smaller the distances over which the data need to be interpolated.

For linear interpolation, input parameters must be adjusted to accommodate various references such as geology and sample size. Nearly 300 soil samples were collected from the 12 coring locations in the plot during each event (predemonstration and postdemonstration), which was the highest number practical within the resources of this project. Appendix A (Section A.1.1) describes how the number and distribution of these sampling points were determined to obtain good coverage of the plot.

The contouring software EarthVision™ uses the same methodology that is used for drawing water level contour maps based on water level measurements at discrete locations in a region. The only difference with this software is that the TCE concentrations are mapped in three

Figure 4-4. Outdoor Cone Penetrometer Test Rig for Soil Coring at Launch Complex 34

Figure 4-5. Indoor Vibra-Push Rig (LD Geoprobe$^{®}$ Series) Used in the Engineering Support Building

dimensions to generate iso-concentration shells (i.e., volumes of soil that fall within a specified concentration range). The average TCE concentration of each shell is multiplied by the volume of the shell (as estimated by the volumetric package in the software) and the bulk density of the soil (1.59 g/cm^3, estimated during preliminary site characterization) to estimate a TCE mass for each shell. The TCE mass in each region of interest (Upper Sand Unit, Middle-Fine-Grained Unit, Lower Sand Unit, and the entire plot) is obtained by adding up the portion of the shells contained in that region. The DNAPL mass is obtained by adding up the masses in only those shells that have TCE concentrations above 300 mg/kg. Contouring provides a single mass estimate for the region of interest.

4.1.2 Kriging

Kriging is a geostatistical interpolation tool that takes into consideration the spatial correlations among the TCE data in making inferences about the TCE concentrations at unsampled points. Spatial correlation analysis determines the extent to which TCE concentrations at various points in the plot are similar or different. Generally, the degree to which TCE concentrations are similar or different is a function of distance and direction. Based on these correlations, kriging determines how the TCE concentrations at sampled points can be optimally weighted to infer the TCE concentrations/masses at unsampled points in the plot or the TCE mass in an entire region of interest (entire plot or stratigraphic unit). Kriging accounts for the uncertainty in each point estimate by calculating a standard error for the estimate. Therefore a range of TCE mass estimates is obtained instead of a single estimate; this range is defined by an average and a standard error or by a confidence interval. The confidence or level of significance required by the project objectives determines the width of this range. A level of significance of 0.2 (or 80% confidence) was determined as necessary at the beginning of the demonstration (Battelle, 1999d).

4.1.3 Interpreting the Results of the Two Mass Removal Estimation Methods

The two data evaluation methods address the spatial variability of the TCE distribution in different ways and, therefore, the resulting mass removal estimates differ slightly between the two methods. This section discusses the implication of these differences.

In both contouring and kriging, TCE mass removal is accounted for on an absolute basis; higher mass removal in a few high-TCE concentration portions of the plot can offset low mass removal in other portions of the plot, to infer a high level of mass removal. Kriging probably provides a more informed inference of the TCE mass removal than contouring because it takes into account the spatial correlations in the TCE distribution and the uncertainties (error) associated with the estimates. At the same time, because a large number of soil samples were collected during each event, the results in Section 5.1 show that contouring was able to overcome the spatial variability to a considerable extent and provide mass estimates that were generally in agreement with the ranges provided by kriging.

4.2 Evaluating Changes in Aquifer Quality

A secondary objective of the performance assessment was to evaluate any short-term changes in aquifer quality due to the treatment. ISCO affects both the contaminant and the native aquifer characteristics. Pre- and postdemonstration measurements conducted to evaluate the short-term impacts of the technology application on the aquifer included:

- CVOC measurements in the groundwater inside the ISCO plot
- Field parameter measurements (pH, Eh, DO, ORP, temperature, and conductivity) in the groundwater
- Inorganic measurements (common cations and anions) in the groundwater
- Selected trace metals
- TDS and 5-day biological oxygen demand (BOD)
- TOC measurements in the soil
- Hydraulic conductivity of the aquifer
- Microbial populations in the aquifer (see Figure 4-6 and Appendix E).

These measurements were conducted primarily in monitoring wells within the plot, but some measurements also were made in the perimeter and distant wells.

4.3 Evaluating the Fate of the TCE/DNAPL Mass Removed

Another secondary objective was to evaluate the fate of the TCE removed from the plot by ISCO treatment. Possible pathways (or processes) for the TCE removed from the plot include oxidation (destruction of TCE) and migration from the ISCO plot (to the surrounding regions). These pathways were evaluated by the following measurements:

Figure 4-6. Collecting and Processing Groundwater Samples for Microbiological Analysis

- Chloride in groundwater (mineralization of CVOCs leads to formation of chloride) and other inorganic constituent in groundwater
- Alkalinity in groundwater (oxidation of CVOCs and native organic matter leads to formation of CO_2 which, in a closed system, forms carbonate)
- Hydraulic gradients (injection of oxidant solution creates gradients indicative of groundwater movement)
- Potassium ion in the ISCO plot and surrounding wells (potassium ion from potassium permanganate addition acts as a semi-conservative tracer for tracking movement of injected solution)
- $KMnO_4$ in groundwater (presence of excess $KMnO_4$ indicates completeness of oxidation in the vicinity of the sample)
- Surface emission tests were conducted as described in Appendix F to evaluate the potential for CVOC losses to the vadose zone and atmosphere (see Figure 4-7)
- CVOC concentration in the semi-confined aquifer below the test plot.

Figure 4-7. Surface Emissions Testing at Launch Complex 34

Potential for Migration to the Semi-Confined Aquifer

During the week of April 2, 2001, Battelle installed three wells into the semi-confined aquifer with a two-stage (dual-casing) drilling and completion process with a mud rotary drill rig provided by Environmental Drilling Services, Inc., from Ocala, Florida. Figure 4-8 shows the location of these wells (PA-20, PA-21, and PA-22). The objective of installing these deeper wells was to evaluate the potential presence of CVOC contamination in the confined aquifer and to assess any effect of the DNAPL remediation demonstration on the confined aquifer.

These wells were first proposed in 1999, but the IDC and Battelle decided to forgo their construction because of NASA's concerns over breaching the relatively thin aquitard (i.e., the Lower Clay Unit). Subsequently, nonintrusive geophysical tests indicated the possibility of DNAPL in the semi-confined aquifer (Resolution Resources, 2000). It was not clear whether any DNAPL in the semi-confined aquifer (approximately 50 to 120 ft bgs) would be related to the demonstration activities. However, the IDC and Battelle decided that there were enough questions about the status of this aquifer that it would be worthwhile taking the risk to characterize the deeper aquifer. Suitable precautions would be taken to mitigate any risk of downward migration of contamination during the well installation.

Westinghouse Savannah River Company (WSRC) sent an observer to monitor the field installation of the wells. The observer verified that the wells were installed properly and that no drag-down of contaminants was created during their installation.

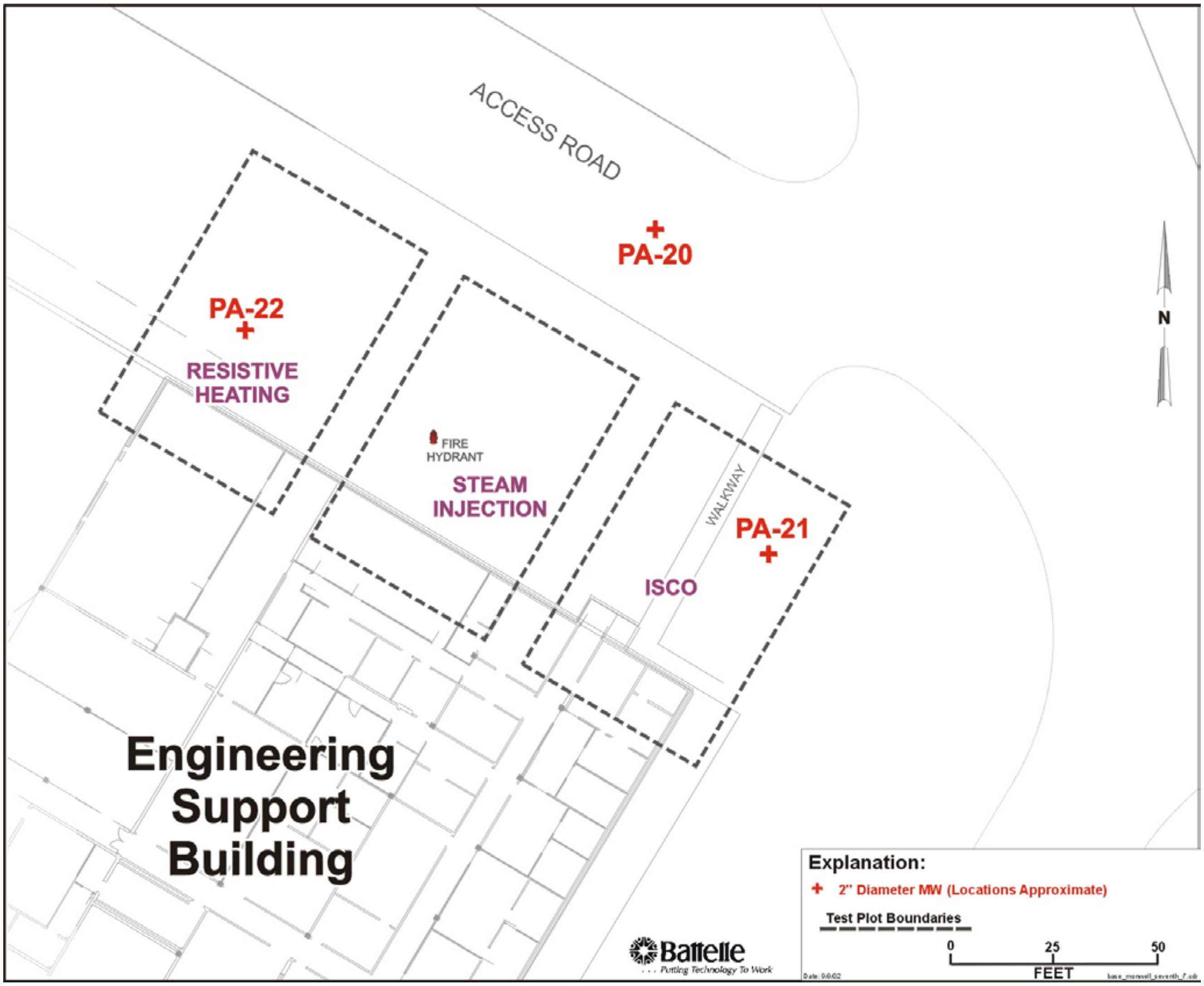


Figure 4-8. Location Map of Semi-Confined Aquifer Wells at Launch Complex 34

4.3.1 Geologic Background at Launch Complex 34

Several aquifers are present at the Launch Complex 34 area, reflecting a barrier island complex overlying coastal sediments (Figure 4-9). The surficial aquifer is comprised of layers of silty sand and shells. It extends down to about 45 ft bgs, where the Lower Clay Unit (aquitard) is encountered. Previous logging suggested that the Lower Clay Unit is 3 ft thick and consists of gray clay with low to medium plasticity. A 40- to 50-ft-thick semi-confined aquifer (Caloosahatchee Marl formation or equivalent) resides under the Lower Clay Unit and is composed of silty to clayey sand and shells. The semi-confined aquifer is confined in the Launch Complex 34 area. Underlying the semi-confined aquifer is the Hawthorne formation, a clayey sand-confining layer. The limestone Floridan Aquifer underlies the Hawthorne formation and is a major source of drinking water for much of Florida. Table 4-2 summarizes the character and water-bearing properties of the hydrostratigraphic units in the area.

4.3.2 Semi-Confined Aquifer Well Installation Method

Figure 4-10 shows the well completion diagram for the three semi-confined aquifer wells. In the first stage of well installation, a 10-inch borehole was advanced to about 45 ft bgs and completed with 6-inch blank stainless steel casing. The surface casing was advanced until it established a key between the "surface" casing and the confining unit (Lower Clay Unit). The borehole was grouted around the surface casing. Once the grout around the 6-inch surface casing had set, in the second stage, a 5⅞-inch borehole was drilled through the inside of the surface casing to a depth of 61 ft bgs. A 2-inch casing with screen was advanced through the deeper borehole to set the well. This borehole also was grouted around the 2-inch casing. These measures were undertaken to prevent any DNAPL from migrating to the confined aquifer. Figure 4-11 shows the surface casing and inner (screened well) casing for the dual-casing wells installed at Launch Complex 34. The detailed installation method for these wells is described in the following paragraphs.

To verify the depth of the confining unit at each well location, a 3⅞-inch pilot hole first was installed to a depth of 40 ft using a tricone roller bit. After this pilot hole was drilled, split-spoon samples were collected in 2-ft (or 1-ft) intervals as soils were observed and logged in search of the top interface of the clay confining unit or aquitard. Upon retrieval of a 2-ft split-spoon sample, the borehole then was deepened to the bottom of the previously spooned interval. Once the previously spooned interval was drilled, the drilling rods and bit were pulled

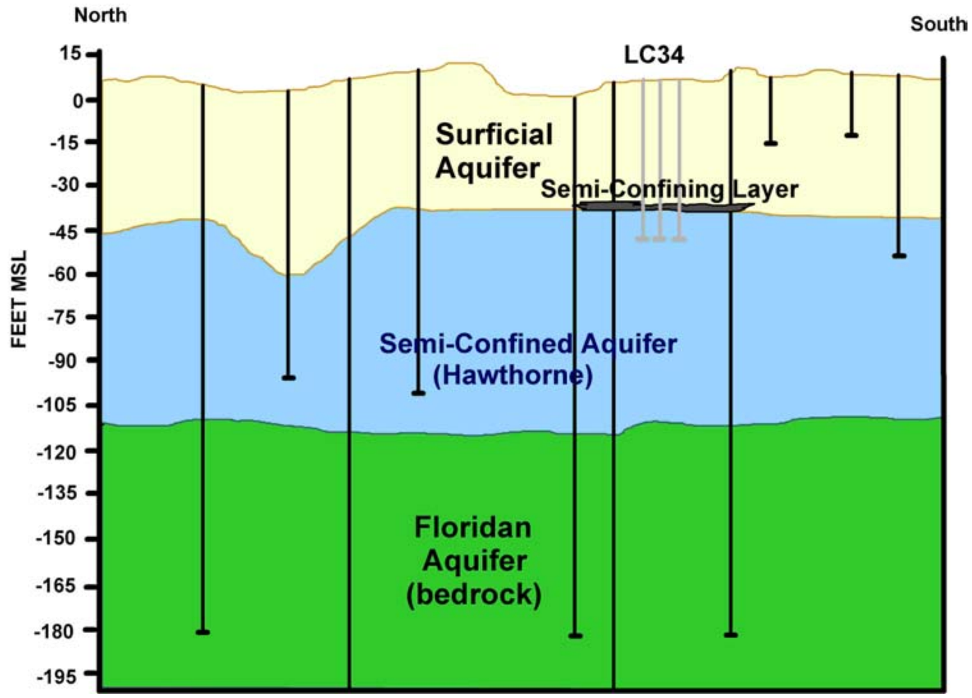
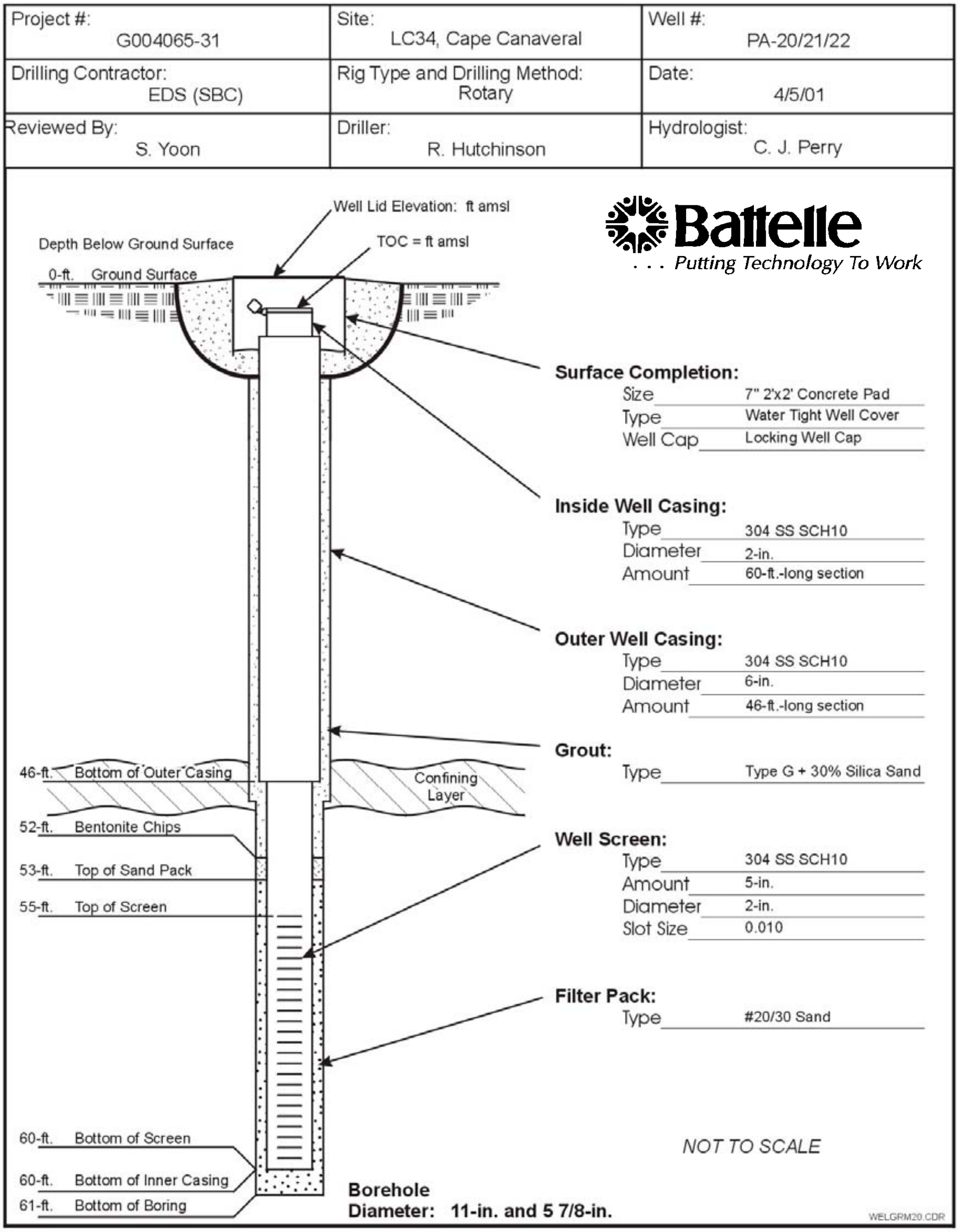


Figure 4-9. Regional Hydrogeologic Cross Section through the Kennedy Space Center Area (after Schmalzer and Hinkle, 1990)

Table 4-2. Hydrostratigraphic Units of Brevard Country, Florida[a]

Geologic Age	Stratigraphic Unit		Approximate Thickness (ft)	General Lithologic Character	Water-Bearing Properties
Recent (0.1 MYA-present)	Pleistocene and Recent Deposits		0-110	Fine to medium sand, coquina and sandy shell marl.	Permeability low due to small grain size, yields small quantities of water to shallow wells, principal source of water for domestic uses not supplied by municipal water systems.
Pleistocene (1.8-0.1 MYA)					
Pliocene (1.8-5 MYA)	Upper Miocene and Pliocene Deposits (Caloosahatchee Marl)		20-90	Gray to greenish gray sandy shell marl, green clay, fine sand, and silty shell.	Permeability very low, acts as confining bed to artesian aquifer, produces small amount of water to wells tapping shell beds.
Miocene (5-24 MYA)	Hawthorne Formation		10-300	Light green to greenish gray sandy marl, streaks of greenish clay, phosphatic radiolarian clay, black and brown phosphorite, thin beds of phosphatic sandy limestone.	Permeability generally low, may yield small quantities of fresh water in recharge areas, generally permeated with water from the artesian zone. Contains relatively impermeable beds that prevent or retard upward movement of water from the underlying artesian aquifer. Basal permeable beds are considered part of the Floridan aquifer.
Eocene (37-58 MYA)	Ocala Group	Crystal River Formation	0-100	White to cream, friable, porous coquina in a soft, chalky, marine limestone.	Floridan aquifer: Permeability generally very high, yields large quantities of artesian water. Chemical quality of the water varies from one area to another and is the dominant factor controlling utilization. A large percentage of the groundwater used in Brevard County is from the artesian aquifer. The Crystal River Formation will produce large quantities of artesian water. The Inglis Formation is expected to yield more than the Williston Formation. Local dense, indurate zones in the lower part of the Avon Park Limestone restrict permeability but in general the formation will yield large quantities of water.
		Williston Formation	10-50	Light cream, soft, granular marine limestone, generally finer grained than the Inglis Formation, highly fossiliferous.	
		Inglis Formation	70+	Cream to creamy white, coarse granular limestone, contains abundant echinoid fragments.	
	Avon Park Limestone		285+	White to cream, purple tinted, soft, dense chalky limestone. Localized zones of altered to light brown or ashen gray, hard, porous, crystalline dolomite.	

(a) Source: Schmalzer and Hinkle (1990).
MYA = million years ago.



Project #: G004065-31	Site: LC34, Cape Canaveral	Well #: PA-20/21/22
Drilling Contractor: EDS (SBC)	Rig Type and Drilling Method: Rotary	Date: 4/5/01
Reviewed By: S. Yoon	Driller: R. Hutchinson	Hydrologist: C. J. Perry

Surface Completion:
Size 7" 2'x2' Concrete Pad
Type Water Tight Well Cover
Well Cap Locking Well Cap

Inside Well Casing:
Type 304 SS SCH10
Diameter 2-in.
Amount 60-ft.-long section

Outer Well Casing:
Type 304 SS SCH10
Diameter 6-in.
Amount 46-ft.-long section

Grout:
Type Type G + 30% Silica Sand

Well Screen:
Type 304 SS SCH10
Amount 5-in.
Diameter 2-in.
Slot Size 0.010

Filter Pack:
Type #20/30 Sand

Borehole Diameter: 11-in. and 5 7/8-in.

Figure 4-10. Well Completion Detail for Semi-Confined Aquifer Wells

out of the hole and replaced with a new split spoon that was driven another 2 ft ahead of the borehole. Standard penetration tests (i.e., blow counts) were conducted and logged during each split-spoon advance. The blow counts were useful in identifying the soil types that are penetrated during spooning. They also were useful in helping to determine the exact interval of soil recovered from spoons that lacked total recovery. The split-spoon soil samples were logged. The soils were visually logged for soil type and description, photoionization detector (PID) scans were run, and at least one soil sample per 2-ft spoon interval was collected for methanol extraction and analysis.

Figure 4-11. Pictures Showing (a) Installation of the Surface Casing and (b) the Completed Dual-Casing Well

Once the top portion (approximately the first 1.5 ft) of the confining unit was retrieved by split spoons in each borehole, the spoon and rods were pulled out of the borehole and the hole was reamed with a 10-inch tricone rotary drill bit to the depth of the lowest spooned interval. Before the 6-inch diameter casing was set in the hole, a PVC slipcap was placed on the bottom of the casing to keep it free of drilling mud and soil. Use of slip caps was an added precaution to prevent any possibility of downward contamination. As the casing was lowered in the hole, it was filled with clean water to prevent it from becoming buoyant. When the casing was set to the drilled depth of about 45 ft, it was grouted in place.

After the grout was allowed to set for at least 24 hours, the slipcap was drilled through with a 5⅞-inch roller bit. Then split-spoon sampling progressed through the remainder of the confining unit and into the confined aquifer. Split-spoon samples were collected totaling 4 ft of lifts before the hole was reamed with the 5⅞-inch bit as fresh drilling mud was circulated in the hole. Split-spooning progressed to a depth of 60 ft. Each hole was reamed an extra foot, to 61 ft, before the screen and casing were set. A sand pack was tremied into place from total depth to 2 ft above the top of the well screen (about 53 ft bgs). A bentonite seal (placed as a slurry) then was tremied in about the sand pack before the remainder of the casing was tremie-grouted into place with a Type G cement and silica flour slurry.

Once the split-spoon samples showed that the Lower Clay Unit had been reached, the 6-inch-diameter surface casing was set and grouted into place with a Type G (heat-resistant) cement and silica flour grout slurry. The drilling mud used for advancing the boreholes consisted of a product called "Super Gel-X bentonite." This powdered clay material was mixed with clean water in a mud pit that was set and sealed to the borehole beneath the drilling platform. The drilling mud was mixed to a density and viscosity that is greater than both groundwater and the bulk density of soil. This mud was pumped down through the drill pipe, out through the drill bit, and then pushed upward (circulated) through the borehole annulus into the mud pit (open space between the drilling rods and borehole wall). Use of the mud stabilizes the borehole, even in sandy soils, enabling advancement of the borehole in depths well below the water table without heaving or caving. The mud seals the borehole walls, preventing the borehole from being invaded by groundwater and contaminants. The mud also lifts all of the cuttings created by the drill bit as the hole is advanced. Once the drilling mud rose to the top of the annulus, it was captured in the mud pit where cuttings were removed by a series of baffles through which the mud was circulated.

The mud pit was monitored with a PID throughout the drilling process. At no time did the PID detect VOCs in the drilling mud, indicating that no significant levels of contamination were entering the borehole and being carried downward into cleaner aquifer intervals as the drilling advanced.

After each well was installed, it was developed using a 3-ft-long stainless steel bailer and a small submersible pump. Bailing was done to surge each well and lift the coarsest sediments. The submersible pump then was used to lift more fines that entered the well as development progressed. A total of at least three well volumes (approximately 27 gal) were lifted from each well. Groundwater sampling was performed following well development. Standard water quality parameters were measured during sampling, and groundwater samples were collected after these parameters became stable.

4.4 Verifying Operating Requirements and Costs

Another secondary objective of the demonstration was to verify the vendor's operating requirements and cost for the technology application. The vendor prepared a detailed report describing the operating requirements and costs of the ISCO application (IT Corporation, 2000). An operating summary based on this report is provided in Section 3.2. Costs of the technology application also were tracked by MSE, the DOE contractor who subcontracted the ISCO vendor. Site characterization costs were estimated by Battelle and TetraTech EM, Inc.

5. Performance Assessment Results and Conclusions

The results of the performance assessment methodology outlined in Section 4 are described in this section.

5.1 Estimating TCE/DNAPL Mass Removal

Sections 2.3 and 4.1 describe the methodology used to estimate the masses of total TCE and DNAPL removed from the plot due to the application of ISCO technology at Launch Complex 34. Intensive soil sampling was the primary tool for estimating total TCE and DNAPL mass removal. Total TCE refers to both dissolved-phase and DNAPL TCE. DNAPL refers to that portion of total TCE in a soil sample that exceeds the threshold concentration of 300 mg/kg (see Section 2.3). Pre- and postdemonstration concentrations of TCE at 12 soil coring locations (nearly 300 soil samples) inside the ISCO plot were tabulated and graphed to *qualitatively* identify changes in TCE/DNAPL mass distribution and efficiency of the ISCO application in different parts of the plot (Section 5.1.1). In addition, TCE/DNAPL mass removal was *quantified* by two methods:

- Contouring (Section 5.1.2)
- Kriging (Section 5.1.3)

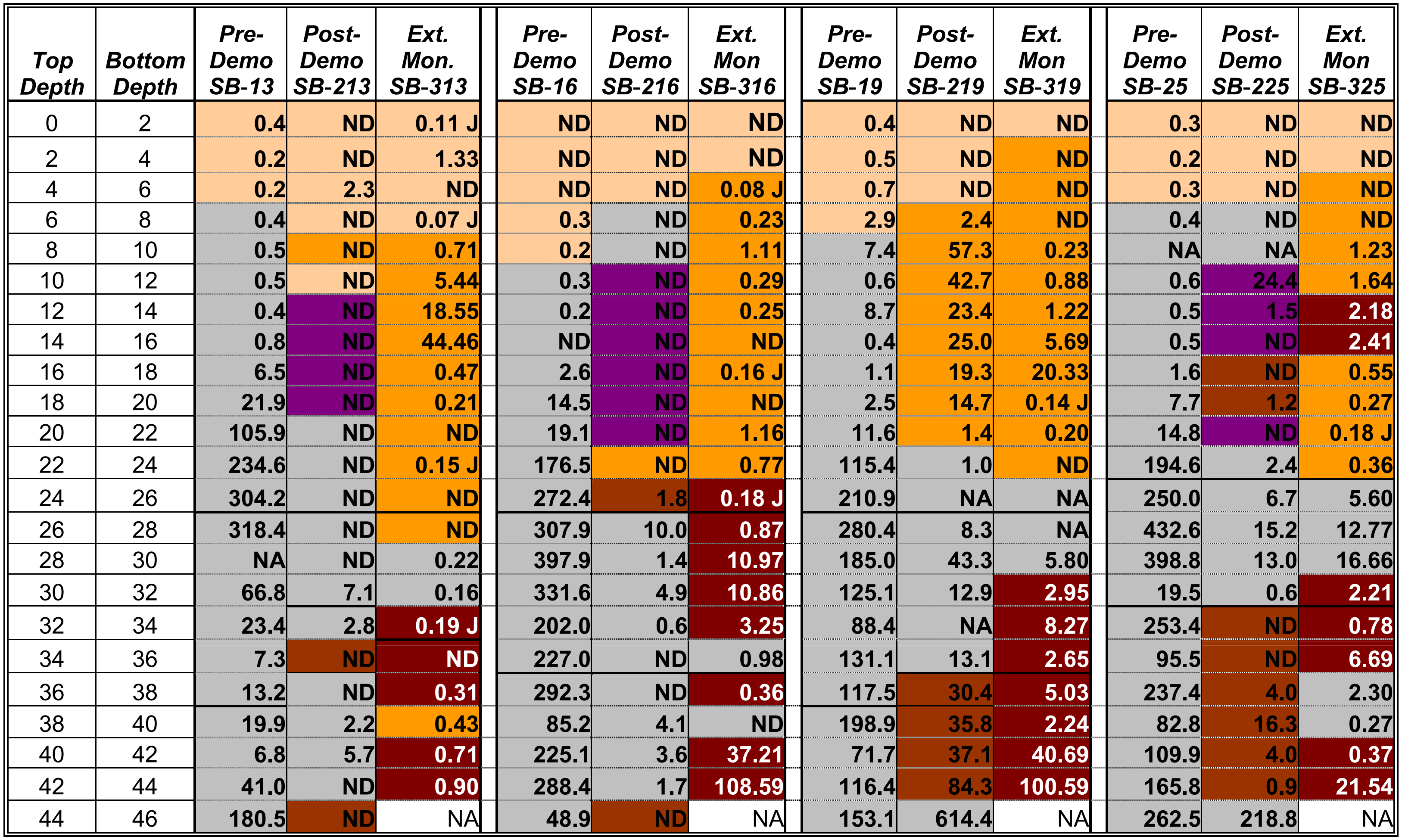
These quantitative techniques for estimating TCE/DNAPL mass removal due to the ISCO application are described in Section 4.1; the results are described in Sections 5.1.2 through 5.1.3.

5.1.1 Qualitative Evaluation of Changes in TCE/DNAPL Distribution

Figure 5-1 charts the concentrations of TCE in the soil samples from the 12 coring locations in the ISCO plot, as measured during the predemonstration, postdemonstration, and extended monitoring events (nine months after end of demonstration). This chart allows a simple comparison of the pre- and postdemonstration (or extended monitoring) TCE concentrations at paired locations. The colors in the chart indicate the color observed in each soil sample at 2-ft intervals. The gray and tan colors are the natural colors of the Launch Complex 34 soil. The orange color indicates mildly oxidizing conditions, when the first trace of oxidant reaches the soil and native iron precipitates out as ferric compounds. The brown color probably indicates moderately oxidizing conditions where MnO_2, a byproduct of TCE and native organic matter oxidation, has formed. The purple color indicates an excess of permanganate.

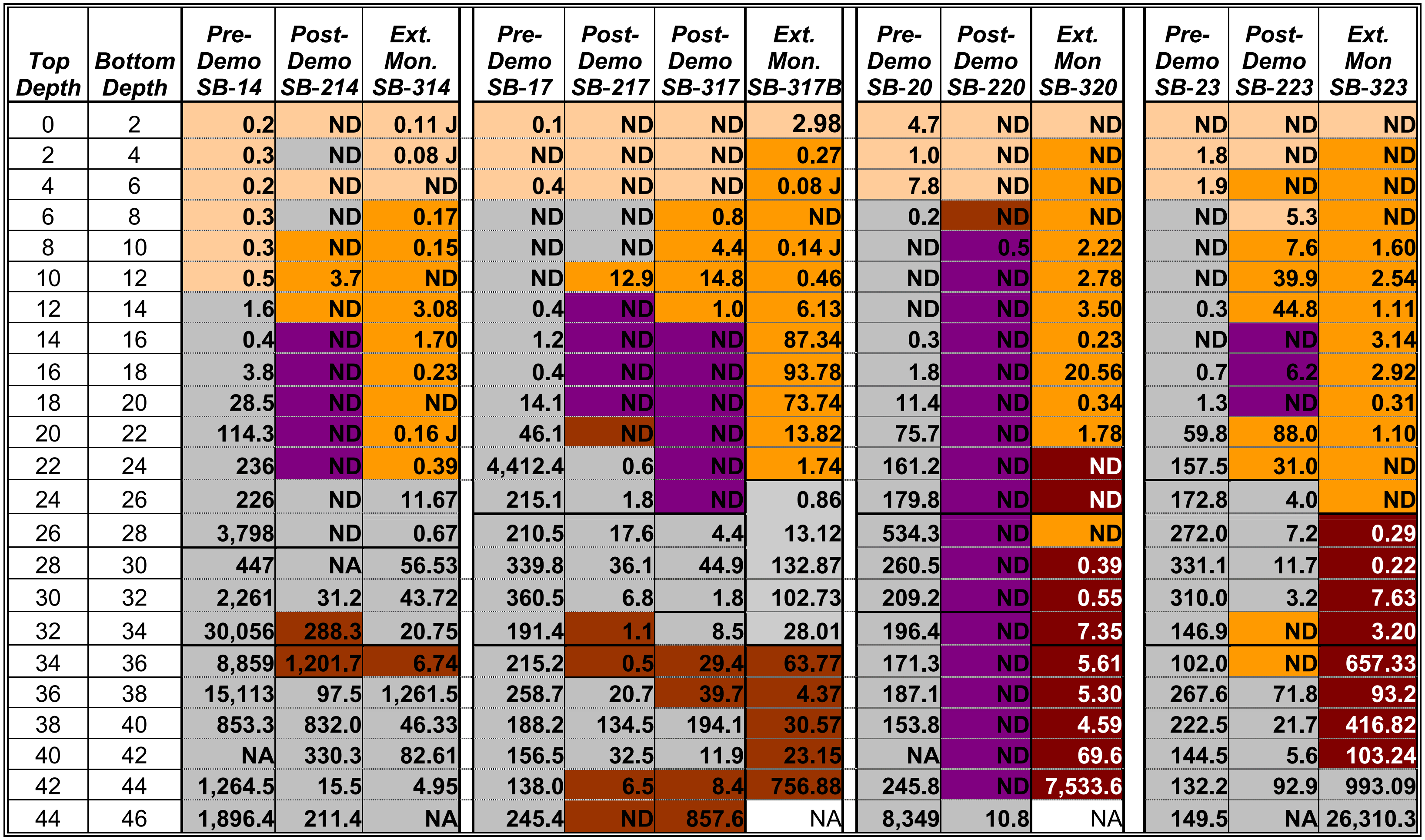
These visual indicators of $KMnO_4$ were not always representative of the level of TCE oxidation/removal observed in the corresponding soil samples. However, the colors (such as purple or brown) did provide preliminary guidance on the extent of oxidant distribution at different points in the plot. Based on the colors, oxidant distribution appeared to be best in the Upper Sand Unit, followed by the Lower Sand Unit. The Middle Fine-Grained Unit showed less penetration of the oxidant than the other two stratigraphic units. Based on the pervasiveness of purple color, the soil core SB-220 in the center of the plot showed the best oxidant distribution at all depths. The predominance of native colors at soil core SB-215, located under the Engineering Support Building, indicated that the soil core sustained less penetration of oxidant than other parts of the plot. In general, access under the building and local geologic heterogeneities appear to have played a considerable role in the efficiency of oxidant distribution.

The chart in Figure 5-1 shows that TCE concentrations were reduced considerably in all three units at several locations in the plot. The thicker horizontal lines in the chart indicate the depths at which the Middle Fine-Grained Unit was encountered at each location. The colors in this figure are indicative of the colors observed visually during sampling. As seen in Figure 5-1, the highest predemonstration contamination detected was 30,056 mg/kg of TCE in SB-14, the soil core located under the Engineering Support Building along the southern edge of the plot, where the contamination was the highest. This hot spot was present at the interface between the Middle Fine-Grained Unit and the Lower



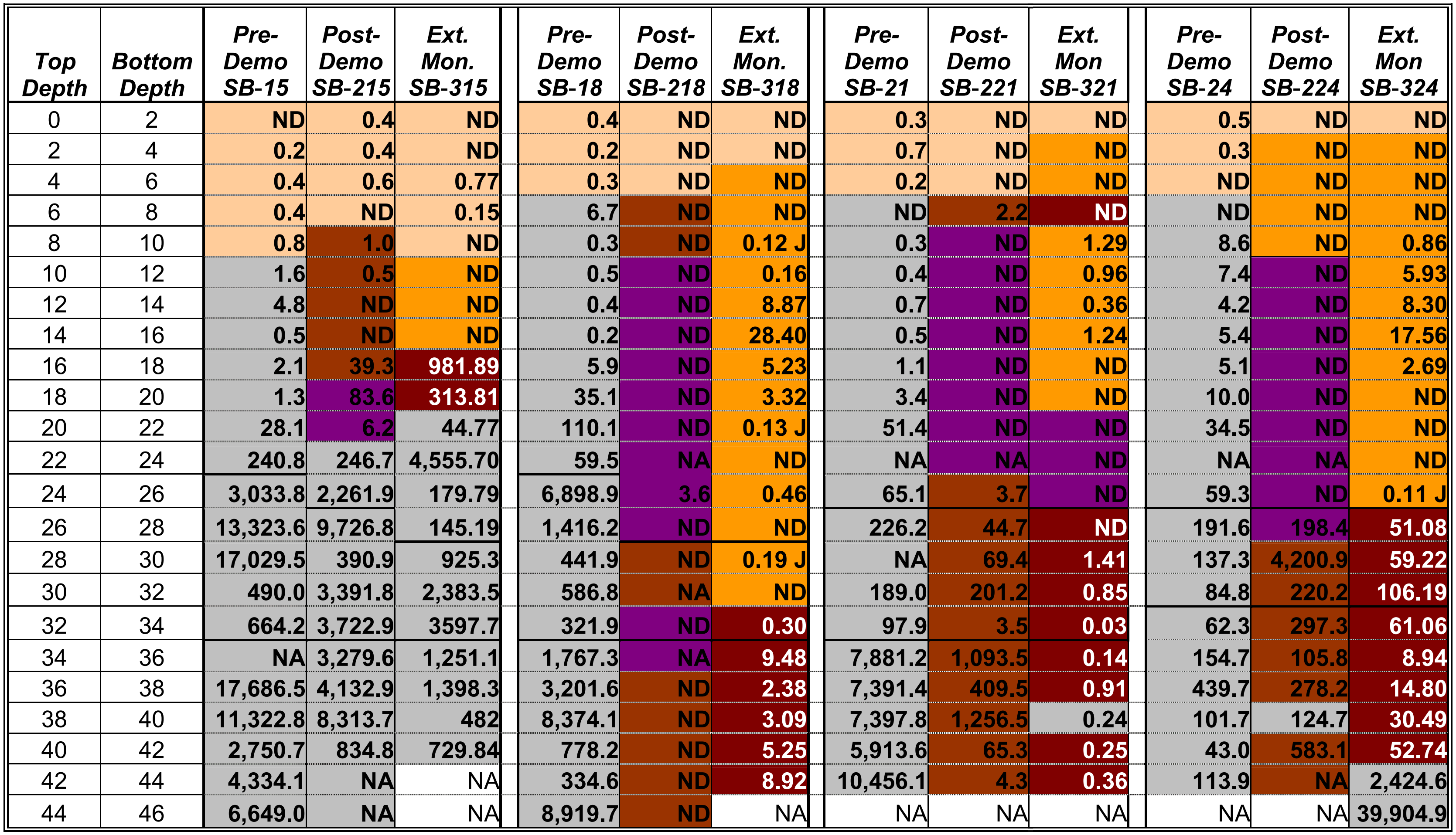
Top Depth	Bottom Depth	Pre-Demo SB-13	Post-Demo SB-213	Ext. Mon. SB-313	Pre-Demo SB-16	Post-Demo SB-216	Ext. Mon SB-316	Pre-Demo SB-19	Post-Demo SB-219	Ext. Mon SB-319	Pre-Demo SB-25	Post-Demo SB-225	Ext. Mon SB-325
0	2	0.4	ND	0.11 J	ND	ND	ND	0.4	ND	ND	0.3	ND	ND
2	4	0.2	ND	1.33	ND	ND	ND	0.5	ND	ND	0.2	ND	ND
4	6	0.2	2.3	ND	ND	ND	0.08 J	0.7	ND	ND	0.3	ND	ND
6	8	0.4	ND	0.07 J	0.3	ND	0.23	2.9	2.4	ND	0.4	ND	ND
8	10	0.5	ND	0.71	0.2	ND	1.11	7.4	57.3	0.23	NA	NA	1.23
10	12	0.5	ND	5.44	0.3	ND	0.29	0.6	42.7	0.88	0.6	24.4	1.64
12	14	0.4	ND	18.55	0.2	ND	0.25	8.7	23.4	1.22	0.5	1.5	2.18
14	16	0.8	ND	44.46	ND	ND	ND	0.4	25.0	5.69	0.5	ND	2.41
16	18	6.5	ND	0.47	2.6	ND	0.16 J	1.1	19.3	20.33	1.6	ND	0.55
18	20	21.9	ND	0.21	14.5	ND	ND	2.5	14.7	0.14 J	7.7	1.2	0.27
20	22	105.9	ND	ND	19.1	ND	1.16	11.6	1.4	0.20	14.8	ND	0.18 J
22	24	234.6	ND	0.15 J	176.5	ND	0.77	115.4	1.0	ND	194.6	2.4	0.36
24	26	304.2	ND	ND	272.4	1.8	0.18 J	210.9	NA	NA	250.0	6.7	5.60
26	28	318.4	ND	ND	307.9	10.0	0.87	280.4	8.3	NA	432.6	15.2	12.77
28	30	NA	ND	0.22	397.9	1.4	10.97	185.0	43.3	5.80	398.8	13.0	16.66
30	32	66.8	7.1	0.16	331.6	4.9	10.86	125.1	12.9	2.95	19.5	0.6	2.21
32	34	23.4	2.8	0.19 J	202.0	0.6	3.25	88.4	NA	8.27	253.4	ND	0.78
34	36	7.3	ND	ND	227.0	ND	0.98	131.1	13.1	2.65	95.5	ND	6.69
36	38	13.2	ND	0.31	292.3	ND	0.36	117.5	30.4	5.03	237.4	4.0	2.30
38	40	19.9	2.2	0.43	85.2	4.1	ND	198.9	35.8	2.24	82.8	16.3	0.27
40	42	6.8	5.7	0.71	225.1	3.6	37.21	71.7	37.1	40.69	109.9	4.0	0.37
42	44	41.0	ND	0.90	288.4	1.7	108.59	116.4	84.3	100.59	165.8	0.9	21.54
44	46	180.5	ND	NA	48.9	ND	NA	153.1	614.4	NA	262.5	218.8	NA

Figure 5-1. Distribution of TCE Concentrations (mg/kg) During Predemonstration, Postdemonstration, and Nine Months after the Demonstration in the ISCO Plot Soil (page 1 of 3)



Top Depth	Bottom Depth	Pre-Demo SB-14	Post-Demo SB-214	Ext. Mon. SB-314	Pre-Demo SB-17	Post-Demo SB-217	Post-Demo SB-317	Ext. Mon. SB-317B	Pre-Demo SB-20	Post-Demo SB-220	Ext. Mon SB-320	Pre-Demo SB-23	Post-Demo SB-223	Ext. Mon SB-323
0	2	0.2	ND	0.11 J	0.1	ND	ND	2.98	4.7	ND	ND	ND	ND	ND
2	4	0.3	ND	0.08 J	ND	ND	ND	0.27	1.0	ND	ND	1.8	ND	ND
4	6	0.2	ND	ND	0.4	ND	ND	0.08 J	7.8	ND	ND	1.9	ND	ND
6	8	0.3	ND	0.17	ND	ND	0.8	ND	0.2	ND	ND	ND	5.3	ND
8	10	0.3	ND	0.15	ND	ND	4.4	0.14 J	ND	0.5	2.22	ND	7.6	1.60
10	12	0.5	3.7	ND	ND	12.9	14.8	0.46	ND	ND	2.78	ND	39.9	2.54
12	14	1.6	ND	3.08	0.4	ND	1.0	6.13	ND	ND	3.50	0.3	44.8	1.11
14	16	0.4	ND	1.70	1.2	ND	ND	87.34	0.3	ND	0.23	ND	ND	3.14
16	18	3.8	ND	0.23	0.4	ND	ND	93.78	1.8	ND	20.56	0.7	6.2	2.92
18	20	28.5	ND	ND	14.1	ND	ND	73.74	11.4	ND	0.34	1.3	ND	0.31
20	22	114.3	ND	0.16 J	46.1	ND	ND	13.82	75.7	ND	1.78	59.8	88.0	1.10
22	24	236	ND	0.39	4,412.4	0.6	ND	1.74	161.2	ND	ND	157.5	31.0	ND
24	26	226	ND	11.67	215.1	1.8	ND	0.86	179.8	ND	ND	172.8	4.0	ND
26	28	3,798	ND	0.67	210.5	17.6	4.4	13.12	534.3	ND	ND	272.0	7.2	0.29
28	30	447	NA	56.53	339.8	36.1	44.9	132.87	260.5	ND	0.39	331.1	11.7	0.22
30	32	2,261	31.2	43.72	360.5	6.8	1.8	102.73	209.2	ND	0.55	310.0	3.2	7.63
32	34	30,056	288.3	20.75	191.4	1.1	8.5	28.01	196.4	ND	7.35	146.9	ND	3.20
34	36	8,859	1,201.7	6.74	215.2	0.5	29.4	63.77	171.3	ND	5.61	102.0	ND	657.33
36	38	15,113	97.5	1,261.5	258.7	20.7	39.7	4.37	187.1	ND	5.30	267.6	71.8	93.2
38	40	853.3	832.0	46.33	188.2	134.5	194.1	30.57	153.8	ND	4.59	222.5	21.7	416.82
40	42	NA	330.3	82.61	156.5	32.5	11.9	23.15	NA	ND	69.6	144.5	5.6	103.24
42	44	1,264.5	15.5	4.95	138.0	6.5	8.4	756.88	245.8	ND	7,533.6	132.2	92.9	993.09
44	46	1,896.4	211.4	NA	245.4	ND	857.6	NA	8,349	10.8	NA	149.5	NA	26,310.3

Figure 5-1. Distribution of TCE Concentrations (mg/kg) During Predemonstration, Postdemonstration, and Nine Months after the Demonstration in the ISCO Plot Soil (page 2 of 3)



Top Depth	Bottom Depth	Pre-Demo SB-15	Post-Demo SB-215	Ext. Mon. SB-315	Pre-Demo SB-18	Post-Demo SB-218	Ext. Mon. SB-318	Pre-Demo SB-21	Post-Demo SB-221	Ext. Mon SB-321	Pre-Demo SB-24	Post-Demo SB-224	Ext. Mon SB-324
0	2	ND	0.4	ND	0.4	ND	ND	0.3	ND	ND	0.5	ND	ND
2	4	0.2	0.4	ND	0.2	ND	ND	0.7	ND	ND	0.3	ND	ND
4	6	0.4	0.6	0.77	0.3	ND	ND	0.2	ND	ND	ND	ND	ND
6	8	0.4	ND	0.15	6.7	ND	ND	ND	2.2	ND	ND	ND	ND
8	10	0.8	1.0	ND	0.3	ND	0.12 J	0.3	ND	1.29	8.6	ND	0.86
10	12	1.6	0.5	ND	0.5	ND	0.16	0.4	ND	0.96	7.4	ND	5.93
12	14	4.8	ND	ND	0.4	ND	8.87	0.7	ND	0.36	4.2	ND	8.30
14	16	0.5	ND	ND	0.2	ND	28.40	0.5	ND	1.24	5.4	ND	17.56
16	18	2.1	39.3	981.89	5.9	ND	5.23	1.1	ND	ND	5.1	ND	2.69
18	20	1.3	83.6	313.81	35.1	ND	3.32	3.4	ND	ND	10.0	ND	ND
20	22	28.1	6.2	44.77	110.1	ND	0.13 J	51.4	ND	ND	34.5	ND	ND
22	24	240.8	246.7	4,555.70	59.5	NA	ND	NA	NA	ND	NA	NA	ND
24	26	3,033.8	2,261.9	179.79	6,898.9	3.6	0.46	65.1	3.7	ND	59.3	ND	0.11 J
26	28	13,323.6	9,726.8	145.19	1,416.2	ND	ND	226.2	44.7	ND	191.6	198.4	51.08
28	30	17,029.5	390.9	925.3	441.9	ND	0.19 J	NA	69.4	1.41	137.3	4,200.9	59.22
30	32	490.0	3,391.8	2,383.5	586.8	NA	ND	189.0	201.2	0.85	84.8	220.2	106.19
32	34	664.2	3,722.9	3597.7	321.9	ND	0.30	97.9	3.5	0.03	62.3	297.3	61.06
34	36	NA	3,279.6	1,251.1	1,767.3	NA	9.48	7,881.2	1,093.5	0.14	154.7	105.8	8.94
36	38	17,686.5	4,132.9	1,398.3	3,201.6	ND	2.38	7,391.4	409.5	0.91	439.7	278.2	14.80
38	40	11,322.8	8,313.7	482	8,374.1	ND	3.09	7,397.8	1,256.5	0.24	101.7	124.7	30.49
40	42	2,750.7	834.8	729.84	778.2	ND	5.25	5,913.6	65.3	0.25	43.0	583.1	52.74
42	44	4,334.1	NA	NA	334.6	ND	8.92	10,456.1	4.3	0.36	113.9	NA	2,424.6
44	46	6,649.0	NA	NA	8,919.7	ND	NA	NA	NA	NA	NA	NA	39,904.9

NA: Not available.
ND: Not detected.
Solid horizontal lines demarcate MFGU.

Figure 5-1. Distribution of TCE Concentrations (mg/kg) During Predemonstration, Postdemonstration, and Nine Months after the Demonstration in the ISCO Plot Soil (page 3 of 3)

Sand Unit; concentrations in the vicinity of this hot spot were reduced considerably by the ISCO application, as seen in the postdemonstration core SB-214. The highest postdemonstration TCE concentration was 9,727 mg/kg, found in soil core SB-215. This high residual contamination was present in the Middle Fine-Grained Unit at a location under the building, probably the region that presented the most geologic and operational difficulty for oxidation treatment through injection points outside the building. The highest TCE concentration found during the extended monitoring event was 39,905 mg/kg, found in soil core SB-324 on the northern edge of the test plot, at a depth right above the clay aquitard. The postdemonstration groundwater concentration in monitoring well BAT-1D, the well closest to soil boring SB-324, shows persistently high levels of TCE (see Appendix C); therefore, the soil and groundwater data are in agreement in this region. During postdemonstration sampling of this location (SB-224), the soil recovery in the sample at this depth was poor and the sample could not be analyzed. This high a level of TCE in SB-324 indicates a DNAPL pocket remaining right above the aquitard after treatment. The color of the soil at this depth in SB-324 is its natural color and visually it does not appear that much permanganate reached this spot. As apparent in Figure 5-1, the TCE concentration was relatively low (52 mg/kg) 2 ft above this DNAPL pocket, where the soil shows discoloration due to permanganate. Except for this one soil boring location (corresponding to the group SB-24, SB-224, and SB-324), the TCE distribution in the rest of the test plot during the three events (predemonstration, postdemonstration, and extended monitoring) was consistent with expectations.

Figures 5-2 to 5-4 show representative pre- and postdemonstration distributions of TCE in soil from the Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit, respectively, in the ISCO plot and surrounding aquifer. A graphical representation of the TCE data illustrates the horizontal and vertical extent of the oxidant distribution and the changes in TCE concentrations. The colors yellow to red indicate DNAPL (TCE >300 mg/kg). In general, the portions of the aquifer under the building (SB-14 and SB-15) and along the western boundary of the ISCO plot (SB-18 and SB-21) had the highest predemonstration contamination, especially in the Middle Fine-Grained Unit and Lower Sand Unit. The postdemonstration coring showed that the ISCO process had caused a considerable decline in TCE concentrations throughout the ISCO plot. Postdemonstration soil cores SB-218 and SB-221, along the western edge of the plot, showed the sharpest declines in TCE/DNAPL concentrations. On the other hand, cores SB-214 and SB-215, collected under the building, contained considerable postdemonstration concentrations of both total TCE and DNAPL. These results indicate that distribution of oxidant under the building was not as efficient as in the rest of the plot.

Figure 5-5 depicts three-dimensional (3-D) DNAPL distributions identified during the pre- and postdemonstration sampling in the ISCO plot. This figure shows that DNAPL was removed from large regions of the test plot. A few pockets of DNAPL remain, primarily under the building and near the northern edge of the test plot, at locations where the permanganate probably experienced difficulty penetrating.

Figures 5-6 to 5-8 show the distribution of potassium permanganate in the shallow, intermediate, and deep wells, respectively, in the Launch Complex 34 aquifer, as measured by spectrophotometry in May 2000, soon after the end of the oxidant injection process. The permanganate levels in the monitoring wells are probably a measure of the excess oxidant in the aquifer; that is, the permanganate left over after the TCE and native organic matter in the vicinity had been oxidized. These figures show that some excess potassium permanganate was present in most parts of the ISCO plot and surrounding aquifer, although some regions seemed to have received a higher oxidant dose than others. Monitoring wells BAT-5S and BAT-5D seemed to have barely measurable levels of permanganate, indicating that preferential pathways may have guided the oxidant flow away from this region. In fact, BAT-5S was the only well inside the ISCO plot that showed an increase in TCE concentration throughout the demonstration (see Section 5.2.1). TCE increased in some of the perimeter wells as described in Section 5.3.2.

5.1.2 TCE/DNAPL Mass Removal Estimation by Linear Interpolation

Section 4.1.1 describes the use of linear interpolation to estimate pre- and postdemonstration TCE/DNAPL masses and calculate TCE/DNAPL mass removal. In this method, EarthVision™, a three-dimensional contouring software, is used to group the TCE concentration distribution in the ISCO plot into three-dimensional shells (or bands) of equal concentration. The concentration in each shell is multiplied by the volume of the shell and the bulk density of the soil to arrive at the TCE mass in that shell. The masses in the individual shells are added up to arrive at a TCE mass for the entire plot; this process is conducted separately for the pre- and postdemonstration TCE distributions in the ISCO plot. The predemonstration TCE/DNAPL mass in the entire plot then can be compared with the postdemonstration mass in the entire plot to estimate TCE/DNAPL removal. The results of this evaluation are described in this section.

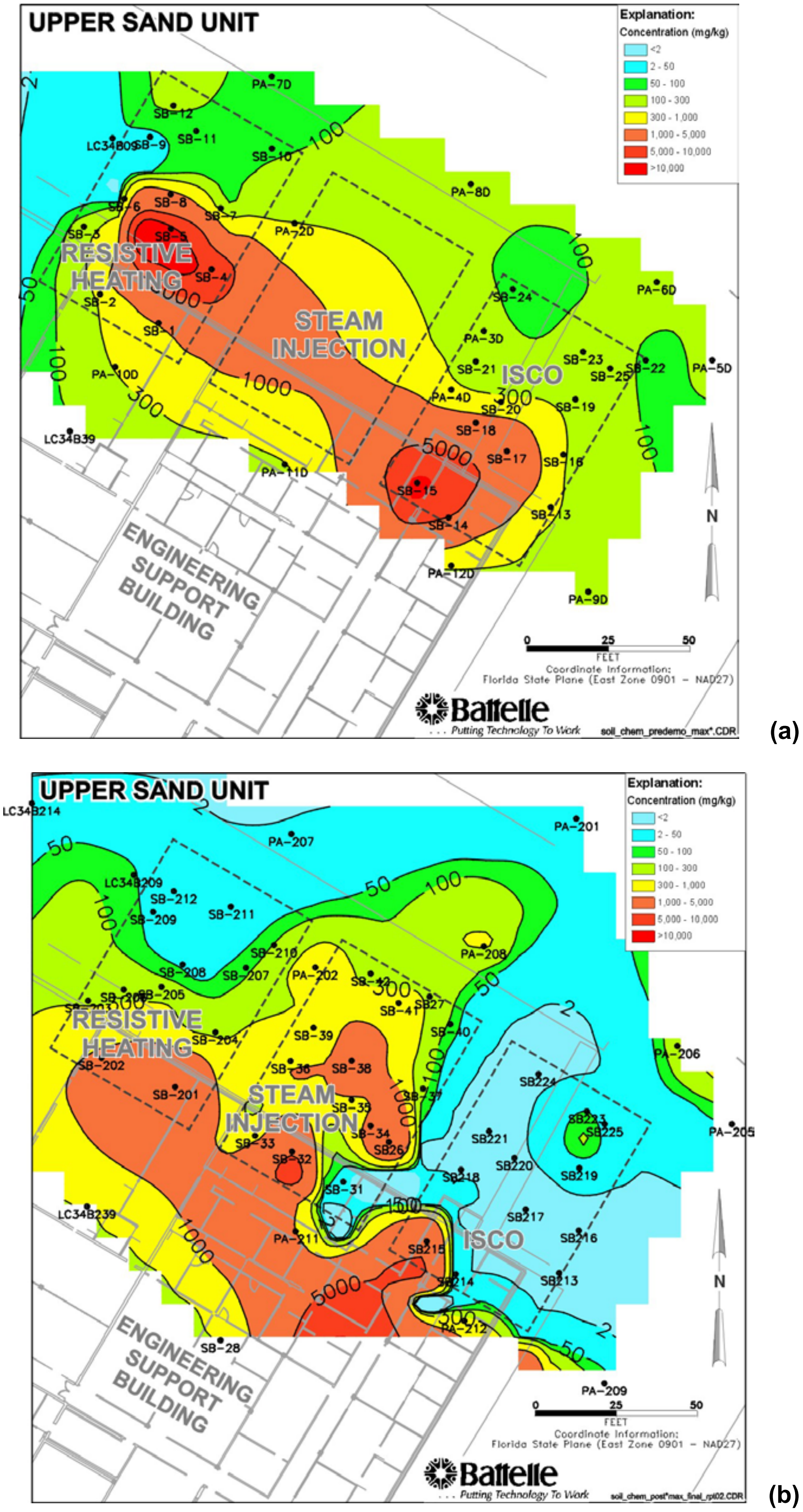


Figure 5-2. Representative (a) Predemonstration (June 1999) and (b) Postdemonstration (May 2000) Horizontal Cross Sections of TCE (mg/kg) in the Upper Sand Unit Soil

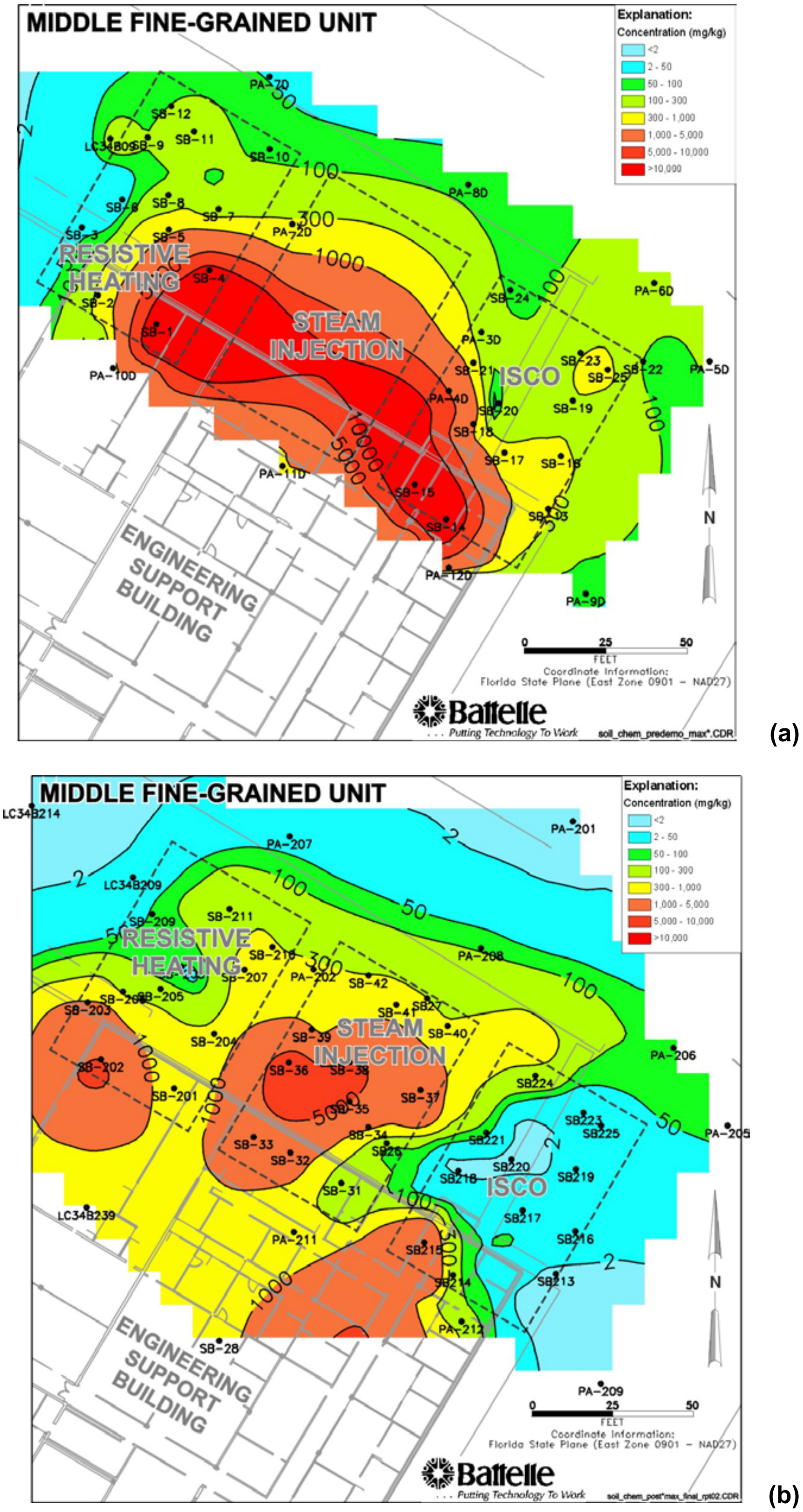


Figure 5-3. Representative (a) Predemonstration (June 1999) and (b) Postdemonstration (May 2000) Horizontal Cross Sections of TCE (mg/kg) in the Middle Fine-Grained Unit Soil

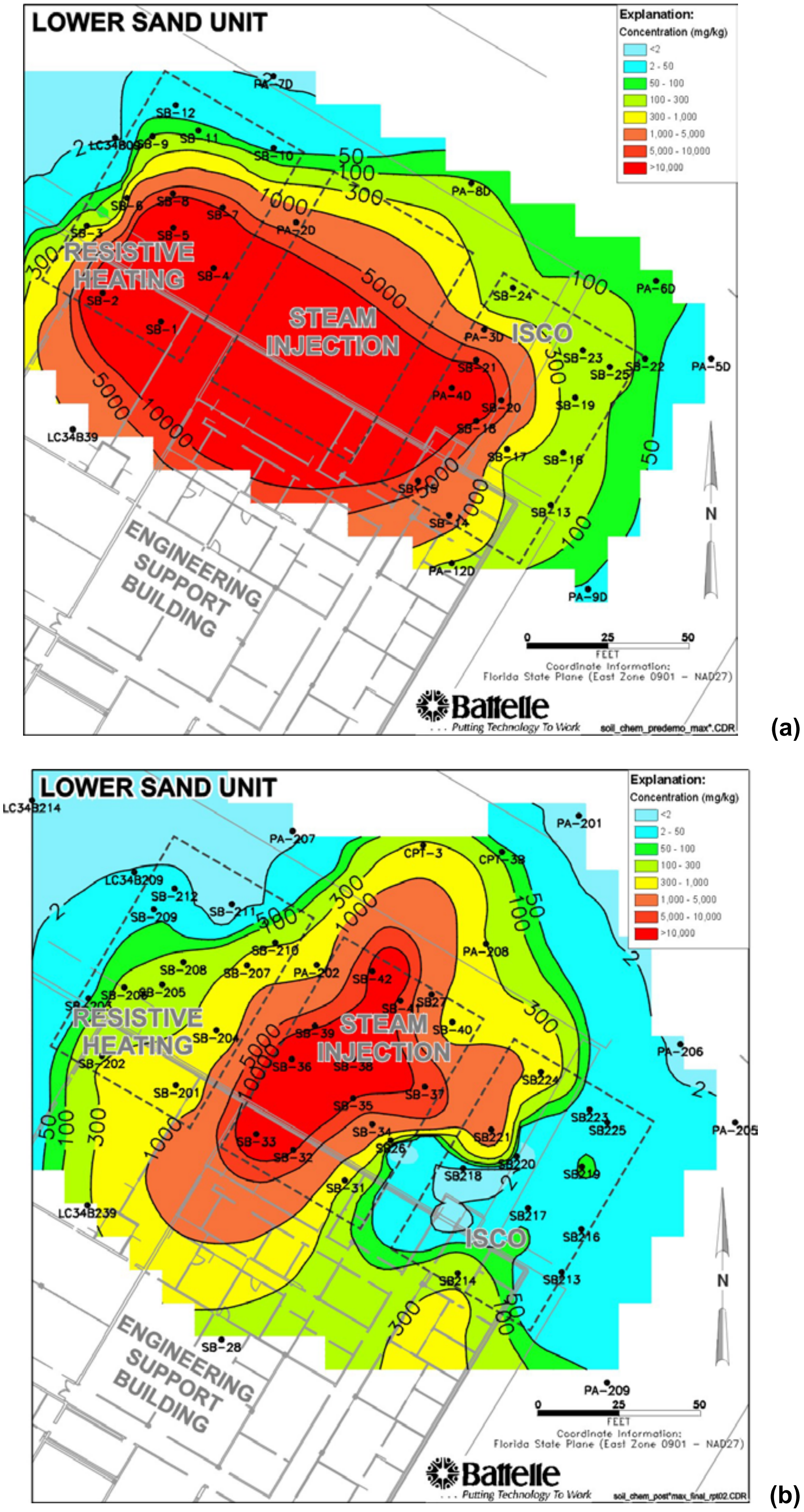


Figure 5-4. Representative (a) Predemonstration (June 1999) and (b) Postdemonstration (May 2000) Horizontal Cross Sections of TCE (mg/kg) in the Lower Sand Unit Soil

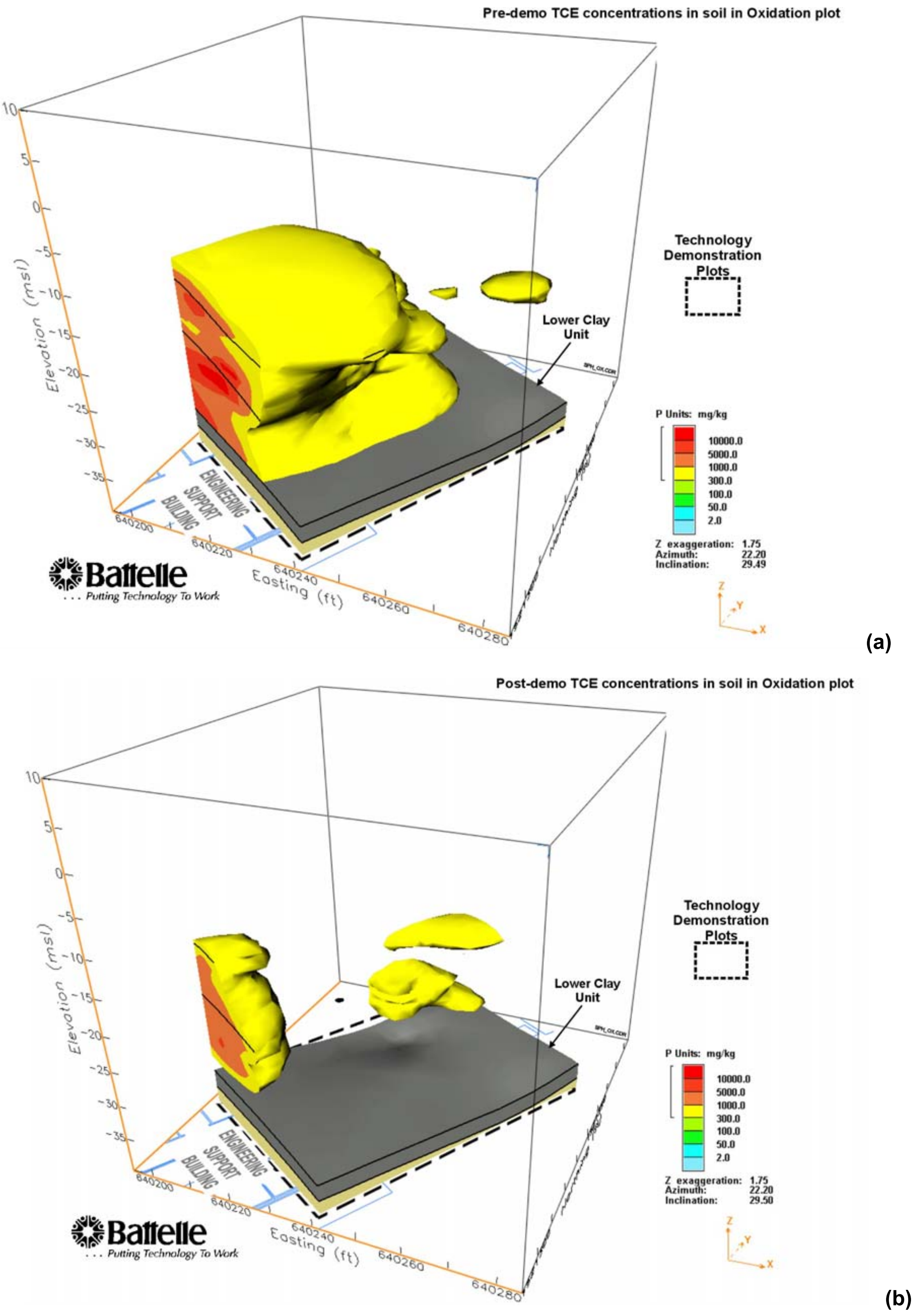


Figure 5-5. Three-Dimensional Distribution of DNAPL in the ISCO Plot Based on (a) Predemonstration (June 1999) and (b) Postdemonstration (May 2000) (mg/kg) Soil Sampling Events

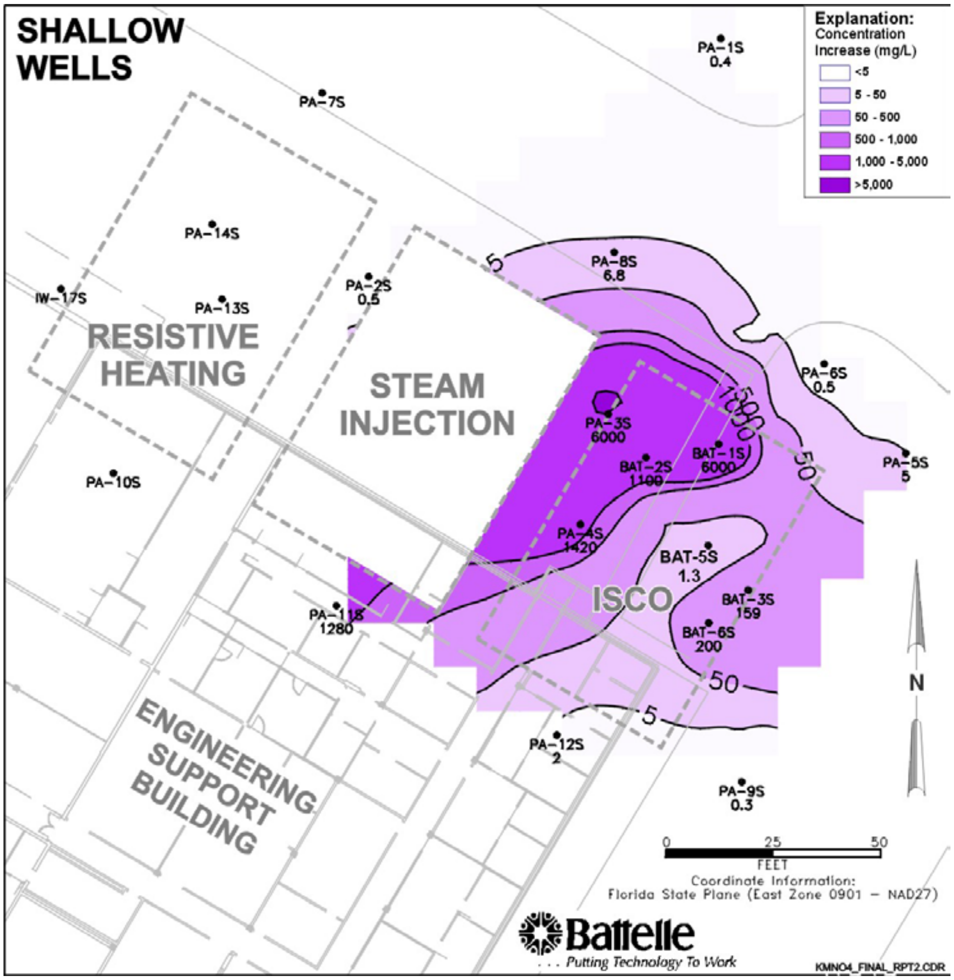


Figure 5-6. Distribution of Potassium Permanganate ($KMnO_4$) in Shallow Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

Table 5-1 presents the estimated masses of total TCE and DNAPL in the ISCO plot and the three individual stratigraphic units. Under predemonstration conditions, soil sampling indicated the presence of 6,122 kg of total TCE (dissolved and free phase), approximately 5,039 kg of which was DNAPL. Following the demonstration, soil sampling indicated that 1,100 kg of total TCE remained in the plot; approximately 810 kg of this remnant TCE was DNAPL. Based on these estimates, 5,022 kg of total TCE, including 4,229 kg of DNAPL, was removed from the plot. Therefore, linear interpolation indicates that the overall mass removal effected by the ISCO process was 82% of total TCE and 84% of DNAPL.

Table 5-1 indicates that the highest mass removal (97% of total TCE and 98% of DNAPL) was achieved in the Upper Sand Unit, followed by the Lower Sand Unit. Substantial TCE/DNAPL mass was removed in the Middle Fine-Grained Unit as well, but the removal efficiency in this finer-grained unit was not as high as in the two sandy units.

When the predemonstration and extended monitoring TCE concentrations are compared, the estimated mass removal is 77% of total TCE and 76% of DNAPL. The lower estimated mass removal during the extended monitoring event is due to an isolated pocket of DNAPL found in soil core SB-323.

5.1.3 TCE Mass Removal Estimation by Kriging

Section 4.1.2 describes the use of kriging to estimate the pre- and postdemonstration TCE masses in the aquifer. Whereas the contouring method linearly interpolates the TCE measurements at discrete sampling points to estimate TCE concentrations at unsampled points in the plot, kriging takes into account the spatial variability and uncertainty of the TCE distribution when estimating TCE concentrations (or masses) at unsampled points. Consequently, kriging provides a range of probable values rather than single TCE concentration estimates. Kriging

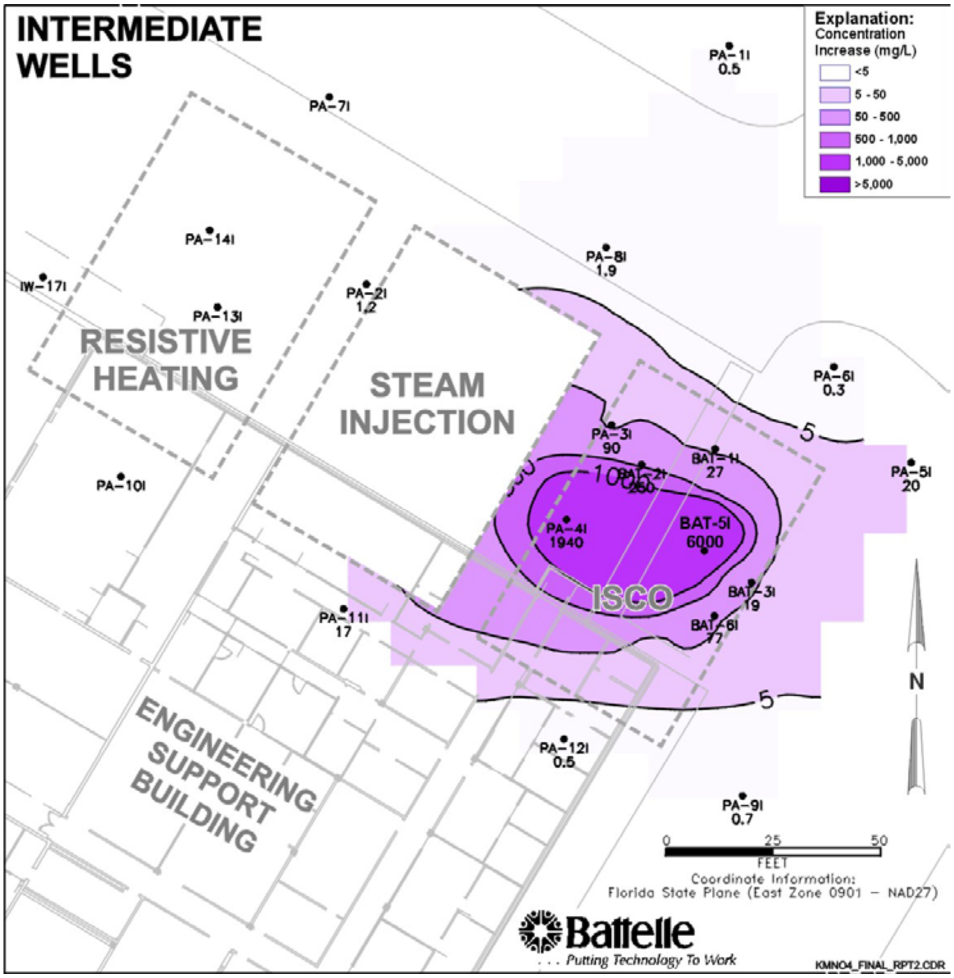


Figure 5-7. Distribution of Potassium Permanganate ($KMnO_4$) in Intermediate Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

is a good way of obtaining a global estimate (estimate for one of the three stratigraphic units or the entire plot) for the parameters of interest (such as pre- and postdemonstration TCE masses), when the parameter is heterogeneously distributed.

Appendix A.1.2 contains a description of the application and results of kriging the TCE distribution in the ISCO plot. Table 5-2 summarizes the total TCE mass estimates obtained from kriging. This table contains an average and range (80% confidence interval) for each global estimate (Upper Sand Unit, Middle Fine-Grained Unit, Lower Sand Unit, and the entire plot). Limiting the evaluation to DNAPL instead of total TCE limits the number of usable data points to those with TCE concentrations greater than 300 mg/kg. To avoid using too small a number of data points (especially for the postdemonstration DNAPL mass estimates), kriging was conducted on total TCE values only.

The pre- and postdemonstration total TCE masses estimated from kriging match the total TCE obtained from linear interpolation relatively well, probably because the high sampling density (almost 300 soil samples in the plot per event) allows linear interpolation to capture much of the variability of the TCE distribution in the plot. Kriging shows that between 62 and 84% (75% on average) of the predemonstration TCE mass was removed from the plot due to the application of ISCO technology. TCE mass removal was highest in the Upper Sand Unit, followed by the Lower Sand Unit. TCE mass removal was lowest in the Middle Fine-Grained Unit. An interesting observation from Table 5-2 is that the estimated ranges for the pre- and postdemonstration TCE masses do not overlap, either for the entire plot or for any of the three stratigraphic units; this indicates that the mass removal due to the ISCO application is significant at the 80% confidence level. The initial 90% DNAPL removal goal set for the demonstration probably was not met due

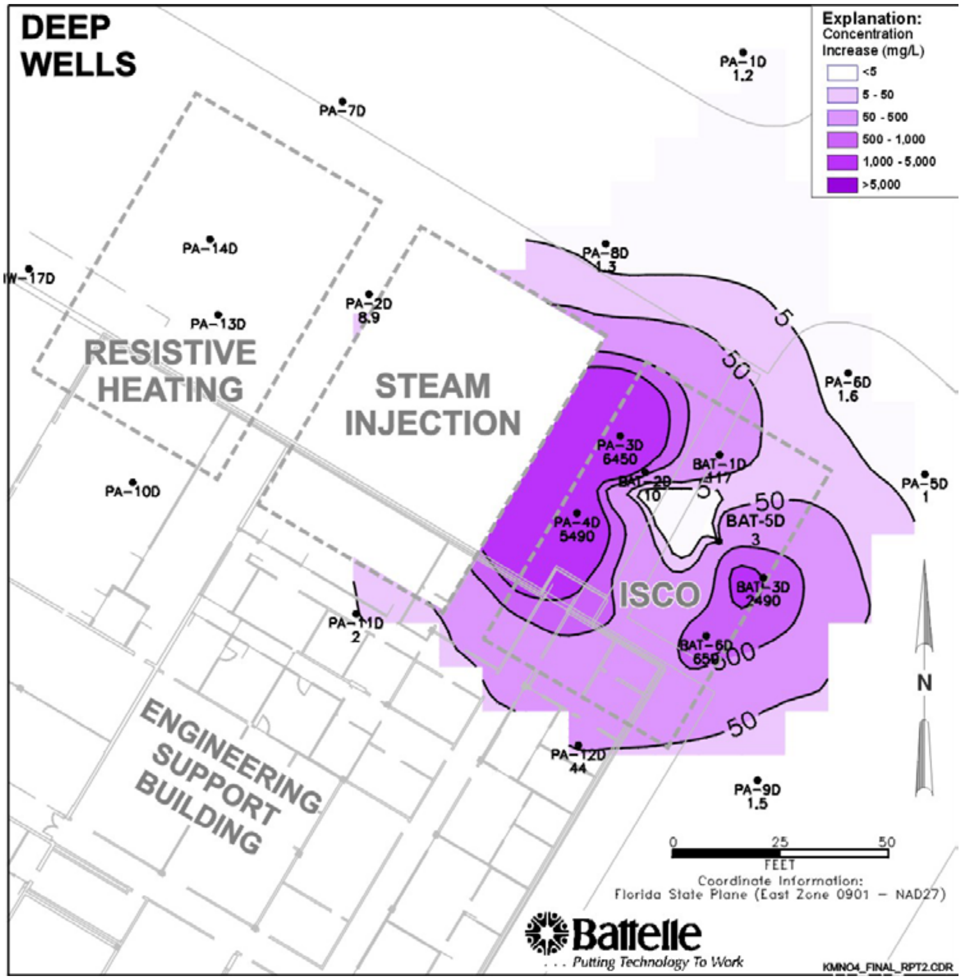


Figure 5-8. Distribution of Potassium Permanganate ($KMnO_4$) in Deep Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

Table 5-1. Linear Interpolation Estimates for the ISCO Demonstration

Stratigraphic Unit	Predemonstration Total TCE (kg)	Predemonstration DNAPL[a] (kg)	Postdemonstration Total TCE (kg)	Postdemonstration DNAPL[a] (kg)	Mass Removal Total TCE (%)	Mass Removal DNAPL (%)
Upper Sand Unit	846	601	23	10	97	98
Middle Fine-Grained Unit	1,048	749	233	163	78	78
Lower Sand Unit	4,228	3,689	844	637	80	83
Total (Entire Plot)	6,122	5,039	1,100	810	82	84

Stratigraphic Unit	Predemonstration Total TCE (kg)	Predemonstration DNAPL[a] (kg)	Extended Monitoring Total TCE (kg)	Extended Monitoring DNAPL[a] (kg)	Mass Removal Total TCE (%)	Mass Removal DNAPL (%)
Upper Sand Unit	846	601	82	57	90	91
Middle Fine-Grained Unit	1,048	749	160	126	85	93
Lower Sand Unit	4,228	3,689	1,172	1,036	72	72
Total (Entire Plot)	6,122	5,039	1,415	1,219	77	76

(a) The DNAPL estimates include only TCE concentrations estimated to be above 300 mg/kg of soil.

Table 5-2. Kriging Estimates for the ISCO Demonstration

	Predemonstration Total TCE[a]			Postdemonstration Total TCE[a]			Total TCE Mass Removal[a]		
Stratigraphic Unit	**Average (kg)**	**Lower Bound (kg)**	**Upper Bound (kg)**	**Average (kg)**	**Lower Bound (kg)**	**Upper Bound (kg)**	**Average (%)**	**Lower Bound (%)**	**Upper Bound (%)**
Upper Sand Unit	454	250	659	26	18	34	94	87	97
Middle Fine-Grained Unit	2,836	1,668	4,005	872	532	1,211	69	27	87
Lower Sand Unit	4,408	3,519	5,298	1,030	788	1,272	77	64	85
Entire Plot[b]	7,699	6,217	9,182	1,928	1,511	2,345	75	62	84

	Predemonstration Total TCE[a]			Extended Monitoring Total TCE[a]			Total TCE Mass Removal[a]		
Stratigraphic Unit	**Average (kg)**	**Lower Bound (kg)**	**Upper Bound (kg)**	**Average (kg)**	**Lower Bound (kg)**	**Upper Bound (kg)**	**Average (%)**	**Lower Bound (%)**	**Upper Bound (%)**
Upper Sand Unit	454	250	659	246	238	254	46	0	64
Middle Fine-Grained Unit	2,836	1,668	4,005	152	140	164	95	90	97
Lower Sand Unit	4,408	3,519	5,298	2,683	2,583	2,782	39	21	51
Entire Plot[b]	7,699	6,217	9,182	3,081	2,980	3,182	60	49	68

(a) Average and 80% confidence intervals (bounds).

(b) The standard error for the entire plot is different from the standard error for the individual stratigraphic units. Therefore, the estimated range of TCE levels in the entire plot are different from the sum total of the TCE estimates in the individual units.

to the limited access to the DNAPL under the building and the limited distribution of oxidant in the Middle Fine-Grained Unit.

When the predemonstration and extended monitoring TCE mass estimates are compared, the total TCE mass removal ranges from 49 to 68%, with an average removal of 60%. The lower removal estimates during the extended monitoring event are due to the isolated pocket of DNAPL discovered in the northern part of the test plot.

5.1.4 TCE/DNAPL Mass Removal Summary

In summary, the evaluation of TCE concentrations in soil indicates the following:

- In the horizontal plane, the highest predemonstration DNAPL contamination was under the Engineering Support Building and along the western boundary of the ISCO plot.
- In the vertical plane, the highest predemonstration DNAPL contamination was associated with the Lower Sand Unit.
- Kriging indicated that between 6,217 and 9,182 kg of total TCE was present in the test plot before the demonstration; and that between 62 and 84% of the total TCE was removed from the test plot by the technology application. When the predemonstration and extended monitoring event TCE mass estimates were compared, kriging indicated that between 49 and 68% of the TCE was removed from the plot. The extended monitoring event was conducted nine months after the end of the oxidant injections. The slightly lower removal estimates during the extended monitoring event are due to an isolated pocket of DNAPL found on the north end of the test plot during extended monitoring. These statistics are significant at the 80% confidence level specified before the demonstration. In summary, it can be said that at about half (at least 49%) of the initial TCE mass in the test plot was removed by the ISCO treatment.
- Linear interpolation of the predemonstration, postdemonstration, and extended monitoring TCE/DNAPL soil concentrations shows that approximately 76% of the estimated predemonstration DNAPL mass in the ISCO plot was removed due to the ISCO application.
- Oxidant was injected at relatively high pressures at several locations and depths within the ISCO plot and this improved the overall TCE/DNAPL mass removal. However, despite the high injection pressures and spatially intensive injection scheme, localized aquifer heterogeneities played a significant role in the eventual oxidant distribution and TCE/DNAPL removal.

- TCE/DNAPL removal efficiency was highest in the Upper Sand Unit, indicating that oxidant was effectively distributed in the more permeable, coarse-grained soil.
- TCE/DNAPL removal efficiency was lowest in the Middle Fine-Grained Unit, indicating that oxidant distribution was difficult in the tighter, fine-grained soil.
- Accessing the 15 ft of plot underneath the Engineering Support Building from oxidant injection points located outside the building proved difficult and resulted in low TCE/DNAPL removal efficiency under the building. This indicates that the radius of influence of the oxidant around the injection points was less than 15 ft.

5.2 Evaluating Changes in Aquifer Quality

This section describes the changes (between the predemonstration and postdemonstration sampling events) in aquifer characteristics created by the ISCO application at Launch Complex 34, as measured by monitoring conducted before, during, and after the demonstration. The affected aquifer characteristics are grouped into four subsections:

- Changes in CVOC levels (see Appendix C for detailed results)
- Changes in aquifer geochemistry (see Appendix D for detailed results)
- Changes in the hydraulic properties of the aquifer (see Appendix B for detailed results)
- Changes in the aquifer microbiology (see Appendix E for detailed results).

Table 5-3 lists selected CVOC concentrations in groundwater at the ISCO plot, and Table 5-4 lists levels of various groundwater parameters that indicate aquifer quality and the impact of the ISCO treatment. The tables summarize the levels from predemonstration, postdemonstration, and one year after the demonstration. Other important organic and inorganic aquifer parameters are discussed in this subsection. A separate microbiological evaluation of the aquifer is described in Appendix E.

5.2.1 Changes in CVOC Levels in Groundwater

The fact that considerable DNAPL mass was removed was expected to reduce CVOC levels in groundwater, at least in the short term. Although influx from surrounding contamination is possible, it was not expected to contribute significantly to the postdemonstration sampling in the short term because through most of the demonstration, hydraulic gradients radiated outward from the plot due to the injection pressures inside the plot. Also, the natural gradient at the site is relatively flat, so any influx of contaminated groundwater into the plot between oxidant injection and postdemonstration sampling was expected to be minimal. Lastly, excess permanganate in many parts of the plot would help control CVOC influx. Therefore, CVOC levels were measured in the ISCO plot wells before, during, and after the demonstration to evaluate changes in CVOC levels in the groundwater.

Table 5-3 shows the changes of TCE and *cis*-1,2-DCE in the ISCO performance monitoring wells. Appendix C tabulates the levels of TCE, *cis*-1,2-DCE and vinyl chloride in the groundwater in the ISCO plot wells. Figures 5-9 to 5-11 show dissolved TCE concentrations in the shallow, intermediate, and deep wells, respectively, in the ISCO plot and perimeter. Before the demonstration, several of the shallow, intermediate, and deep wells in the plot had concentrations close to the solubility of TCE (1,100 mg/L). Immediately after the demonstration, TCE concentrations in several of these wells (e.g., BAT-1S, BAT-2S, BAT-2I, and BAT-6D) declined by 99% or more. The only anomalous well was the Upper Sand Unit Well BAT-5S. Both during and after the demonstration, BAT-5S showed increased TCE concentrations, at times approaching saturation levels. SB-219, the soil core closest to BAT-5S (the only monitoring well that showed an increase in TCE concentrations throughout the demonstration) did not indicate any substantial amounts of DNAPL (see Figure 5-1). These results suggest the following possibilities:

Table 5-3. CVOC Concentrations in Groundwater from the ISCO Plot

	TCE (µg/L)			***cis*-1,2-DCE (µg/L)**		
Well ID	**Predemonstration**	**Postdemonstration**	**Extended Monitoring**	**Predemonstration**	**Postdemonstration**	**Extended Monitoring**
BAT-2S	1,110,000	<5	19 J	4,900J	<5	<20
BAT-2I	970,000	880	937 D	4,700J	<77	7
BAT-2D	1,160,000	220,000	388,000 D	NA	<10,000	7,770
BAT-5S	298,000	410,000	13,300 D	12,500	<17,000	5,300 D
BAT-5S-DUP	240,000	NA	11,100 D	9,100J	NA	5,020 D
BAT-5I	868,000	<10	356,000 D	5,220	<10	540 J
BAT-5D	1,140,000	52,000	436,000 D	NA	<1,700	1,090

Table 5-4. Predemonstration, Postdemonstration, and Extended Monitoring Levels of Groundwater Parameters Indicative of Aquifer Quality

Groundwater Parameter (applicable groundwater standard, if any) (mg/L)	Aquifer Depth	Predemonstration (mg/L)[a]	Postdemonstration (mg/L)[a]	Extended Monitoring (mg/L)[a]
TCE (0.003)	Shallow	298 to 1,140	<0.005 to 630	0.019J to 13.3
	Intermediate	868 to 1,190	<0.005 to 360	0.937 to 356
	Deep	752 to 1,160	<0.005 to 220	388 to 436
DCE (0.070)	Shallow	3.9 to 12.5	<0.005 to 52.0	<0.02 to 5.3
	Intermediate	4.1 to 21.3	<0.005 to 0.015	0.007 to 0.54J
	Deep	9.18 to 44.5	<0.005 to <17.0	1.09 to 7.77
Vinyl chloride (0.001)	Shallow	<5.0	<0.010 to <33.0	<0.02
	Intermediate	<5.0	<0.010 to <33.0	<0.001 to <0.1
	Deep	<5.0	<0.010 to <20.0	<1
pH	Shallow	7.0 to 7.4	7.2	7.5
	Intermediate	7.3 to 7.6	6.6	6.8 to 7.7
	Deep	7.4 to 7.5	6.4	5.5 to 7.0
ORP[b]	Shallow	–149 to –25 mV	–2 mV	–40 to 469 mV
	Intermediate	–165 to –38 mV	–97 to 384 mV	–103 to –29 mV
	Deep	–150 to –22 mV	–84 mV	–171 to 166 mV
DO	Shallow	<0.5 to 2.7	<0.5	0.92
	Intermediate	0.50 to 0.9	<0.5 to 3.1	0.72
	Deep	<0.5 to 0.9	0.7	0.06 to 0.92
Calcium	Shallow	70	4 to 70	1 to 7
	Intermediate	41	4 to 49	24 to 85
	Deep	84 to 88	210 to 349	71 to 1,020
Magnesium	Shallow	53	2 to 111	0.3 to 23
	Intermediate	59	3 to 19	32 to 45
	Deep	82 to 84	53 to 203	83 to 201
Alkalinity as $CaCO_3$	Shallow	269 to 316	1,060 to 1,500	1,700 to 2,010
	Intermediate	291 to 323	1,280	1,060 to 1,860
	Deep	204 to 208	1,300 to 2,140	359 to 1,610
Chloride (250)	Shallow	38 to 53	236 to 237	126 to 531
	Intermediate	57 to 181	238 to 582	186 to 452
	Deep	722 to 752	1,360 to 1,730	1,010 to 5,070
Manganese (0.05)	Shallow	0.016 to 1.1	2 to 235	0.25 to 33
	Intermediate	<0.015 to 0.018	98 to 516	1.46 to 7.41
	Deep	0.015 to 0.025	9 to 10	3.47 to 488
Iron (0.3)	Shallow	0.3 to 2.5	<0.05	<0.1 to 0.263
	Intermediate	<0.05 to 0.5	<0.1	<0.1 to 4.06
	Deep	0.1 to 0.3	<0.05 to 1.1	2.84 to 35.6
Sulfate in mg SO_4/L	Shallow	29 to 46	483	778 to 1,330
	Intermediate	49 to 138	1,380	618 to 1,810
	Deep	67 to 103	379 to 535	517 to 781
TDS (500)	Shallow	387 to 499	2,860 to 6,790	5,170 to 5,980
	Intermediate	517 to 760	5,280 to 13,000	3,640 to 4,750
	Deep	1,490 to 1,550	5,990 to 6,410	5,250 to 8,280
BOD	Shallow	<3	<3 to 112	<2 to 18
	Intermediate	<3 to 16	<3	8.6 to >74
	Deep	13	16 to 108	15 to >74
TOC	Shallow	4 to 6	157 to 422	51 to 95
	Intermediate	6 to 16	86 to 2,110	24 to 109
	Deep	10 to 11	10 to 131	32 to 233

(a) All reported quantities are in mg/L, except for pH, which is in log units, and ORP, which is in mV.

(b) ORP (469 mV) measured in the shallow well during the extended monitoring period may have been affected by interference from $KMnO_4$.

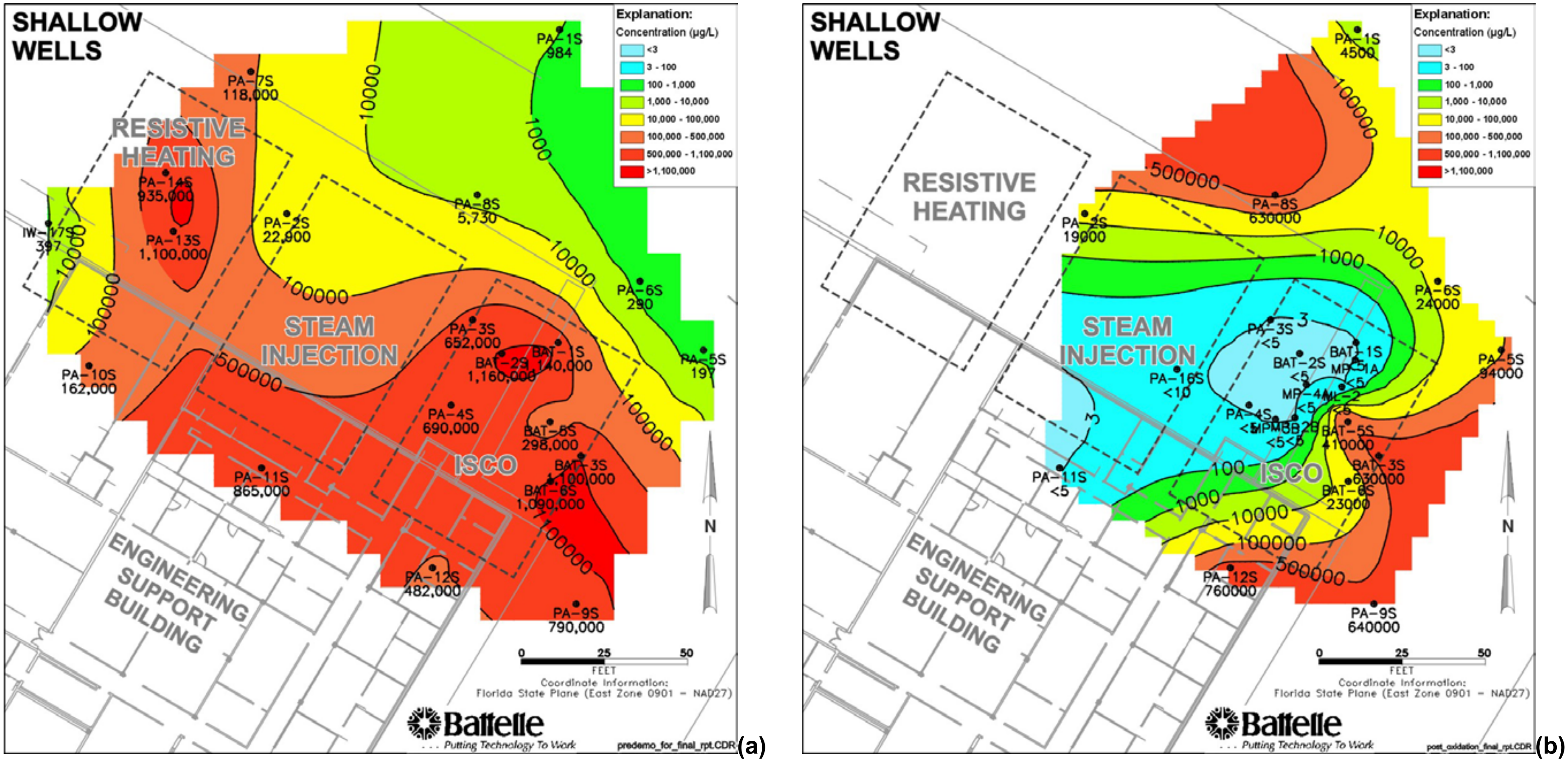


Figure 5-9. Dissolved TCE Concentrations (µg/L) during (a) Predemonstration (August 1999) and (b) Postdemonstration (May 2000) Sampling of Shallow Wells

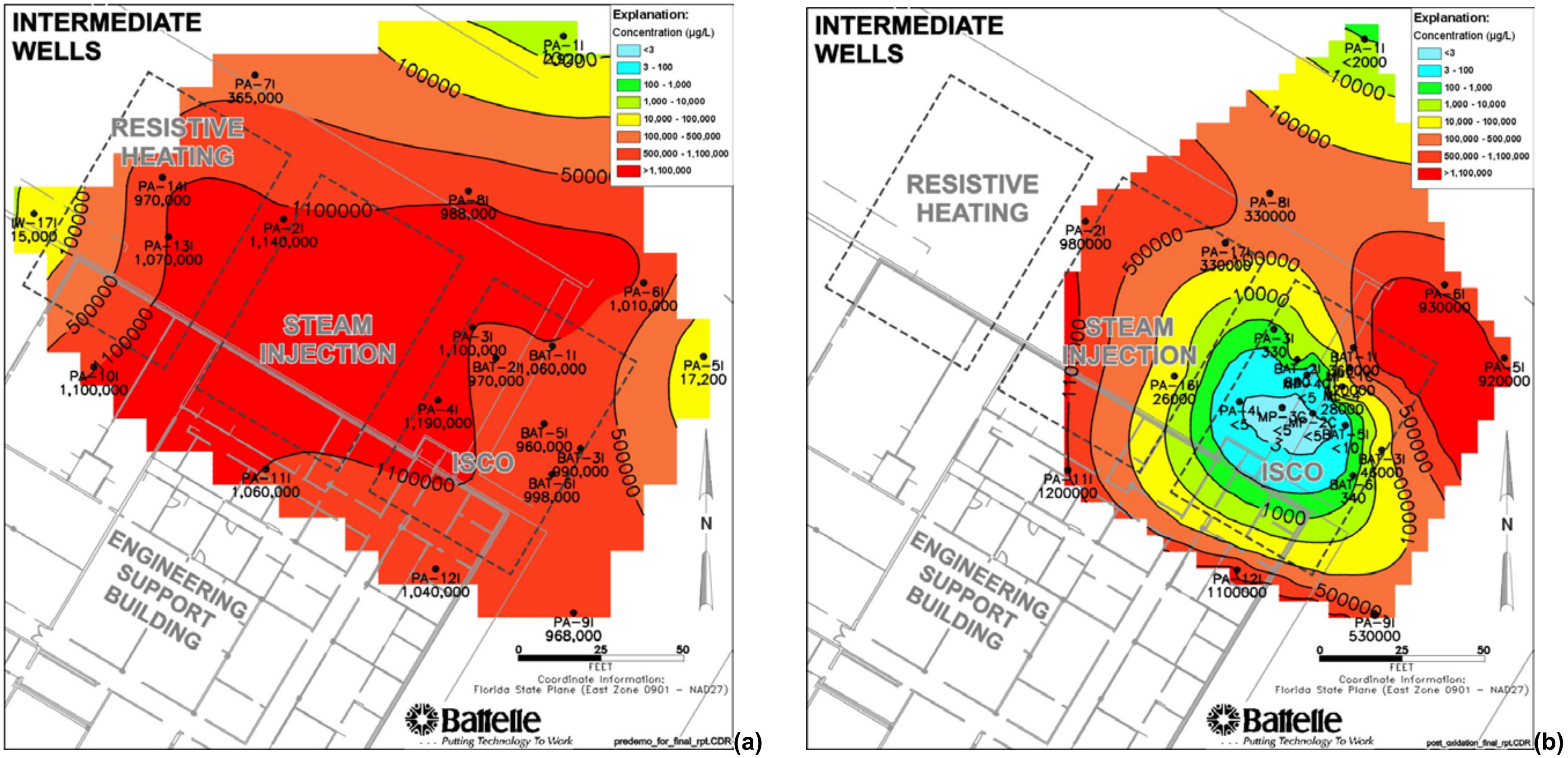


Figure 5-10. Dissolved TCE Concentrations (µg/L) during (a) Predemonstration (August 1999) and (b) Postdemonstration (May 2000) Sampling of Intermediate Wells

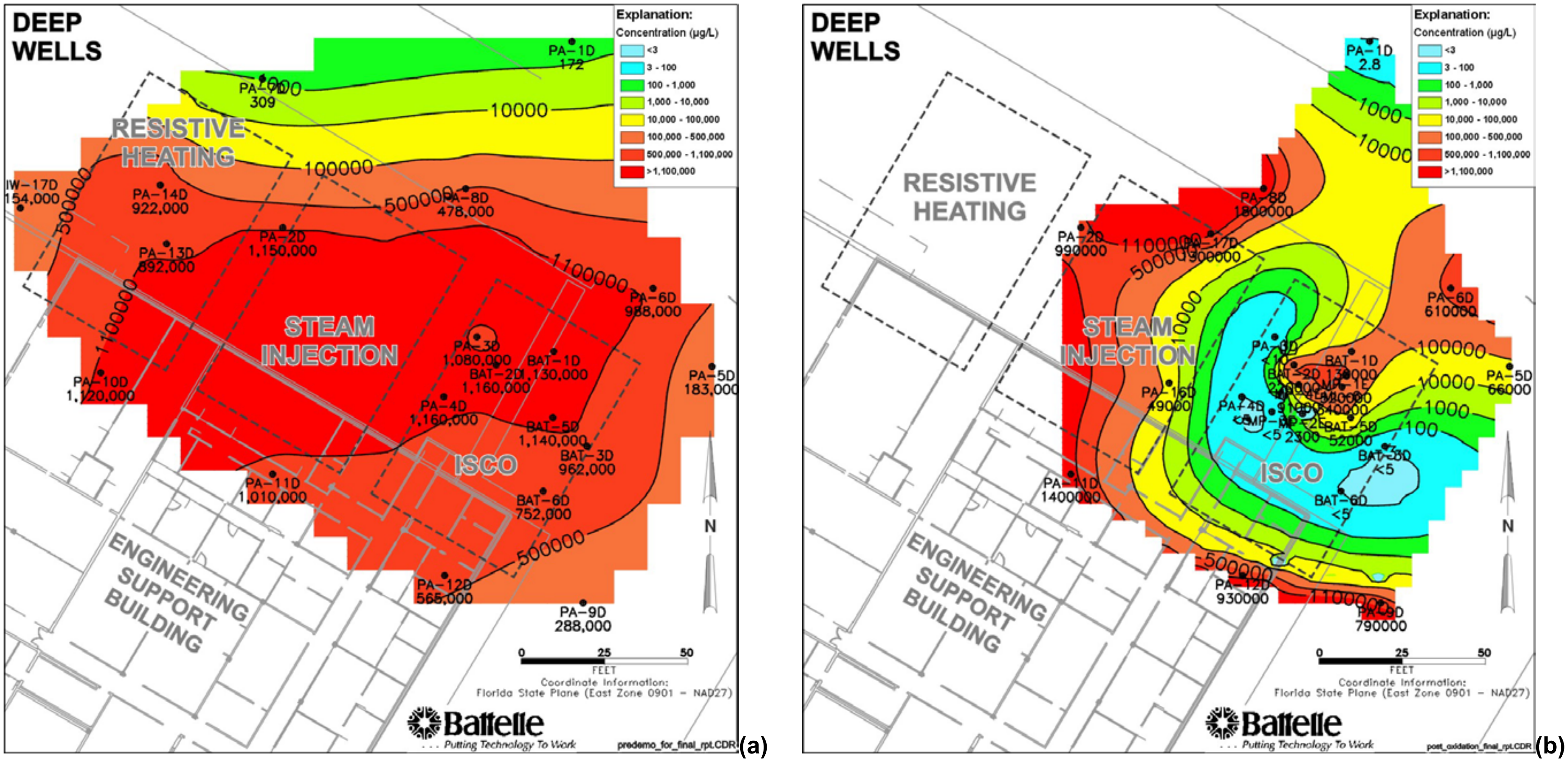


Figure 5-11. Dissolved TCE Concentrations (µg/L) during (a) Predemonstration (August 1999) and (b) Postdemonstration (May 2000) Sampling of Deep Wells

- Local heterogeneities near BAT-5S may have prevented sufficient oxidant from reaching this region, as well as perhaps other regions in the plot. In many wells inside the ISCO plot, the water turned purple during the demonstration, indicating excess permanganate and good oxidant distribution. However, in some wells in the plot (such as BAT-5, which is relatively close to one of the injection points), the water never turned purple, indicating that preferential pathways dominated flow and oxidant distribution on the scale of the plot. Local heterogeneities may limit the amount of oxidant encountered through advective flow in certain regions of the plot; some of these regions may be relatively close to oxidant injection points. Another possibility is that the injected oxidant encountered so much DNAPL and natural organic matter that it was depleted prior to reaching a neighboring monitoring well. Over time, it is possible that permanganate may persist in the vicinity long enough to penetrate into such difficult spots by diffusion. In fact, during the extended monitoring event (see Table 5-3), there were signs that TCE levels in BAT-55 were beginning to decline.
- Redistribution of residual DNAPL within the plot due to hydraulic gradients is unlikely; residual DNAPL does not move out of pores by hydraulic gradient alone. On the other hand, some mobile DNAPL in the plot may have migrated into the BAT-5S well early during the injection and subsequently created elevated TCE levels in the well.
- Another possibility is that the sharp increase in TCE in BAT-5S and some perimeter wells (see Section 5.2.2) is due to the increased groundwater flow through previously less permeable regions of the DNAPL source zone. Partial removal of DNAPL by oxidation increases the permeability of the DNAPL source regions to groundwater flow (Pankow and Cherry, 1996). Therefore, DNAPL mass removal, if it is not 100%, can initially elevate dissolved TCE concentrations, although reduced dissolved-TCE levels will result over subsequent years.

The concentration of *cis*-1,2-DCE declined considerably in several wells (e.g., BAT-1S, BAT-2S, BAT-3D, BAT-6D, PA-4S, and PA-4I) within the plot. Vinyl chloride was not detected in several wells both before and after the demonstration, primarily because of the analytical limitations associated with samples containing higher levels of TCE.

5.2.2 Changes in Aquifer Geochemistry

Among the field parameter measurements (tabulated in Table 5-4 and Appendix D) conducted in the affected aquifer before, during, and after the demonstration, the following trends were observed:

- Groundwater *temperature* ranged from 26 to 29°C before the demonstration to 27 to 29°C after the demonstration (relatively unchanged). This was expected as there is no exothermic reaction involved with permanganate, as with some other oxidants.
- Groundwater *pH* ranged from 7.0 to 7.6 before the demonstration to 6.4 to 7.7 after the demonstration, with some fluctuation during the demonstration. A pH drop would be expected in an unbuffered system as the oxidation reaction produces hydrogen ions and CO_2. However, as discussed in Section 5.3.1, the native groundwater alkalinity and carbonate shell materials provide a buffer, and limit any change in pH.
- *ORP* increased from −22 to −165 mV before the demonstration to −171 to 469 mV after the demonstration, with some fluctuation during the demonstration. The higher ORP is indicative of the oxidizing conditions created in the plot.
- *DO* ranged from <0.5 to 2.7 mg/L before the demonstration to <0.5 to 3.1 mg/L after the demonstration, with some fluctuation during the demonstration. Some DO may have been introduced into the aquifer through the hydrant water used to make up the permanganate solution. Due to the limitations of measuring DO with a flowthrough cell, groundwater with DO levels below 1.0 is considered anaerobic. Except for the shallower regions, the aquifer was mostly anaerobic through the demonstration.
- *Conductivity* increased from 0.5 to 2.7 mS/cm before the demonstration to 6.7 to 14.6 mS/cm after the demonstration (see Appendix D-1). The increase is attributed to a buildup of dissolved ions formed from the mineralization of organic matter and CVOCs. Also, this possibly resulted from residual permanganate in solution.

Other groundwater measurements indicative of aquifer quality included inorganic ions, BOD, and TOC. The results of these measurements are as follows:

- *Calcium* and *magnesium* levels remained relatively unchanged in the shallow and intermediate wells, but increased in the deep wells. In the deep wells, predemonstration levels of calcium (84 to 88 mg/L) and magnesium (82 to 84 mg/L) rose to postdemonstration levels of 210 to 349 mg/L (calcium) and 53 to 203 mg/L (magnesium). Calcium levels further increased to 1,020 mg/L during the extended monitoring, nine months after the demonstration.

Groundwater *alkalinity* increased from 204 to 323 mg/L before the demonstration to 1,060 to 2,140 mg/L after the demonstration. The sharp changes in calcium, magnesium, and alkalinity can be attributed to the oxidation of organic matter and CVOCs that leads to CO_2 generation in the aquifer, and the interaction of this CO_2 with shell material and groundwater in open (shallow aquifer) and closed (deep aquifer) systems, as described in Section 5.3.1.

- *Chloride* levels were already relatively high in the aquifer due to saltwater intrusion, especially in the deeper units. Despite relatively high native chloride levels in the aquifer and despite the dilution effect of hydrant water containing 94 mg/L that was used to make up the permanganate injection solution, chloride concentrations increased noticeably in the three stratigraphic units. In the shallow wells, chloride increased from 38 to 53 mg/L before the demonstration to 126 to 531 mg/L after the demonstration. In the deep wells, chloride levels increased from 722 to 752 mg/L before the demonstration to 1,360 to 1,730 mg/L after the demonstration. Nine months after the demonstration, chloride levels in the deep wells had increased to as high as 5,070 mg/L. These increased chloride levels are a primary indicator of CVOC destruction due to ISCO. The secondary drinking water limit for chloride is 250 mg/L.
- *Manganese* levels in the plot rose from <0.015 to 1.1 mg/L before the demonstration to as high as 516 mg/L in BAT-5I after the demonstration; manganese has a secondary drinking water limit of 0.05 mg/L, which was exceeded during and after the demonstration. Perimeter wells also showed elevated levels of manganese. Dissolved manganese consists of the species Mn^{7+} (from excess permanganate ion) and Mn^{2+} (generated when MnO_2 is reduced by native organic matter). Mn^{7+} levels are expected to subside over time, as excess permanganate precipitates out as MnO_2 and normal groundwater flow re-establishes in the plot. Mn^{2+} is generated when MnO_2 enters a reducing environment. Mn^{2+} is not a health hazard, but it can cause discoloration of the water above 0.05 mg/L. As the water enters a more aerobic environment (as may be present outside the CVOC plume), Mn^{2+} will precipitate out as MnO_2. Manganese levels declined considerably with distance from the plot (see Table D-2 in Appendix D).
- *Iron* levels in the ISCO plot remained relatively unchanged at levels of <0.05 to 2.5 mg/L in the native groundwater and <0.05 to 1.1 mg/L in the postdemonstration water. In the extended monitoring, iron levels had increased to as high as 35.6 mg/L in one well. The secondary drinking water limit for iron is 0.3 mg/L, which was exceeded during and after the demonstration. Precipitation of ferric iron on soil was visually noted (as orange color) and the expectation was that dissolved iron levels would decrease. Some dissolution of iron from underground materials could have occurred that replenished dissolved iron. The monitoring wells are made of stainless steel and are fairly resistant to the oxidant; however, chloride may corrode stainless steel and dissolve some iron and, perhaps, chromium and nickel.
- *Sulfate* levels increased sharply from 29 to 138 mg/L before the demonstration to 379 to 1,380 mg/L in postdemonstration water. In the extended monitoring, sulfate levels increased to 1,810 mg/L in one well. This increase in sulfate may be due to oxidation of reduced sulfur species in the native soil.
- *TDS* levels increased considerably in all three units. In the shallow wells, TDS levels rose from 387 to 499 mg/L before the demonstration to 2,860 to 6,790 mg/L after the demonstration; in the intermediate wells, TDS rose from 517 to 760 mg/L before to 3,640 to 13,000 mg/L after the demonstration; in the deep wells, TDS rose from 1,490 to 1,550 mg/L before to 5,250 to 8,280 mg/L after the demonstration. During extended monitoring, TDS levels remained high. The secondary drinking water limit for TDS is 500 mg/L, which was exceeded both before and after the demonstration.
- Table 5-5 shows the groundwater cleanup target levels issued by the State of Florida for 12 *trace metals*. The primary drinking water limits for chromium, nickel, and thallium were exceeded in some of the ISCO plot wells during and after the demonstration. Chromium (PA-3S, PA-5S, and PA-12D) and nickel (PA-5S and PA-12 cluster) limits were also exceeded in some of the perimeter wells. The secondary drinking water standard for aluminum was exceeded on one occasion during the demonstration, but subsided after the demonstration.

  Metals of concern that are minor ingredients in the industrial-grade $KMnO_4$ batch used at Launch Complex 34 are listed in Table 5-6 (see Appendix I for the technical specification sheet from the manufacturer). This table also shows the expected concentrations in the groundwater, if the metals entering the aquifer stay within the test plot (a worst case scenario). When the expected concentrations are compared with the actual concentrations in the groundwater before and after ISCO treatment, the increases in concentrations of chromium and nickel are difficult to attribute to the injected permanganate

Table 5-5. Postdemonstration Concentrations of Trace Metals in Groundwater at Launch Complex 34 versus the State of Florida Standards (issued May 26, 1999)

Trace Metal	Maximum Concentration Measured in Treated Aquifer (μg/L)	State of Florida Drinking Water Limit (μg/L)	Standard
Aluminum	<200	200	Secondary
Antimony	<6	6	Primary
Arsenic	21	50(a)	Primary
Barium	<200	2,000	Primary
Beryllium	<10	4	Primary
Chromium	193,000	100	Primary
Copper	<25	1,000	Secondary
Lead	12	15	Primary
Nickel	10,600	100	Primary
Silver	38	100	Secondary
Thallium	20	2	Primary
Zinc	56	5,000	Secondary

(a) The federal arsenic standard for drinking water standard was recently lowered to 10 μg/L.

Shading denotes the metals that are exceeding the State of Florida drinking water standard.

Table 5-6. Contribution from the Industrial-Grade $KMnO_4$ to Elevated Levels of Trace Metals in the ISCO Plot

Metals	Metal Concentration in the Industrial-Grade $KMnO_4$ Used (mg/kg)	Expected Metal Concentration in Aquifer(a) (mg/L)	Maximum Concentration in Untreated Aquifer (mg/L)	Maximum Concentration Measured in Treated Aquifer (mg/L)
Aluminum	61.6	1.17	<0.2	<0.2
Antimony	0.8	0.02	<0.006	<0.006
Arsenic	3.3	0.06	1.11	0.021
Barium	11.1	0.21	<0.1	<0.2
Beryllium	<0.8	0.01	<0.005	<0.01
Chromium	10	0.19	<0.01	193
Copper	25.3	0.48	<0.025	<0.25
Iron	24.7	0.47	1.1	35.6
Lead	1.4	0.03	<0.003	0.012
Nickel	4.2	0.08	0.066	10.6
Silver	<0.8	0.01	<0.01	0.038
Thallium	3.4	0.06	<0.01	0.02
Zinc	3.8	0.07	<0.02	0.056

(a) The expected metal concentration due to $KMnO_4$ was calculated based on the volume (1,274,265 L) of porewater in the ISCO plot (porosity of 0.3) and the mass (66,956 kg) of $KMnO_4$ used for the ISCO demonstration.

chemical. Other possible sources of chromium and nickel could be the aquifer itself (metals extracted from the soil particles by the action of the strong oxidant) or the stainless steel (Fe-Ni-Cr alloy) monitoring wells. Iron levels increased sharply in some wells, too.

On the other hand, actual thallium levels in the posttreatment aquifer are of the same approximate order as the expected levels. Given the fact that some injected thallium would migrate outside the test plot, the elevated thallium concentrations in the test plot could be attributed to the injected permanganate. Elevated levels of trace metals in the treated aquifer are expected to eventually subside by advection and diffusion over time. To a certain extent, the manganese dioxide formed when permanganate reacts with organic matter, can itself adsorb some of the trace metals released. Elevated levels of trace metals are an issue that needs further investigation in the context of industrial-grade potassium permanganate application to the subsurface.

- *TOC and BOD* data were difficult to interpret. TOC in groundwater ranged from 4 to 16 mg/L before the demonstration and from 10 to 2,110 mg/L after the demonstration. BOD declined in some wells, increased in other wells, and remained unchanged in some wells, indicating the variations in the efficiency of oxidant distribution in different regions of the plot. BOD increased sharply in BAT-5S and BAT-5D, from <3 to 13 mg/L before the demonstration to <2 to 112 mg/L after the demonstration. The increase in groundwater TOC and BOD may indicate greater dissolution of native organic species in the groundwater due to oxidation. TOC levels measured in soil remained relatively unchanged, ranging from 0.9 to 1.8% before the demonstration and from 0.8 to 1.8% after the demonstration.

In addition to measuring inorganic parameters in the ISCO plot wells, they also were measured in the perimeter wells surrounding the plot and selected distant wells to see how far the influence of the ISCO would progress. In addition to the geochemistry, the effect of the ISCO treatment on the aquifer microbiology was evaluated in a separate study as described in Appendix E.

5.2.3 Changes in the Hydraulic Properties of the Aquifer

Table 5-7 summarizes the results (see Appendix B) of slug tests conducted in the ISCO plot before and after the demonstration. Hydraulic conductivity of the aquifer ranged from 1.3 to 6.4 ft/day before the demonstration to 1.4 to 5.0 ft/day after the demonstration. There was no noticeable difference in the hydraulic conductivity due to

Table 5-7. Pre- and Postdemonstration Hydraulic Conductivity at ISCO Plot Aquifer

	Hydraulic Conductivity (ft/day)	
Well	**Predemonstration**	**Postdemonstration**
BAT-5S	4.0	5.0
BAT-6S	5.1	Poor response
BAT-3I	1.6	2.4
BAT-5I	6.4	1.5
BAT-6I	1.4	3.7
BAT-3D	1.3	Poor response
BAT-6D	2.3	1.4

the ISCO treatment. Any buildup of MnO_2 or other solids due to the chemical oxidation process does not seem to have affected the hydraulic properties of the aquifer. It is possible that the lack of change in hydraulic conductivity is due to the fact that any porosity loss caused by generation of MnO_2 solids is offset by the porosity gain from calcium carbonate solids that go into solution because of the CO_2 generated in the oxidation process. Also, if the MnO_2 solids are small enough, they could have been transported out of the test plot with the groundwater flow.

5.2.4 Changes in Microbiology of ISCO Plot

Microbiological analysis of soil and groundwater samples was conducted to evaluate the effect of the ISCO application on the microbial community (see Appendix E for details). Samples were collected before, six months after (as postdemonstration monitoring), and nine months after the ISCO technology demonstration. For each monitoring event, soil samples were collected from five locations in the plot and five locations in a control (unaffected) area. At each location, four depths were sampled—capillary fringe, Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit. The results are presented in Appendix E.

Table 5-8 summarizes the soil analysis results. The geometric mean typically is the mean of the five samples collected in each stratigraphic unit in the plot. Because microbial counts can be highly variable, only order-of-magnitude changes in counts were considered significant. Figure 5-12 illustrates the live/dead stain analysis of soil samples (see Appendix E for detailed data).

In the Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit, aerobic microbial populations decreased immediately following the demonstration. In the capillary fringe, aerobic counts increased. Anaerobic microbial populations decreased in the Upper Sand Unit, but increased in the Lower Sand Unit. In other stratigraphic units, the populations appeared to be relatively constant. The postdemonstration microbial counts indicate that microbial populations may have declined during the ISCO treatment. In some parts of the plot, both aerobic and anaerobic counts declined to below detection, immediately after the oxidant injections. The live/dead stain analysis (Appendix E) also appears to indicate a decline in the percentage of live cells immediately after the demonstration, although the variability in the results is quite high. However, the microbial counts during the extended monitoring event indicate that microbial populations rebound quickly and re-establish in all parts of the plot.

Table 5-8. Geometric Mean of Microbial Counts in the ISCO Plot (Full Range of Replicate Sample Analyses Given in Parentheses)

ISCO Plot	**Pre-demonstration Aerobic Heterotrophic Counts (CFU/g)**	**Post-demonstration Aerobic Heterotrophic Counts (6 months after) (CFU/g)**	**Extended Monitoring Aerobic Heterotrophic Counts (9 months after) (CFU/g)**	**Pre-demonstration Anaerobic Heterotrophic Counts (cells/g)**	**Post-demonstration Anaerobic Heterotrophic Counts (6 months after) (cells/g)**	**Extended Monitoring Anaerobic Heterotrophic Counts (9 months after) (cells/g)**
Capillary Fringe	66,069 (3,981 to 1,584,893)	11,220,184 (3,162,278 to 100,000,00)	1,096,478 (19,952 to 63,095.7)	57,543 (5,012 to 1,584,893)	1,584,893 (1,584,893 to >1,584,893)	3,019,952 (251,188.6 to >31,622,776.6)
Upper Sand Unit	39,810.7 (1,259 to 100,000)	420.9 (<316.2 to 7,943)	478,630 (7,943 to 7,943,282)	85,770 (2,512 to 316,228)	8 (<1.78 to 6,310)	1,737,800 (199,526 to 19,952,623)
Middle Fine-Grained Unit	14,125 (501 to 125,893)	15,841 (<316.2 to 1,584,893)	316,227 (15,848.9 to 1,258,925)	7,499 (794 to 79,432.8)	12,879 (<1.78 to 1,584,893	457,088 (7,943 to 3,162,277)
Lower Sand Unit	6,309.6 (316 to 316,228)	218,776 (7,943 to 7,943,282)	114,815 (19,952 to 316,227.8)	4,365 (251 to 63,096)	239,883 (1,259 to >1,584.9)	416,869 (50,118.7 to 3,981,071)

CFU = colony-forming unit.

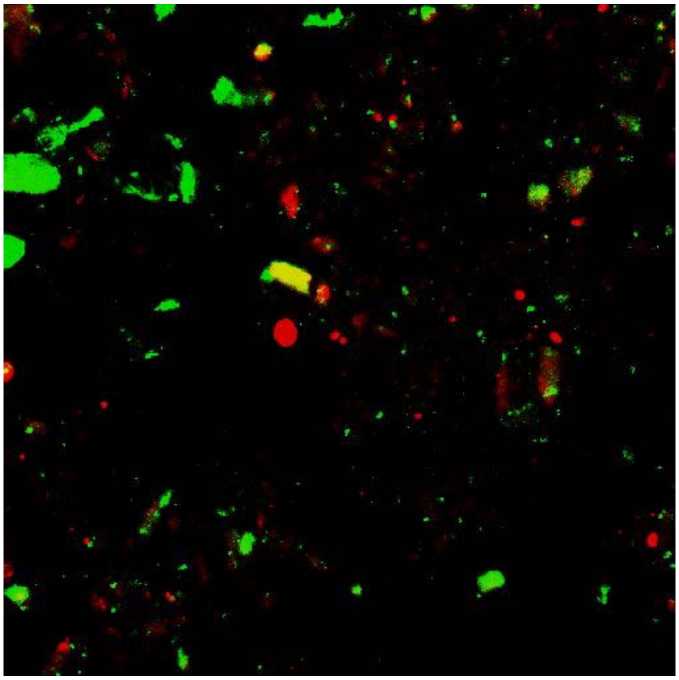


Figure 5-12. Representative Live/Dead Stain Analysis of Microorganisms in Soil (green indicating live, red indicating dead, and yellow indicating injured microorganisms)

5.2.5 Summary of Changes in Aquifer Quality

In summary, application of the ISCO technology created the following changes in the aquifer:

- Dissolved TCE levels declined sharply in several monitoring wells in the ISCO plot, with some wells showing postdemonstration concentrations of less than 5 µg/L, the federal drinking water standard. Achievement of the State of Florida groundwater target cleanup level of 3 µg/L could not be determined because excessive permanganate in several of the postdemonstration groundwater samples caused analytical interference and required dilution. In some wells within the ISCO plot, TCE levels declined, but stayed above 5 µg/L. In one of the shallow wells, TCE levels rose through the demonstration, indicating that local heterogeneities (limited oxidant distribution) or redistribution of groundwater flow due to partial DNAPL removal may have affected dissolved TCE levels. *cis*-1,2-DCE levels in all monitoring wells declined to below 70 µg/L. Vinyl chloride levels in some wells declined to less than 1 µg/L, the State of Florida target; in some wells, higher TCE levels elevated the detection limits of vinyl chloride. This indicated that ISCO considerably improved groundwater quality in the short term. There are some signs of a rebound in TCE and *cis*-1,2-DCE concentrations in the test plot during the extended monitoring that was conducted nine months after the end of the injections. Although TCE and *cis*-1,2-DCE levels rebounded to some extent in the nine months following the demonstration, they were still below the predemonstration levels in most wells. In any case, DNAPL mass removal is expected to lead to eventual and earlier disappearance of the plume over the long term. There is also the possibility that even in the medium term, as normal groundwater flow is reestablished, a weakened plume may be generated and the resulting CVOC levels may be amenable to natural attenuation.
- Temperature, pH, and DO remained relatively stable through the demonstration. ORP and conductivity of the groundwater increased, indicating oxidizing conditions and accumulation of dissolved ions.
- Calcium and magnesium levels rose in the deeper groundwater, indicating interactions with the shell material in the lower stratigraphic units (see Section 5.3.1).
- Alkalinity, chloride, and total dissolved solids levels rose sharply, indicating oxidation of TCE and native organic matter with carbon dioxide generation (see Section 5.3.1). High chloride and TDS levels both before and after the demonstration cause the groundwater to be classified as brackish.
- Dissolved manganese levels in the plot rose above secondary drinking water limits following the demonstration.
- Dissolved sulfate levels rose, indicating possible interactions between the oxidant and soil matter.
- Some trace metals, namely chromium, nickel, and thallium, exceeded State of Florida drinking water limits following the demonstration. The source of these metals is unclear. They could have been released from the soil matrix or the stainless steel monitoring wells. Some contribution from the industrial-grade permanganate is likely. Nine months after the end of the oxidant injections, the levels of these metals in the test plot were still elevated. The elevated levels of these trace metals are expected to subside over time, as flow is reestablished. The levels of these metals decline significantly as the water reaches the monitoring wells surrounding the plot, probably due to adsorption on the aquifer solids and on the newly generated manganese dioxide.
- The geochemical interactions between the oxidant and the aquifer are relatively complex, and not all of

the aquifer changes were easy to explain. The persistence of dissolved iron, the variability of 5-day BOD, the increase in sulfate, and the persistence of TOC in the postdemonstration aquifer are difficult to explain without further research.

5.3 Evaluating the Fate of the TCE/DNAPL Mass Removed

This part of the performance assessment was the most difficult because there are several pathways that the DNAPL could take when subjected to the ISCO treatment. These pathways were evaluated as follows:

5.3.1 DNAPL Destruction through Oxidation of TCE

As described in Equations 5-1 and 5-2, oxidation of TCE and other CVOCs by permanganate leads to the formation of chloride, carbon dioxide, hydrogen ion, and manganese dioxide. Any manganese dioxide generated is insoluble in water and is expected to deposit on the soil surfaces — the brown discoloration of soil observed in some soil samples indicates the formation of manganese dioxide. The soluble or partially soluble species — chloride, carbon dioxide, carbonate (alkalinity), and hydrogen ion (pH) — are more amenable to more direct measurement.

$$\begin{gathered} C_2HCl_3 + 2MnO_4^- \rightarrow \\ 3Cl^- + 2CO_2 + H^+ + 2MnO_2\ (s) \end{gathered} \qquad (5\text{-}1)$$

$$\begin{gathered} C_2H_2Cl_2 + 2MnO_4^- \rightarrow \\ 2Cl^- + 2CO_2 + 2H^+ + 2MnO_2\ (s) \end{gathered} \qquad (5\text{-}2)$$

Chloride is the strongest indicator of TCE oxidation, because it is directly traceable to TCE; because of the high injection pressures (and high water levels) in the ISCO plot during ISCO treatment, not much chloride intrusion is expected from tidal influence over the time period of the demonstration. Chloride generation due to oxidation would be expected to cause chloride levels to rise in the aquifer. Appendix D shows the pre- and postdemonstration chloride levels in the ISCO plot and surrounding aquifer. The increased chloride concentrations are noticeable in all three units — Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit — even though predemonstration chloride levels were high to begin with. Chloride levels in the aquifer increased to levels that were above the concentration level of water from the hydrant (94 mg/L chloride content) used to make up the oxidant solution.

Figures 5-13 to 5-15 show the distribution of excess chloride in the shallow, intermediate, and deep wells, respectively, as measured in May 2000, towards the end of the ISCO treatment. The chloride concentrations in these figures are the differences in chloride levels between the treated (postdemonstration) and native (predemonstration) levels of chloride. The strongest increase in chloride was observed in the deep wells (Lower Sand Unit), where the predemonstration DNAPL mass was highest. Most of the chloride increase in the test plot is attributable to oxidation of TCE by the permanganate. Because oxidation of TCE occurs in the aqueous phase, the treatment kinetics may be driven by the rate of dissolution of DNAPL, rather than the oxidation of dissolved TCE, which is a relatively fast process. There are reports that addition of permanganate increases the rate of dissolution of TCE by as much as a factor of 10 (Siegrist et al., 2001). There is very little possibility of chloride migrating into the ISCO plot from the resistive heating plot, because strong hydraulic gradients have been measured emanating radially outward from the ISCO plot during most of the ISCO application period. Some of the chloride formed probably migrated out of the ISCO plot under the strong hydraulic gradients created by the oxidant injection.

Carbon dioxide is an indicator of oxidation, although not of TCE alone. Native organic matter that is oxidized also releases carbon dioxide as indicated in Equation 5-3, which is a simplified illustration. However, TOC levels in the predemonstration groundwater and soil were relatively unchanged, or increased slightly (see Section 5.2.2), possibly due to the formation of new organic species from the complex native humic matter in the soil. Formation of carbon dioxide is an encouraging sign that TCE and native organic matter are being oxidized.

$$\begin{gathered} 3C_{organic} + 4MnO_4^- + 4H^+ \rightarrow \\ 3CO_2 + 4MnO_2\ (s) + 2H_2O \end{gathered} \qquad (5\text{-}3)$$

In an unbuffered system, the CO_2 generated may be expected to lower the *pH* of the aquifer. Dissolution of gaseous CO_2 in water can be expressed according to the following mass action equation:

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO^*_{3(aq)} \qquad (5\text{-}4)$$

where H_2CO_3* represents both dissolved CO_2 ($CO_{2(aq)}$) and carbonic acid (H_2CO_3). The predominant carbon species are H_2CO_3 below pH 6.3; HCO_3^- between pH 6.3 and 10.3, and CO_3^{-2} above pH 10.3. The presence of *carbonate* species in the Launch Complex 34 groundwater provides buffering capacity, which attenuates the effects of the accumulating acidic species (CO_2) in the water due to the oxidation treatment.

The other major factor in the geochemical scenario at Launch Complex 34 is the abundance of shell material in the aquifer soil. Carbonate rocks and biological shell

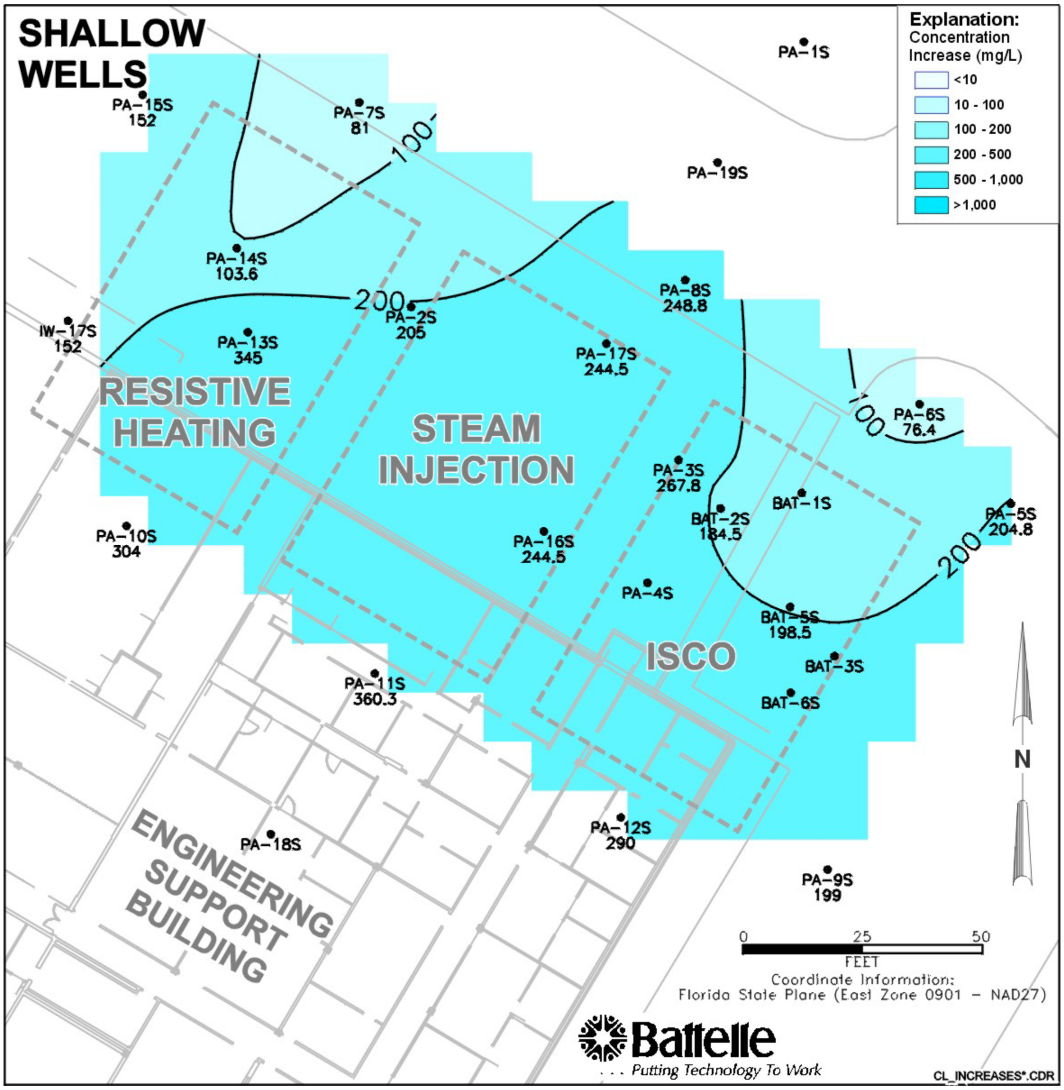


Figure 5-13. Distribution of Chloride Produced by ISCO Technology in Shallow Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

material are composed primarily of calcium carbonate, and minor amounts of other metals, such as magnesium, iron, and manganese. Equilibrium between calcium carbonate (typically calcite or aragonite mineral forms) and water in the presence of CO_2 can be expressed as Equation 5-5 (Appelo and Postma, 1994).

$$CaCO_{3(solid)} + CO_{2(g)} + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (5\text{-}5)$$

If a source of CO_2 is available, calcite will dissolve. Oxidation of organic matter by permanganate causes generation of CO_2. During the continuous oxidation, the partial pressure of CO_2 is probably high enough to cause a release of substantial amounts of calcium and bicarbonate ions into solution from the shell material. This could explain the sharp increase in alkalinity in all the ISCO plot wells, as well as the increase in dissolved *calcium* in some wells. Note that if calcite (shell material) were not available in the soil, the reaction in Equation 5-4 would apply, and the groundwater pH would have decreased accordingly. Therefore, despite the persistence of neutral pH and relatively low ORP in the posttreatment groundwater, the geochemistry indicates that a large amount of carbon dioxide was produced and a large portion of the organic matter (probably including the organic contaminants) was oxidized. The sharp increase in alkalinity and the substantial increase in inorganic chloride are encouraging signs that a significant proportion of the DNAPL removal was due to oxidation.

From a long-term perspective, it is important to note that after the CO_2 is exhausted, the system may not return to its original state, even though equilibrium is regained. In general, the aquifer environment is an open system, so

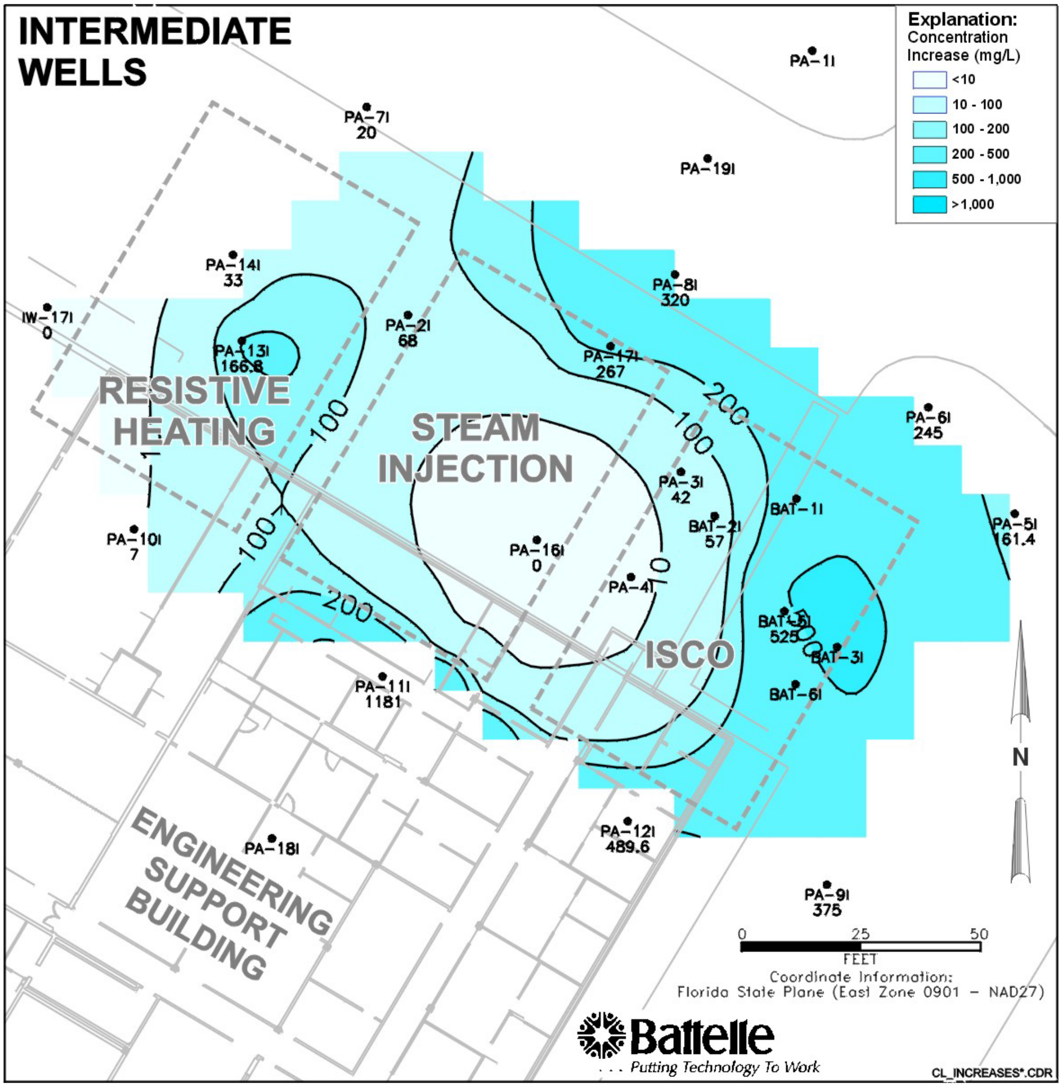


Figure 5-14. Distribution of Chloride Produced by ISCO Technology in Intermediate Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

the partial pressure of CO_2 does return to its normal level after oxidation subsides. However, during the period when CO_2 is being produced, the HCO_3^- content increases logarithmically with pH, so that the final bicarbonate concentration at equilibrium is completely controlled by the initial partial pressure of CO_2 and the solubility of the calcite in the shell material. Therefore, the only way for the alkalinity and calcium levels in the groundwater to return to pretreatment levels is through dilution with the groundwater from the surrounding aquifer. In the relatively stagnant aquifer at Launch Complex 34, this could take a long time. Rainfall and recharge from the ground surface also could play a role in the rebound.

One aspect of the ISCO application that was not addressed during this demonstration is the formation of byproducts from incomplete oxidation of CVOCs and natural organic matter. This issue may best be addressed on a bench scale.

In summary, all the geochemical indicators examined point to oxidation as a pathway that contributed substantially to the removal of TCE/DNAPL from the ISCO plot. These geochemical indicators include:

- Considerable rise in chloride levels in the treated aquifer
- Considerable increase in groundwater alkalinity (as indicative of carbon dioxide generation)
- Rise in calcium levels in the deeper portions of the aquifer.

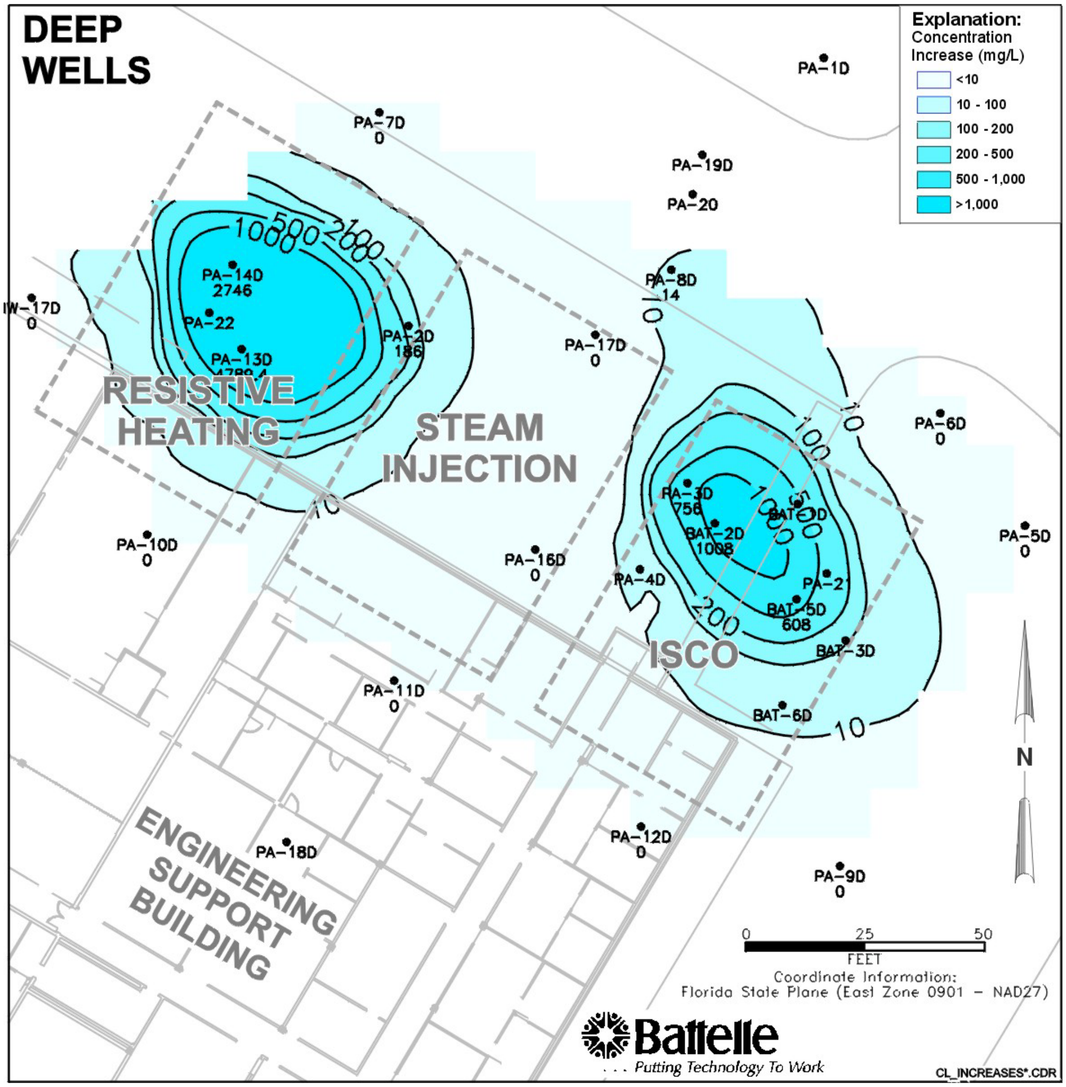


Figure 5-15. Distribution of Chloride Produced by ISCO Technology in Deep Wells near the Engineering Support Building at Launch Complex 34 (May 2000)

5.3.2 Potential for DNAPL Migration from the ISCO Plot

The six measurements conducted to evaluate the potential for migration of DNAPL, as well as dissolved vapor and nonaqueous phase, to the surrounding aquifer include:

- Hydraulic gradient in the aquifer
- Distribution of dissolved potassium in the aquifer
- TCE measurements in perimeter wells
- TCE concentrations in the surrounding aquifer soil cores
- TCE concentrations in the vadose zone soil cores
- TCE concentrations in surface emissions to the atmosphere.

As mentioned in Section 5.2, predemonstration *hydraulic gradients* in the Launch Complex 34 aquifer are relatively flat in all three stratigraphic units. During the demonstration, hydraulic gradients (see Figures 5-16 to 5-18) were measured in April 2000 in the shallow, intermediate, and deep wells, respectively, while the third and final oxidant injection was under way in the Lower Sand Unit. Water level measurements in the deep wells showed a sharp hydraulic gradient emanating radially from the ISCO plot because of the injection pressures. Interestingly, the gradient was not as strong in the shallow and intermediate wells while oxidant was being injected in the deeper layers, indicating that the Middle Fine-Grained Unit acts as a conspicuous hydraulic barrier.

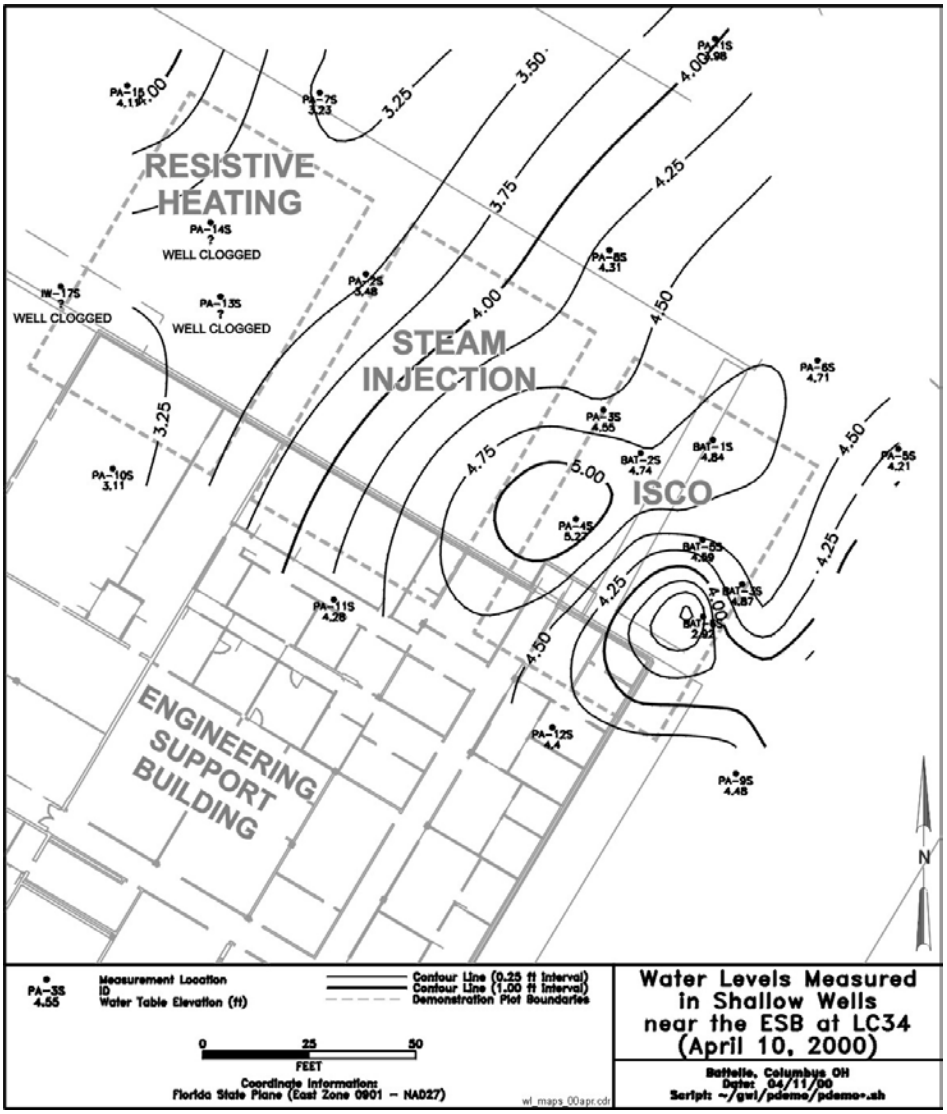


Figure 5-16. Water Levels Measured in Shallow Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

Residual DNAPL cannot migrate due to hydraulic gradient alone, no matter how strong. However, if mobile DNAPL was present in the aquifer, strong injection pressures could have caused DNAPL movement from the plot.

Migration of groundwater and dissolved groundwater constituents from the ISCO plot are exemplified by the movement of *potassium ion* in the aquifer, as shown in Figures 5-19 to 5-21. Because there were no monitoring wells at the time in the steam injection plot, this area is blanked out in these figures to avoid interpolating over relatively large distances. Potassium, originating from the injected oxidant, acts as a semiconservative tracer for tracking groundwater movement. Figures 5-19 to 5-21 show the excess potassium (above predemonstration levels) in the groundwater at Launch Complex 34. The vapor extraction occurring in the resistive heating plot could have exacerbated the effect of the westward hydraulic gradient and increased the migration of water and ions from the ISCO plot. Also, vaporization of water in the resistive heating plot could have caused dissolved ion levels in the resistive heating plot and vicinity to increase. Because more monitoring wells are present on the western side of the ISCO plot, movement seems to be occurring to the west; however, similar groundwater transport probably occurred in all directions from the plot. This migration of groundwater and dissolved species from the ISCO plot is an important aspect of injecting oxidant without concomitant extraction or hydraulic control, and may need to be reviewed on a site-specific basis.

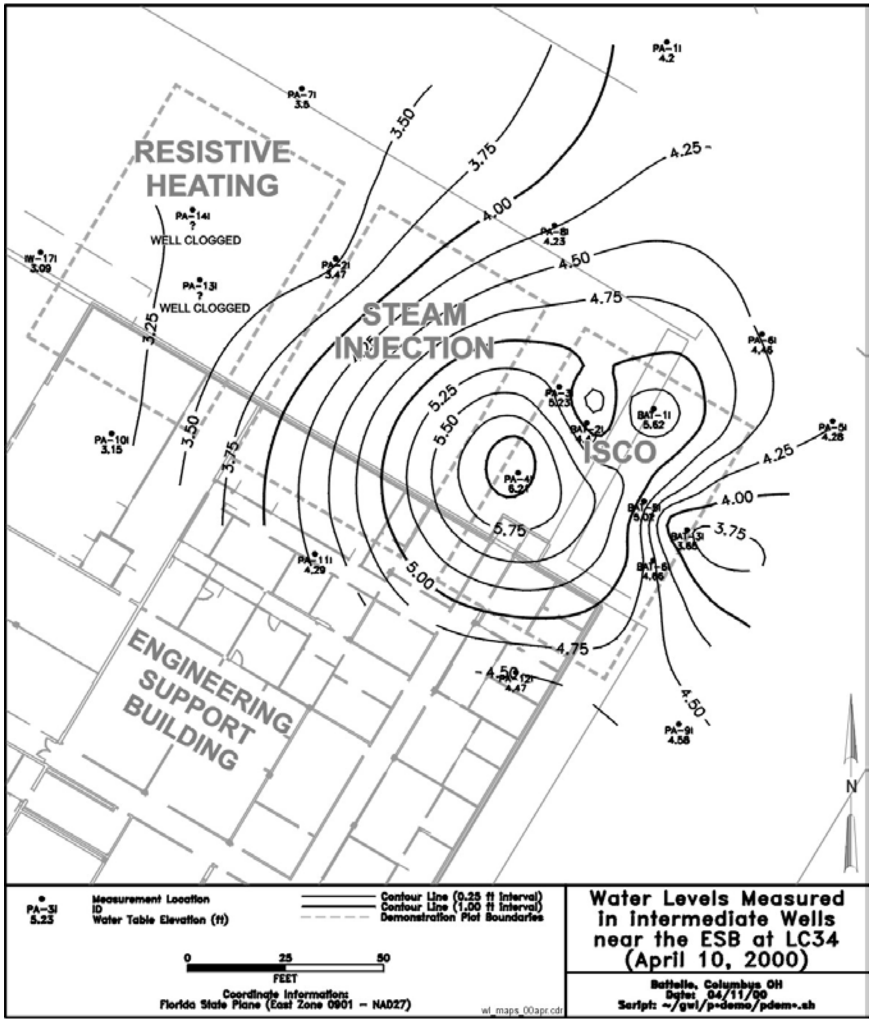


Figure 5-17. Water Levels Measured in Intermediate Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

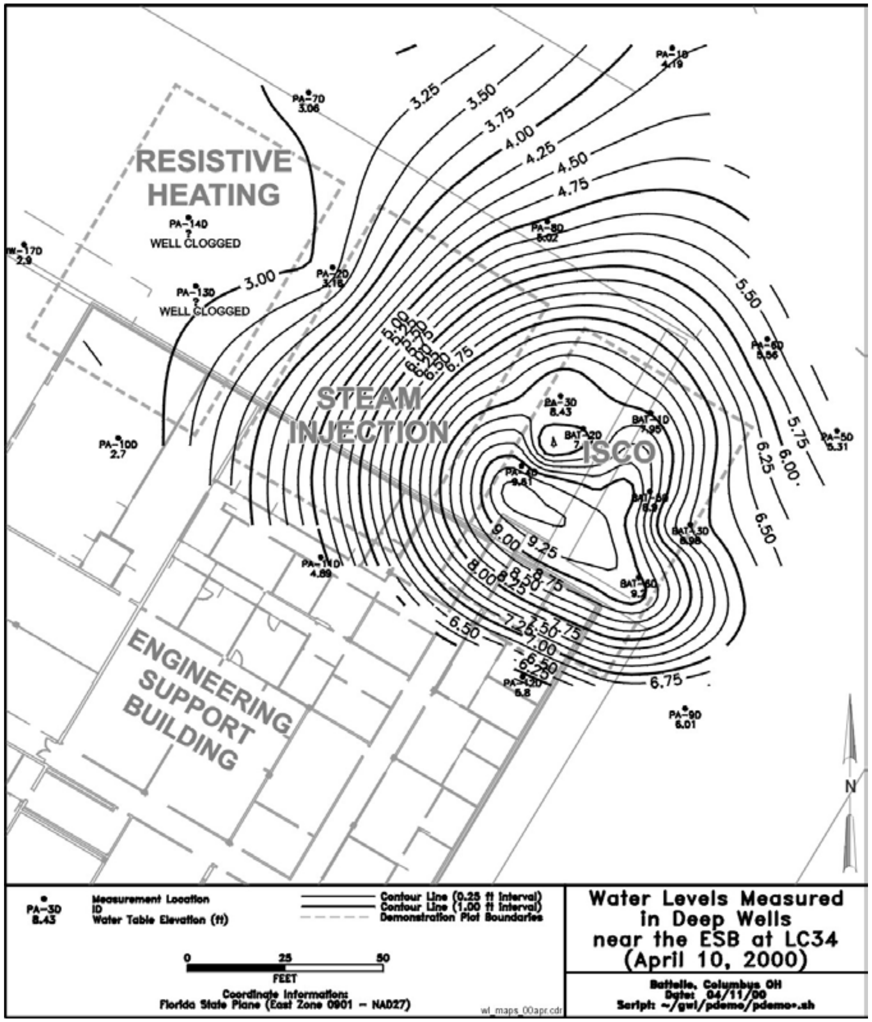


Figure 5-18. Water Levels Measured in Deep Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

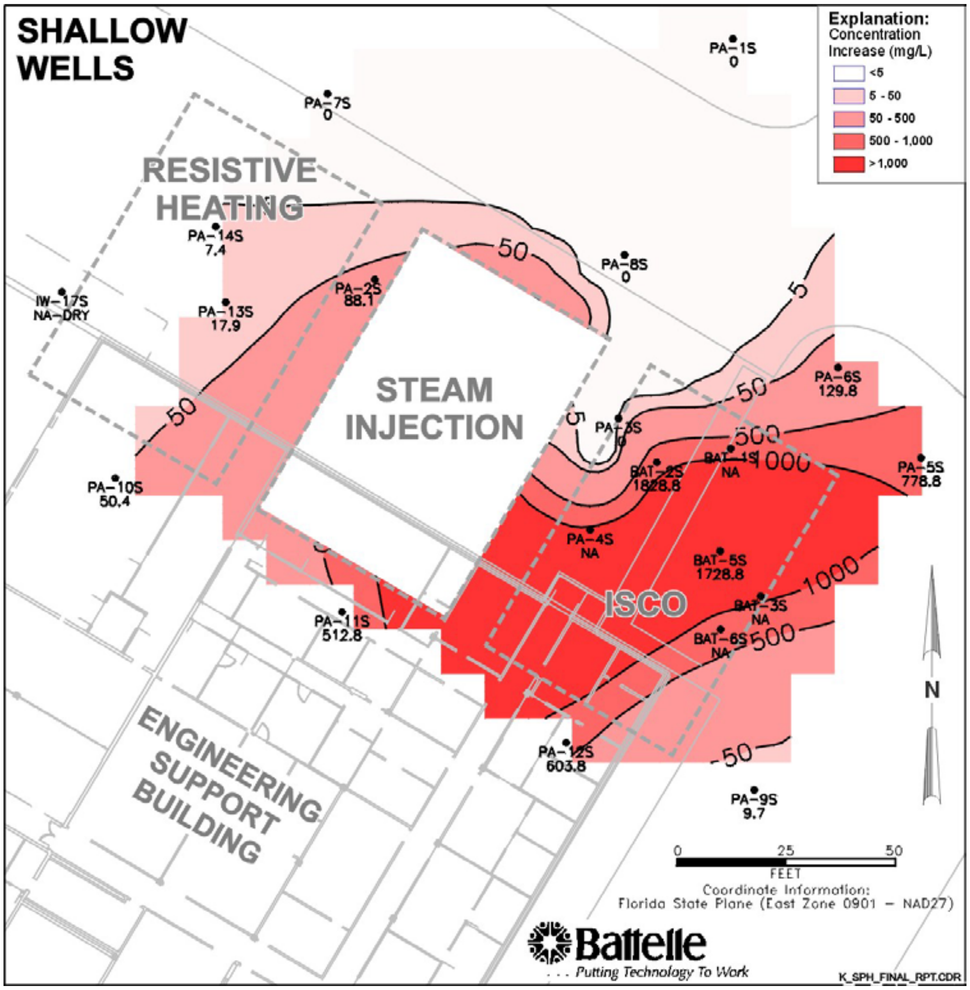


Figure 5-19. Distribution of Potassium (K) Produced by ISCO Technology in Shallow Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

TCE and other CVOCs are among the dissolved species that migrated from the ISCO plot as indicated by the TCE measurements in perimeter and distant wells (see Appendix C). Figures 5-22 to 5-24 show the TCE trends observed in the *perimeter wells*. TCE levels in perimeter wells PA-5S, PA-5I, and PA-6S (on the northeast side of the ISCO plot) and in a somewhat distant well PA-8S (northwest of the ISCO plot) rose sharply when the oxidation treatment started and an increase of more than an order of magnitude was sustained through the end of the demonstration. In other perimeter wells, TCE levels either declined sharply or showed a mild increase. A sharp temporary increase in TCE concentrations in the monitoring wells would signify that dissolved-phase TCE has migrated. A sharp sustained increase may signify that DNAPL has redistributed within the plot or outside it. Another possibility, as mentioned in Section 5.2, is that the sharp increase in TCE in some ISCO plot and perimeter wells is due to the increased groundwater flow through previously less permeable regions of the DNAPL source zone; an increase in permeability can result in regions of the aquifer that experience partial removal of DNAPL.

Figure 5-25 shows the TCE trends observed in *distant well* clusters PA-8 and PA-1. PA-8 is closer to the ISCO plot on the northwest side. PA-1 is further away towards the north-northwest side. The PA-8 cluster showed a significant increase in TCE concentrations in the shallow and deep wells. After the ISCO and resistive heating demonstrations started, DNAPL was observed for the first time in distant wells PA-11D, PA-2I, and PA-2D, all of which are on the west side of the ISCO plot. DNAPL had not been previously found in any of the monitoring wells before the demonstration. This indicates that some free-phase TCE movement occurred in the aquifer due to the application of the two technologies. It is unclear which of the two technologies contributed to the DNAPL movement and whether or not this DNAPL was initially in mobile or residual form. Mobile DNAPL could have

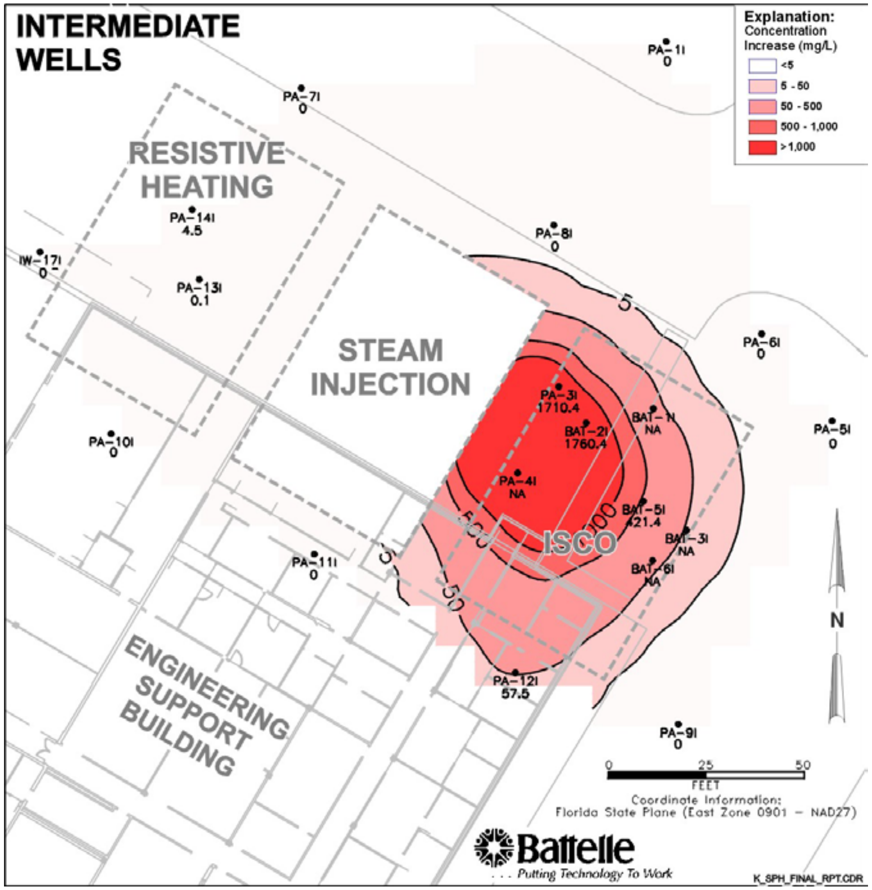


Figure 5-20. Distribution of Potassium (K) Produced by ISCO Technology in Intermediate Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

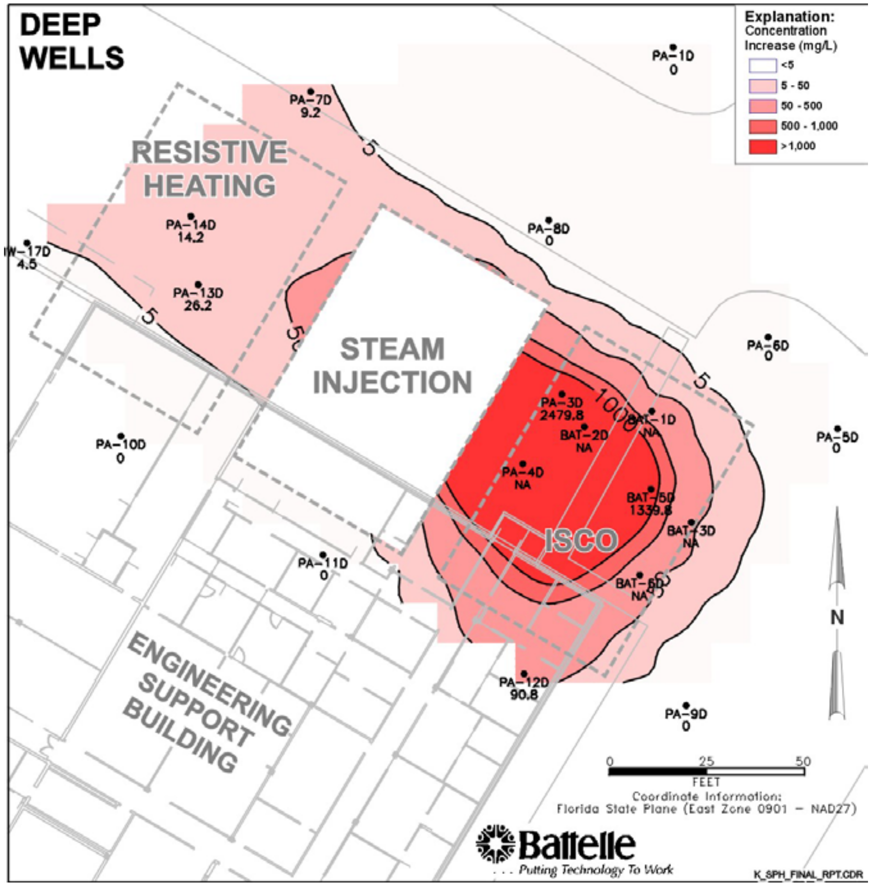


Figure 5-21. Distribution of Potassium (K) Produced by ISCO Technology in Deep Wells near the Engineering Support Building at Launch Complex 34 (April 2000)

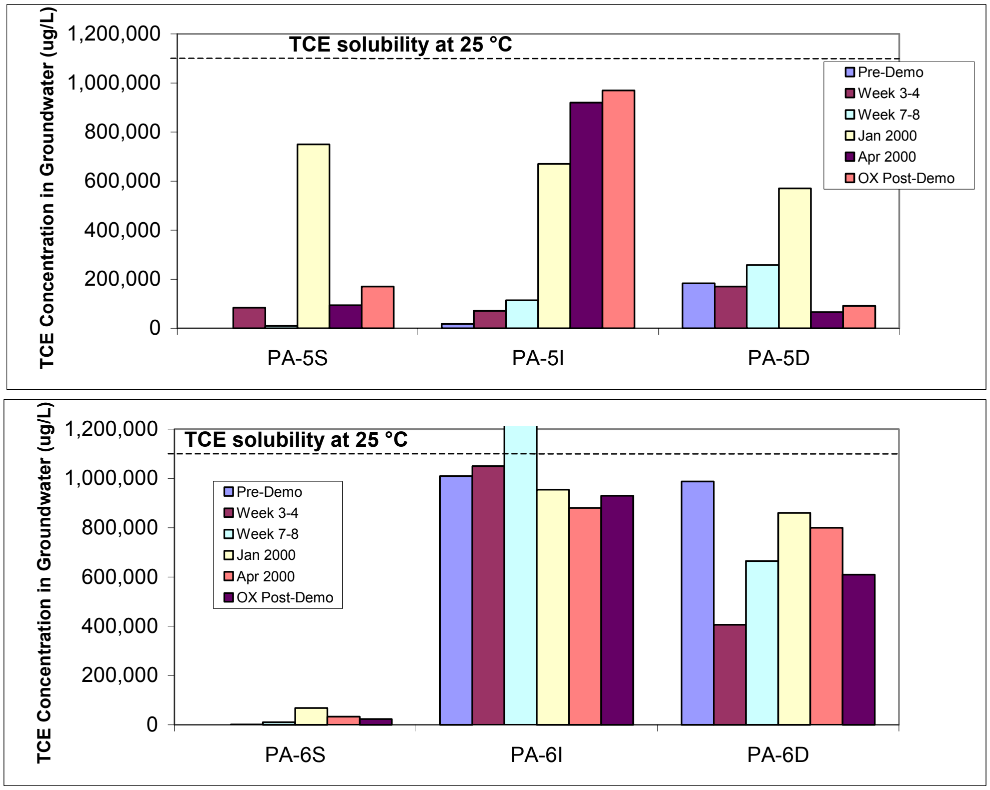


Figure 5-22. Dissolved TCE Levels (µg/L) in Perimeter Wells on the Northeastern Side of the ISCO Plot

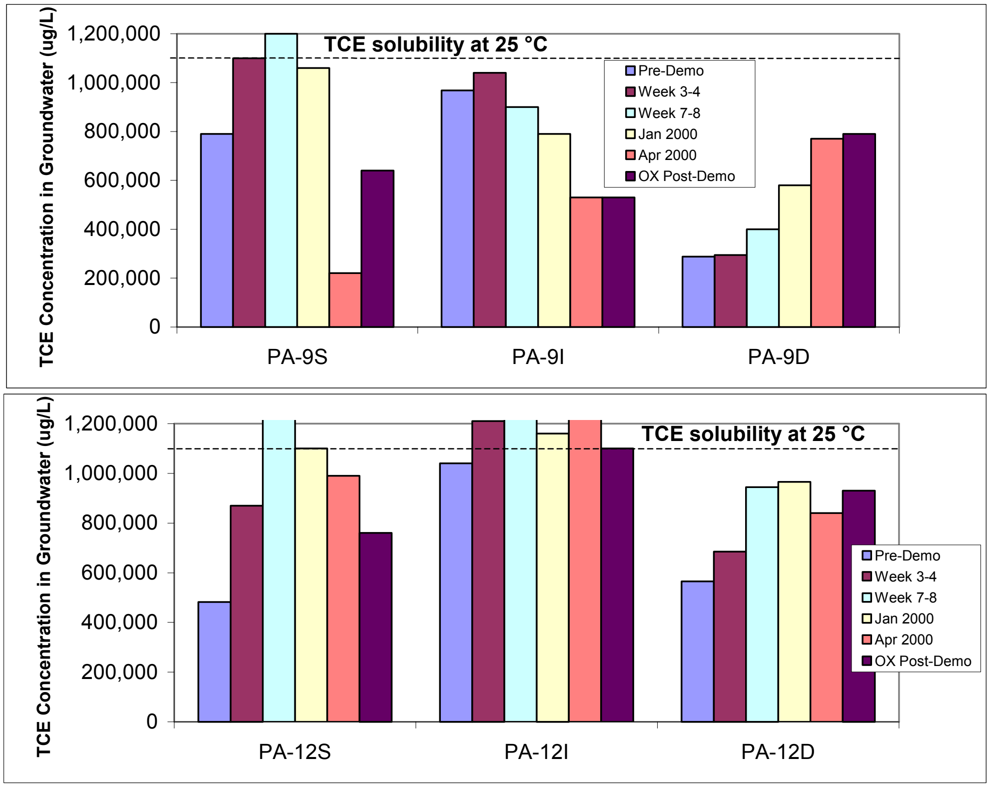


Figure 5-23. Dissolved TCE Levels (µg/L) in Perimeter Wells on the Southern Side of the ISCO Plot

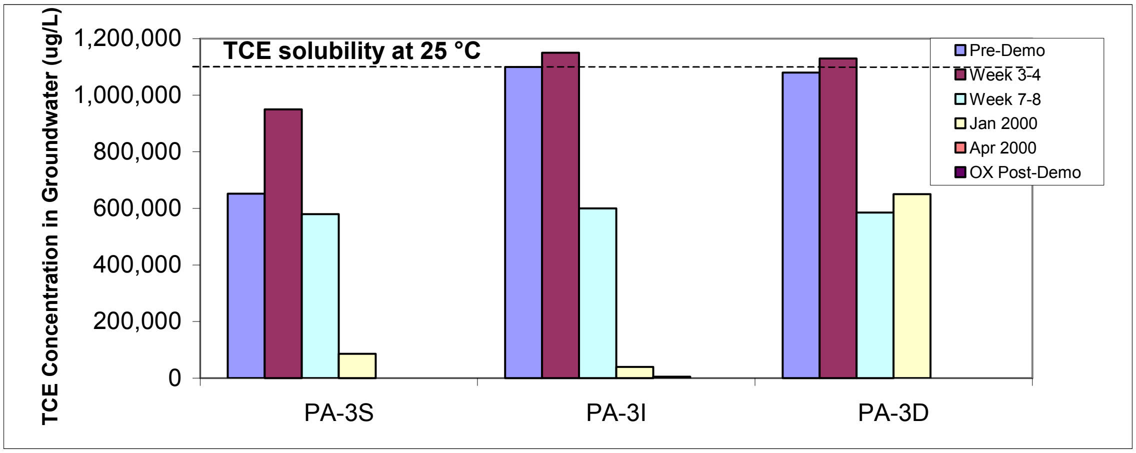


Figure 5-24. Dissolved TCE Levels (µg/L) in Perimeter Wells on the Western Side of the ISCO Plot

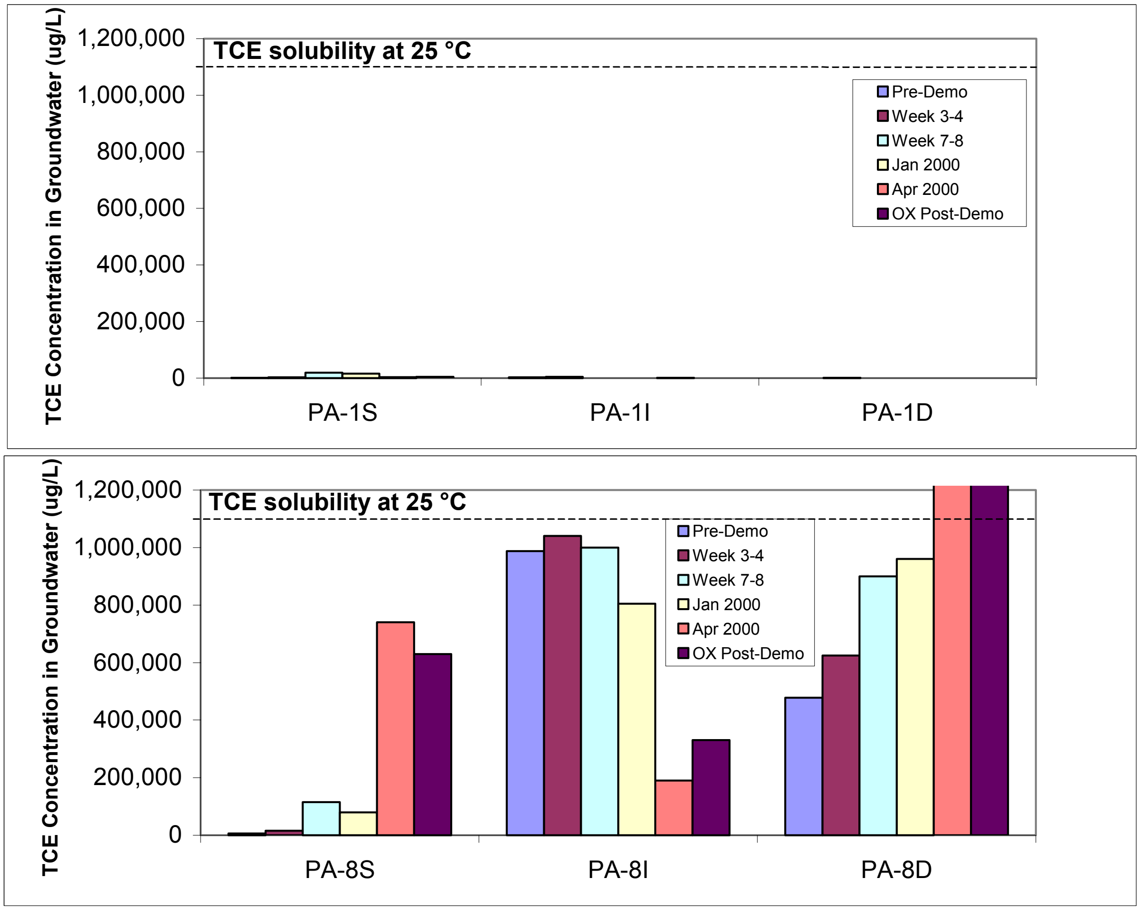


Figure 5-25. Dissolved TCE Levels (µg/L) in Distant Wells on the Northwestern Side of the ISCO Plot

moved under the influence of the sharp hydraulic gradient induced by the oxidant injection pressures. Residual DNAPL, by nature, would not be expected to move. PA-2I and PA-2D are closer to the resistive heating plot than to the ISCO plot and it is possible that the DNAPL migrated into these wells due to the resistive heating operation.

When the groundwater data indicated that DNAPL movement had occurred, additional postdemonstration *soil cores* were collected from areas surrounding the ISCO plot — at locations PA-206, PA-205, PA-209, PA-212, PA-211 and PA-208 (see Figure 4-3). These locations were selected because these were the only locations in the immediate vicinity of the ISCO plot where predemonstration soil core data were available for comparison. No noticeable increase in TCE or DNAPL concentration was found in any of these soil samples following the demonstration. The sampling density of the soil cores surrounding the plot is not as high as the sampling density inside the plot; therefore, the effort was more exploratory than definitive.

To evaluate the possibility of TCE/DNAPL migration to the *vadose zone*, all pre- and postdemonstration soil cores in the ISCO plot included soil samples collected at 2-ft intervals in the vadose zone. As seen in Figure 5-1, no noticeable deposition of TCE was found in vadose zone soils due to the ISCO treatment. *Surface emission* tests were conducted as described in Appendix F to evaluate the possibility of solvent losses to the atmosphere. As seen in Table 5-9, there was no noticeable difference in TCE concentrations between surface emission samples collected in the ISCO plot and at background locations at various times during and after the demonstration. Unlike some technologies that involve exothermic reactions or applied heating, permanganate oxidation does not cause volatilization of the targeted solvents and therefore there is very little probability of TCE losses to the vadose zone or atmosphere.

Table 5-9. Results for Surface Emission Tests

Sample ID	Sample Date	TCE (ppb [v/v])
	ISCO Plot	
OX-SE-1	9/30/1999	1.6
OX-SE-2	9/30/1999	2.4
OX-SE-3	10/1/1999	3.4
OX-SE-4	10/25/1999	0.68
OX-SE-5	10/25/1999	1.1
OX-SE-6	10/25/1999	1.4
OX-SE-7	1/17/2000	11
OX-SE-8	1/17/2000	7.6
OX-SE-9	1/17/2000	5.8
OX-SE-10	4/11/2000	2.6
OX-SE-11	4/11/2000	0.69
OX-SE-12	4/11/2000	1.7
	Background	
DW-SE-1	10/1/1999	<0.42
DW-SE-2	10/8/1999	<0.44
DW-SE-3	10/25/1999	0.44
DW-SE-4	10/22/1999	6,000(a)
DW-SE-5	1/17/2000	<0.38
DW-SE-6	4/11/2000	0.43
DW-SE-7	4/11/2000	0.86
DW-SE-8	4/11/2000	0.79
	***Ambient Air at Shoulder Level*(b)**	
SPH-SE-14	5/9/2000	<0.39(c)
SPH-SE-15	5/9/2000	<0.39(c)
SPH-SE-C27	9/1/2000	<0.88
DW-C1	4/11/2000	2.1
DW-C2	5/9/2000	<0.39
DW-C3	5/9/2000	<0.39

(a) Background sample (10/22/99) was collected immediately after a sample was collected at the resistive heating plot that had an unexpectedly high concentration of 13,000 ppbv. This may indicate condensation of TCE in the emissions collection box at levels that could not be removed by the standard decontamination procedure of purging the box with air for two hours. In subsequent events (1/17/2000 background), special additional decontamination steps were taken to minimize carryover.

(b) A Summa canister was held at shoulder level to collect an ambient air sample to evaluate local background air quality.

(c) SPH-SE-14/15 samples were collected at an ambient elevation at the east and west edges of the resistive heating plot without using an air collection box.

ppb (v/v): parts per billion by volume.

Because of NASA's concerns about breaching the relatively thin aquitard, no monitoring wells were installed before the demonstration into the Lower Clay Unit or in the aquifer below. After the resistive heating and ISCO demonstrations, the possibility of the historical presence of DNAPL under the Lower Clay Unit was revisited and specially designed wells with telescopic casing were designed and installed in the semi-confined aquifer below. Section 4.3 describes the installation and monitoring of these deeper wells. Figure 3-1 in Section 3.3.1 shows the locations of these three deeper wells (PA-20, PA-21, and PA-22) in the semi-confined aquifer. Tables 5-10 and 5-11 show the results of the analysis of soil and water samples from these wells. The soil samples were collected when these wells were being installed. At least in the soil and water samples in PA-21, the well directly under the ISCO plot, TCE levels do not indicate the presence of DNAPL. The absence of baseline (predemonstration) data in these wells makes interpretation difficult. However, most of the DNAPL-level TCE concentrations appear to be in the Lower Clay Unit and have not penetrated to the semi-confined aquifer below. Therefore, the data do not indicate that any migration of DNAPL occurred into the semi-confined aquifer portion below the ISCO plot, either before or during the ISCO demonstration.

5.3.3 Summary Evaluation of the Fate of TCE/DNAPL

In summary, the field measurements indicate that DNAPL movement has occurred in the Launch Complex 34

Table 5-10. Results of TCE Concentrations of Soil Analysis at Launch Complex 34

Approximate Depth (ft bgs)	TCE (mg/kg)[(a)]		
	SB-50 (PA-20)	SB-51 (PA-21)	SB-52 (PA-22)
39-40		66	
40-41			20
41-42	174	6,578	
42-43			21
43-44	72		
44-45		3,831	37
45-46	19	699	138
46-47	39	2,857	466
47-47.5			330
47.5-48			310
48-49	5	46	132
49-50			367
50-51	1	49	473
51-52			707
52-53	<1	3	
53-54			
54-55	<1	<1	8,496; 10,700
55-56			
56-57	2	<1	40,498
57-58			
58-59	<1	<1	122
59-60			

(a) Shaded cells represent the Lower Clay Unit.

Table 5-11. Results of CVOC Analysis in Groundwater from the Semi-Confined Aquifer

TCE

Well ID	Feb 2001	Apr 2001	May 2002	Jun 2001	Aug 2001	Nov 2001	Feb 2002
PA-20	67.1	447	111	350	19	15	181
PA-20-DUP	58.4	N/A	N/A	N/A	N/A	N/A	N/A
PA-21	7,840	15,700	6,400	5,030	790	1,640	416
PA-22	736,000	980,000	877,000	801,000	1,000,000	1,110,000	1,240,000
PA-22-DUP	N/A	N/A	939,000	N/A	1,000,000	N/A	N/A

cis-1,2-DCE

Well ID	Feb 2001	Apr 2001	May 2002	Jun 2001	Aug 2001	Nov 2001	Feb 2002
PA-20	21.7	199	37.4	145	10	52	66
PA-20-DUP	18.5	N/A	N/A	N/A	N/A	N/A	N/A
PA-21	1,190	5,790	1,490	1,080	330	5,140	315
PA-22	8,130	8,860	11,000	11,900	12,000 J	14,900	13,300
PA-22-DUP	N/A	N/A	10,700	N/A	12,000 J	N/A	N/A

trans-1,2-DCE

Well ID	Feb 2001	Apr 2001	May 2002	Jun 2001	Aug 2001	Nov 2001	Feb 2002
PA-20	<0.1	1.45	0.24J	0.38	<1.0	0.48J	0.3J
PA-20-DUP	<0.1	N/A	N/A	N/A	N/A	N/A	N/A
PA-21	<1	51.7	6 J	5	<33	<10	2
PA-22	<100	<1,000	<1,120	<100	<17,000	<100	<1,000
PA-22-DUP	N/A	N/A	<1,090	N/A	<17,000	N/A	N/A

Vinyl Chloride

Well ID	Feb 2001	Apr 2001	May 2002	Jun 2001	Aug 2001	Nov 2001	Feb 2002
PA-20	<0.1	0.36J	<1.08	<0.1	<2.0	<0.10	<1.0
PA-20-DUP	<0.1	N/A	N/A	N/A	N/A	N/A	N/A
PA-21	<1	4.22	<22.2	<1	<67	1,050	<1.0
PA-22	<100	<1,000	<1,120	<100	<33,000	<100	260J
PA-22-DUP	N/A	N/A	<1,090	N/A	<33,000	N/A	N/A

N/A: Not analyzed.
J: Estimated value, below reporting limit.

aquifer due to the demonstrations of resistive heating and ISCO technologies. It is unclear as to which of these two technologies caused this movement. It is also unclear as to whether the migrating DNAPL was initially present as mobile or residual form. If all the DNAPL was initially present in residual form, the strong hydraulic gradient created by the oxidant injection alone would not be sufficient to cause DNAPL to migrate. If some DNAPL was present in mobile form, the hydraulic gradient created by the injection pressures would cause it to migrate. In general, for future applications, the strong hydraulic gradients generated by the oxidant injection would necessitate that one of the following measures be implemented:

- The DNAPL source zone boundary should be delineated as accurately as possible so that oxidant injection can be applied without extraction or other hydraulic control.
- The oxidant injection pressures should be reduced in favor of higher injection point density and/or longer injection times.
- The oxidant should be injected from the outside in (injection in the perimeter of the DNAPL source zone, followed by injection in the interior of the source zone).

All of these measures pose their own challenges. In the first measure, a definitive identification of the DNAPL source boundary may be difficult or expensive to achieve. In the second measure, increasing the spatial density of injection points or using longer injection times may increase the cost of the application. Extraction of injected fluids may make the application more expensive due to the increased cost of extracting, treating, and disposing/reinjecting the recovered fluids. In the third option, some oxidant could be lost to surrounding regions. At Launch Complex 34, the vendor was constrained to some extent by the conditions of the demonstration, in which only a portion of the DNAPL source was targeted for treatment, as well as by regulatory/economic restraints against extraction/reinjection.

5.4 Verifying Operating Requirements and Cost

Section 3 contains a description of the ISCO field operations at Launch Complex 34. Section 7 contains the costs and economic analysis of the technology.

6. Quality Assurance

A QAPP (Battelle, 1999d) prepared before the demonstration outlined the performance assessment methodology and the QA measures to be taken during the demonstration. The results of the field and laboratory QA for the critical soil and groundwater CVOC (primary) measurements and groundwater field parameter (secondary) measurements are described in this section. The results of the QA associated with other groundwater quality (secondary) measurements are described in Appendix G. The focus of the QA measures is on the critical TCE measurement in soil and groundwater, for which, in some cases, special sampling and analytical methods were used. For other measurements (chloride, calcium, etc.), standard sampling and analytical methods were used to ensure data quality.

6.1 QA Measures

This section describes the data quality in terms of representativeness and completeness of the sampling and analysis conducted for technology performance assessment. Chain-of-custody procedures also are described.

6.1.1 Representativeness

Representativeness is a measure that evaluates how closely the sampling and analysis represents the true value of the measured parameters in the target matrices. The critical parameter in this demonstration is TCE concentration in soil. The following steps were taken to achieve representativeness of the soil samples:

- Statistical design for determining the number and distribution of soil samples in the 75-ft × 50-ft ISCO plot, based on the horizontal and vertical variability observed during a preliminary characterization event (see Section 4.1). Twelve locations (one in each cell of a 4 × 3 grid in the plot) were cored before and after the demonstration and a continuous core was collected and sampled in 2-ft sections from ground surface to aquitard at each coring location. At the 80% confidence level, the pre- and postdemonstration TCE mass estimates in the plot (see Section 5.1) were within relatively narrow intervals that enabled a good judgment of the mass removal achieved by the ISCO technology.
- Sampling and analysis of duplicate postdemonstration soil cores to determine TCE concentration variability within each grid cell. Two complete cores (SB-217 and SB-317) were collected within about 2 ft of each other in the postdemonstration ISCO plot, with soil sampling at every 2-ft interval (see Figure 5-1 for the TCE analysis of these cores). The resulting TCE concentrations showed a relatively close match (±30%) between the duplicate core TCE levels. This indicated that dividing the ISCO plot into 12 grid cells enabled a sampling design that was able to address the horizontal variability in TCE distribution.
- Continuous sampling of the soil column at each coring location enabled the sampling design to address the vertical variability in the TCE distribution. By extracting and analyzing the complete 2-ft depth in each sampled interval, essentially every vertical depth was sampled.
- Use of appropriate modifications to the standard methods for sampling and analysis of soil. To increase the representativeness of the soil sampling, the sampling and extraction procedures in EPA Method 5035 were modified so that an entire vertical section of each 2-ft core could be sampled and extracted, instead of the 5-g aliquots specified in the standard method (see Section 4.1). This was done to maximize the capture of TCE/DNAPL in the entire soil column at each coring location.

Steps taken to achieve representativeness of the groundwater samples included:

- Installation and sampling of six well clusters in the 75-ft × 50-ft ISCO plot. Each cluster consisted of three wells screened in the three stratigraphic units — Upper Sand Unit, Middle Fine-Grained Unit, and Lower Sand Unit.

- Use of standard methods for sampling and analysis. Disposable tubing was used to collect samples from all monitoring wells to avoid persistence of TCE in the sample tubing after sampling wells with high TCE (DNAPL) levels.

6.1.2 Completeness

All the regular samples planned in the QAPP were collected and analyzed, plus additional samples were collected when new requirements were identified as the demonstration progressed. Additional groundwater samples were collected from all ISCO plot and surrounding wells to better evaluate the generation and migration of chloride, potassium ion, and potassium permanganate. One additional soil core was collected during postdemonstration sampling to evaluate the variability within the same grid cell.

All the QC samples planned in the QAPP were collected and analyzed, except for the equipment rinsate blanks during soil coring. Equipment rinsate blanks were not planned in the draft QAPP and were not collected during the predemonstration soil coring event. These blanks were later added to the QAPP and were prepared during the postdemonstration soil coring event. Based on the preliminary speed of the soil coring, one rinsate blank per day was thought to be sufficient to obtain a ratio of one blank per 20 samples (5%). However, as the speed of the soil coring increased, this frequency was found to have fallen slightly short of the desired ratio of blanks to samples. The same rinsing procedure was maintained for the soil core barrel through the pre- and postdemonstration sampling. None of the blanks contained any elevated levels of CVOCs.

6.1.3 Chain of Custody

Chain-of-custody forms were used to track each batch of samples collected in the field and delivered either to the on-site mobile laboratory or to the off-site analytical laboratory. Copies of the chain-of-custody records can be found in Appendix G. Chain-of-custody seals were affixed to each shipment of samples to ensure that only laboratory personnel accessed the samples while in transit. Upon arrival at the laboratory, the laboratory verified that the samples were received in good condition and the temperature blank sample sent with each shipment was measured to ensure that the required temperature was maintained during transit. Each sample received was then checked against the chain-of-custody form, and any discrepancies were brought to the attention of field personnel.

6.2 Field QC Measures

The field QC checks included calibration of field instruments, field blanks (5% of regular samples), field duplicates (5% of regular samples), and trip blanks; the results of these checks are discussed in this section.

Table 6-1 summarizes the instruments used for field groundwater measurements (pH, ORP, DO, temperature, water levels, and conductivity) and the associated calibration criteria. Instruments were calibrated at the beginning and end of the sampling period on each day. The field instruments were always within the acceptance criteria during the demonstration. The DO membrane was the most sensitive, especially to extremely high (near saturation) levels of chlorinated solvent or permanganate in the groundwater and this membrane had to be changed more frequently. Because of interference with DO and other measurements, field parameter measurements in deeply purple (high permanganate level) samples were avoided, as noted in Appendix G.

6.2.1 Field QC for Soil Sampling

Soil extractions were conducted in the field and the extracts were sent to the off-site laboratory for CVOC analysis. A surrogate compound was initially planned on being spiked directly into a fraction of the soil samples collected, but the field surrogate addition was discontinued at the request of the off-site laboratory because of interference and overload of analytical instruments at the

Table 6-1. Instruments and Calibration Acceptance Criteria Used for Field Measurements

Instrument	Measurement	Acceptance Criteria
YSI Meter Model 6820	pH	3 point, ±20% difference
YSI Meter Model 6820	ORP	1 point, ±20% difference
YSI Meter Model 6820	Conductivity	1 point, ±20% difference
YSI Meter Model 6820	Dissolved Oxygen	1 point, ±20% difference
YSI Meter Model 6820	Temperature	1 point, ±20% difference
OHaus Weight Balance	Soil – Dry/Wet Weight	3 point, ±20% difference
Hermit Water Level Indicator	Water Levels	±0.01 ft

detection limits required. Surrogate addition was instead conducted by the analytical laboratory, which injected the surrogate compound into 5% of the methanol extracts prepared in the field. As an overall determination of the extraction and analytical efficiency of the soil sampling, the modified EPA Method 5035 methanol extraction procedure was evaluated before the demonstration by spiking a known amount of TCE into soil samples from the Launch Complex 34 aquifer. A more detailed evaluation of the soil extraction efficiency was conducted in the field by spiking a surrogate compound (1,1,1-TCA) directly into the intact soil cores retrieved in a sleeve. The injection volume of 1,1,1-TCA was approximately 10 µL. The spiked soil samples were handled in the same manner as the remaining soil samples during the extraction procedure. Of the 13 soil samples spiked with 1,1,1-TCA, 12 were within the acceptable range of precision for the postdemonstration soil sampling, calculated as the relative percent difference (RPD), where RPD is less than 30%. The results indicate that the methanol extraction procedure used in the field was suitable for recovering CVOCs. Extraction efficiencies ranged from 84 to 113% (92% average) (Tables G-1 and G-2 in Appendix G). For this evaluation, soil samples from the predemonstration soil core PA-4 were homogenized and spiked with pure TCE. Replicate samples from the spiked soil were extracted and analyzed; the results are listed in Appendix G (Table G-3). For the five replicate soil samples, the TCE spike recoveries were in the range of 72 to 86%, which fell within the acceptable range (70-130%) for quality assurance of the extraction and analysis procedure.

Duplicate soil samples were collected in the field and analyzed for TCE to evaluate sampling precision. Duplicate soil samples were collected by splitting each 2-ft soil core vertically in half and subsequently collecting approximately 250 g of soil into two separate containers, marked as SB#-Depth#-A and B. Appendix G (Table G-4) shows the result of the field soil duplicate analysis and the precision, calculated as the RPD for the duplicate soil cores, which were collected before and after the demonstration. The precision of the field duplicate samples was generally within the acceptable range (±30%) for the demonstration, indicating that the sampling procedure was representative of the soil column at the coring location. The RPD for three of the duplicate soil samples from the predemonstration sampling was greater than 30%, but less than 60%. This indicated that the repeatability of some of the predemonstration soil samples was outside targeted acceptance criteria, but within a reasonable range, given the heterogeneous nature of the contaminant distribution. The RPDs for six of the duplicate soil samples from the postdemonstration sampling were greater than 30%; five of the six samples had an RPD above 60%. This indicates that the ISCO treatment created greater variability in the contaminant distribution. Part of the reason for the higher RPD calculated in some postdemonstration soil samples is that TCE concentrations tended to be low (often near or below the detection limit). For example, the RPD between duplicate samples, one of which is below detection and the other is slightly above detection, tends to be high. In general, though, the variability in the two vertical halves of each 2-ft core was in a reasonable range, given the typically heterogeneous nature of the DNAPL distribution.

Field blanks for the soil sampling consisted of rinsate blank samples and methanol blank samples. The rinsate blank samples were collected once per drilling borehole (approximately 20 soil samples) to evaluate the decontamination efficiency of the sample barrel used for each soil boring. Decontamination between samples consisted of a three-step process where the core barrel was emptied, washed with soapy water, rinsed in distilled water to remove soap and debris, and then rinsed a second time with distilled water. The rinsate blank samples were collected by pouring distilled water through the sample barrel, after the barrel had been processed through the routine decontamination procedure. As seen in Appendix G (Table G-5), TCE levels in the rinsate blanks were always below detection (<5.0 µg/L), indicating that the decontamination procedure was helping control carryover of CVOCs between samples.

Methanol method blank samples (5%) were collected in the field to evaluate the soil extraction process. The results are listed in Appendix G (Table G-6). These samples were generally below the targeted detection limit of 1 mg/kg of TCE in dry soil. Detectable levels of TCE were present in methanol blanks sampled on 6/23/99 (1.8 mg/kg), 6/29/99 (8.0 mg/kg), and 7/16/99 (1.2 mg/kg) during the predemonstration phase of the project, but were still relatively low. The slightly elevated levels may be due to the fact that many of the soil samples extracted on these days were from high-DNAPL regions and contained extremely high TCE concentrations. The TCE concentrations in these blanks were below 10% of the concentrations in the associated batch of soil samples. All the postdemonstration methanol blanks were below detection.

6.2.2 Field QC for Groundwater Sampling

QC checks for groundwater sampling included field duplicates (5%), field blanks (5%), and trip blanks. Field duplicate samples were collected once every 20 wells sampled. Appendix G (Tables G-7 and G-8) contains the analysis of the field duplicate groundwater samples that were collected before, during, and after the demonstration. The RPD (precision) calculated for these samples always met the QA/QC target criteria of ±30%.

Decontamination of the sample tubing between groundwater samples initially consisted of a detergent rinse and two distilled water rinses. However, initial groundwater sampling results revealed that, despite the most thorough decontamination, rinsate blanks contained elevated levels of TCE, especially following the sampling of wells containing TCE levels near or greater than its solubility (1,100 mg/L); this indicated that some free-phase solvent may have been drawn into the tubing. When TCE levels in such rinsate blanks refused to go down, even when a methanol rinse was added to the decontamination procedure, a decision was made to switch to disposable Teflon® tubing. Each new piece of tubing was used only for sampling each well once and then discarded, despite the associated costs. Once disposable sample tubing was used, TCE levels in the rinsate blanks (Appendix G, Tables G-9 and G-10) were below the targeted detection limit (3.0 µg/L) throughout the demonstration. The only exception was one rinsate blank collected during the postdemonstration sampling event on May 20, 2000; this rinsate blank contained 11 µg/L of TCE, which was less than 10% of the TCE concentrations in the regular samples in this batch.

TCE levels in trip blank samples were always below 5 µg/L (Appendix G, Table G-11), indicating the integrity of the samples was maintained during shipment. In some batches of groundwater samples, especially when excess permanganate was present in the sample, detection limits were raised from 3 to 5 µg/L to avoid instrument interference.

6.3 Laboratory QC Measures

The on-site mobile and off-site analytical laboratories performed QA/QC checks consisting of 5% matrix spikes (MS) or laboratory control spikes (LCS), as well as the same number of matrix spike duplicates (MSD) or laboratory control spike duplicates (LCSD). The analytical laboratories generally conducted MS and MSD whenever the groundwater samples were clear, in order to determine accuracy. However, when excess permanganate was present in the samples, as with many postdemonstration samplers, LCS and LCSD were conducted. MS and MSD or LCS and LCSD were used to calculate analytical accuracy (percent recovery) and precision (RPD between MS and MSD or LCS and LCSD).

6.3.1 Analytical QC for Soil Sampling

Analytical accuracy for the soil samples (methanol extracts) analyzed were generally within acceptance limits (70-130%) for the predemonstration period (Appendix G, Table G-12). Matrix spike recoveries were outside this range for three of the MS/MSD samples conducted during the postdemonstration sampling period (Appendix G, Table G-13), but still within 50 to 150%; this indicates that although there may have been some matrix effects, the recoveries were still within a reasonable range, given the matrix interference from the permanganate. Matrix spike recovery was 179% for one of the matrix spike repetitions on 06/01/00. The precision between MS and MSD was always within acceptance limits (±25%). Laboratory control spike recoveries and precision were within the acceptance criteria (Appendix G, Tables G-14 and G-15).

The laboratories conducted surrogate spikes in 5% of the total number of methanol extracts prepared from the soil samples for CVOC analysis. Table 6-2 lists the surrogate and matrix spike compounds used by the on-site laboratory to perform the QA/QC checks. Table 6-3 lists the surrogate and matrix spike compounds used by the off-site laboratory to perform the QA/QC checks. Surrogate and matrix spike recoveries were always within the specified acceptance limits. Method blank samples were run at a frequency of at least one for every 20 samples analyzed in the pre- and postdemonstration periods

Table 6-2. List of Surrogate and Matrix Spike Compounds and Their Target Recoveries for Groundwater Analysis by the On-Site Laboratory

Surrogate Compound DHL	**Matrix Spike Compound DHL**
a,a,a-Trifluorotoluene (75-125%)	*cis*-1,2-DCE (70-130%)
	trans-1,2-DCE (70-130%)
	Vinyl chloride (65-135%)
	TCE (70-130%)

Table 6-3. List of Surrogate and Laboratory Control Sample Compounds and Their Target Recoveries for Soil and Groundwater Analysis by the Off-Site Laboratory

Surrogate Compound STL	**Matrix Spike Compound STL**
Dibromofluoromethane (66-137%)	Vinyl chloride (56-123%)
1,2-Dichloroethane – d4 (61-138%)	Carbon tetrachloride (60-136%)
Toluene – d8 (69-132%)	Benzene (70-122%)
Bromofluorobenzene (59-145%)	1,2-Dichloroethane (58-138%)
	TCE (70-130%)
	1,2-Dichloropropane (68-125%)
	1-1,2-Trichloroethane (63-123%)
	Tetrachloroethane (70-125%)
	1,2-Dibromoethane (66-126%)
	Bromoform (60-131%)
	1,4-Dichlorobenzene (70-120%)
	cis-1,3-Dichloropropane (65-132%)

(Appendix G, Tables G-16 and G-17). CVOC levels in the method blanks were always below detection.

6.3.2 Laboratory QC for Groundwater Sampling

Pre- and postdemonstration MS and MSD results for groundwater are listed in Appendix G (Table G-18). The MS and MSD recoveries (70 to 130%) and their precision (±25%) were generally within acceptance criteria. The only exceptions were the samples collected on 08/03/99 and 01/14/00 during the ongoing demonstration phase which had MS and MSD recoveries that were outside the range due to high initial TCE concentrations in the samples. Recoveries and RPDs for LCS and LCSD samples (Appendix G, Tables G-19 and G-20) were always within the acceptance range.

Method blanks (Appendix G, Tables G-21 and G-22) for the groundwater samples were always below the targeted 3-μg/L detection limit.

6.3.3 Analytical Detection Limits

Detection limits for TCE in soil (1 mg/kg) and groundwater (3 μg/L) generally were met. The only exceptions were samples that had to be diluted for analysis, either because one of the CVOC compounds (e.g., TCE) was at a relatively high concentration as compared to another VOC compound (e.g., *cis*-1,2-DCE) or because excessively high levels of permanganate in the sample necessitated dilution to protect instruments. The proportionately higher detection limits are reported in the CVOC tables in Appendix C. The detection limits most affected were those for *cis*-1,2-DCE and vinyl chloride, due to the masking effect of high levels of TCE. Additionally, the laboratories verified and reported that analytical instrumentation calibrations were within acceptable range on the days of the analyses.

6.4 QA/QC Summary

Given the challenges posed by the typically heterogeneous TCE distribution in a DNAPL source zone, the collected data were an acceptable representation of the TCE distribution in the Launch Complex 34 aquifer before, during, and after the demonstration.

- Sufficient number of locations (12) were sampled within the plot to adequately capture the horizontal variability in the TCE distribution. The continuous sampling of the soil at each coring location ensured that the vertical variability of the TCE distribution was captured. Sampling and analytical procedures were appropriately modified to address the expected variability. At the 80% confidence level, the soil sampling provided pre- and postdemonstration confidence intervals (range of TCE mass estimates) that were narrow enough to enable an acceptable judgment of the TCE and DNAPL mass removal achieved by the ISCO technology.
- Standard sampling and analysis methods were used for all other measurements to ensure that data were comparable between sampling events.
- Accuracy and precision of the soil and groundwater measurements were generally in the acceptable range for the field sampling and laboratory analysis. In the few instances that QC data were outside the targeted range, the reason was generally interference from excessive permanganate in the sample. In some cases, extremely low (near detection) or extremely high levels of TCE in the sample caused higher deviation in the precision (repeatability) of the data.
- The masking effect of high TCE levels on other CVOCs and the need for sample dilution because of the presence of excessive permanganate caused detection limits for TCE, in some cases, to rise to 5 μg/L (instead of 3 μg/L). However, postdemonstration levels of dissolved TCE in many of the monitoring wells in the ISCO plot were considerably higher than the 3-μg/L detection and regulatory target.
- Field blanks associated with the soil samples generally had acceptably low or undetected levels of TCE. After suitable modifications to account for the persistence of DNAPL in groundwater sampling tubing, TCE levels in field blanks were acceptably low or below detection.

7. Economic Analysis

The cost estimation for the ISCO technology application involves the following three major components:

- Treatment cost of ISCO at the demonstration site. Costs of the technology application at Launch Complex 34 were tracked by the ISCO vendor and by MSE, the DOE contractor who subcontracted the vendor.
- Site preparation costs incurred by the owner. NASA and MSE tracked the site preparation costs; that is, the costs incurred by the site owner.
- Site characterization and performance assessment costs. Battelle and TetraTech EM, Inc. estimated these costs based on the site characterization and performance assessment that was generally based on U.S. EPA's SITE Program guidelines.

An economic analysis for an innovative technology generally is based on a comparison of the cost of the innovative technology with a conventional alternative. In this section, the economic analysis involves a comparison of the ISCO cost with the cost of a conventional pump-and-treat system.

7.1 ISCO Treatment Costs

Table 7-1. ISCO Cost Summary Provided by Vendor

Item	Actual Cost
Final design and specifications	$ 48,301
Plans and permits	$ 23,367
Procurement	$ 15,696
Mobilization[(a)]	$ 410,412
Well installation	$ 46,675
Precharacterization sampling	$ 3,292
Tracer test	$ 48,846
Phase 1 injection and monitoring	$ 124,883
Phase 2 injection and monitoring	$ 38,737
Phase 3 injection and monitoring	$ 104,566
Process monitoring	$ 1,554
Cost reporting	$ 24,270
Design/cost modeling	$ 9,919
Final technical report	$ 49,161
Project management/proposal	$ 64,268
Total	$1,013,947

(a) Mobilization includes chemical costs for permanganate and major project equipment rentals and purchases. The total chemical cost is approximately $274,000.

Source: IT Corporation, 2000.

The costs of the ISCO technology were tracked and reported by both the vendor and MSE, the DOE contractor who subcontracted the vendor. Table 7-1 summarizes the major cost components for the application including the costs of chemicals at $274,000. The chemical cost consists of the purchase of 66,956 kg (150,653 lb) of potassium permanganate at an average price of \$4/kg (\$2/lb). The total cost of the ISCO demonstration was approximately $1 million. This total includes the design, permitting support, implementation, process monitoring, and reporting costs incurred by the vendor. The total does not include the costs of site characterization, which was conducted by other organizations (Remedial Investigation/Feasibility Study [RI/FS] study by NASA, preliminary characterization by WSRC, and detailed characterization by Battelle/TetraTech EM, Inc./U.S. EPA). The vendor estimated that approximately 15 to 20% of the total cost was demonstration-related and would not be incurred in an actual remediation application. The vendor documented that the demonstration cost was approximately \$187/yd^3 for the total treatment plot soil volume (IT, 2000). A higher unit cost may be anticipated if greater DNAPL removal (percentage) is required.

A subsequent monitoring event indicated that some rebound in TCE concentrations occurred in the ISCO plot. Based on the DNAPL masses estimated during the predemonstration and extended monitoring events, the unit cost for the treatment was estimated by the DOE contractor at $109/lb of TCE removed (MSE, 2002).

7.2 Site Preparation Costs

Many of the site preparation costs were incurred by NASA and are not included in the treatment costs listed by the vendor in Table 7-1. Site preparation costs for the ISCO technology were relatively minor, compared to the other two technologies demonstrated. For ISCO, site preparation involved the provision of power and water for the demonstration. NASA estimated the site preparation costs at $2,800. NASA did not incur any waste disposal costs associated with this technology because injected fluids did not have to be extracted. Except for the disposal of some mobilization- and operation-related nonhazardous solid wastes, there was no waste disposal requirement.

7.3 Site Characterization and Performance Assessment Costs

This section describes two categories of costs:

- **Site characterization costs.** These are the costs for the effort to bridge the gap between the general site information in an RI/FS or RFI report and the more detailed information required for DNAPL source delineation and remediation technology design. This cost component is perhaps the most reflective of the type of costs incurred when a site of the size and geology of Launch Complex 34 undergoes site characterization in preparation for remediation. Presuming that groundwater monitoring and plume delineation at a site indicates the presence of DNAPL, these site characterization costs are incurred in an effort to define the boundaries of the DNAPL source zone, obtain an order-of-magnitude estimate of the DNAPL mass present, and define the local hydrogeology and geochemistry of the DNAPL source zone.
- **Performance assessment costs.** These are primarily demonstration-related costs. Most of these costs were incurred in an effort to further delineate the portion of the DNAPL source contained in the ISCO plot and determine the TCE/DNAPL mass removal achieved by ISCO. Only a fraction of these costs would be incurred during full-scale deployment of this technology; depending on the site-specific regulatory requirements, only the costs related to determining compliance with cleanup criteria would be incurred in a full-scale deployment.

Table 7-2 summarizes the costs incurred by Battelle for the February 1999 site characterization. The February 1999 site characterization event was a suitable combination of soil coring and groundwater sampling, organic and inorganic analysis, and hydraulic testing (water levels and slug tests) that may be expected to bridge the gap between the RI/FS or RFI data usually available at a site and the typical data needs for DNAPL source delineation and remediation design.

Table 7-3 lists performance assessment costs incurred jointly by Battelle and TetraTech EM, Inc.

Table 7-2. Estimated Site Characterization Costs

Activity	Cost
Site Characterization Work Plan • Additional characterization to delineate DNAPL source • Collect hydrogeologic and geochemical data for technology design	$ 25,000
Site Characterization • Drilling – soil coring and well installation (12 continuous soil cores to 45 ft bgs; installation of 36 monitoring wells) • Soil and groundwater sampling (36 monitoring wells; 300 soil samples collection and field extraction) • Laboratory analysis (organic and inorganic analysis) • Field measurements (water quality; hydraulic testing)	$ 165,000
Data Analysis and Site Characterization Report	$ 65,000
Total	**$ 255,000**

Table 7-3. Estimated Performance Assessment Costs

Activity	Cost
Predemonstration Assessment • Drilling – 12 continuous soil cores, installation of 18 monitoring wells • Soil and groundwater sampling for TCE/DNAPL boundary and mass estimation (36 monitoring wells; 300 soil samples collection and field extraction) • Laboratory analysis (organic and inorganic analysis) • Field measurements (water quality; hydraulic testing)	$208,000
Demonstration Assessment • Groundwater sampling (ISCO plot and perimeter wells) • Laboratory analysis (organic and inorganic analysis) • Field measurements (water quality; hydraulic testing; ISCO plot and perimeter wells)	$240,000
Postdemonstration Assessment • Drilling – 12 continuous soil cores • Soil and groundwater sampling (36 monitoring wells; 300 soil samples collection and field extraction) • Laboratory analysis (organic and inorganic analysis) • Field measurements (water quality; hydraulic testing)	$215,000
Total	**$ 663,000**

7.4 Present Value Analysis of ISCO and Pump-and-Treat System Costs

DNAPL, especially of the magnitude present at Launch Complex 34, is likely to persist in the aquifer for several decades or centuries. The resulting groundwater contamination and plume also will persist for several decades. The conventional approach to this type of contamination has been the use of pump-and-treat systems that extract and treat the groundwater above ground. This conventional technology is basically a plume control technology and would have to be implemented as long as groundwater contamination exists. ISCO is an innovative in situ technology that seeks to replace the conventional pump-and-treat approach. The economic analysis therefore compares the costs of these two alternatives.

Because a pump-and-treat system would have to be operated for the next several decades, the life-cycle cost of this long-term treatment has to be calculated and compared with the cost of ISCO, a short-term treatment. The present value (PV) of a long-term pump-and-treat application is calculated as described in Appendix H. The PV analysis is conducted over a 30-year period, as is typical for long-term remediation programs at Superfund sites. Site characterization and performance (compliance) assessment costs are assumed to be similar for both alternatives and are not included in this analysis.

For the purpose of comparison, it is assumed that a pump-and-treat system would have to treat the plume emanating from a DNAPL source the size of the ISCO plot. Recent research (Pankow and Cherry, 1996) indicates that the most efficient pump-and-treat system for source containment would capture all the groundwater flowing through the DNAPL source region. For a 75-ft-long × 50-ft-wide × 40-ft-deep DNAPL source region at Launch Complex 34, a single well cluster (with two wells, one screened in the Upper Sand Unit and the other screened in the Lower Sand Unit) pumping at 2 gpm is assumed to be sufficient to contain the source in an aquifer where the hydraulic gradient (and therefore, the groundwater flow velocity) is extremely low. This type of minimal containment pumping ensures that the source is contained without having to extract and treat groundwater from cleaner surrounding regions, as would be the case in more aggressive conventional pump-and-treat systems. The extracted groundwater is treated with an air stripper and polishing carbon. The air effluent from the air stripper is treated with a catalytic oxidizer before discharge to the atmosphere.

As shown in Appendix H, the total capital investment for an equivalent pump-and-treat system would be approximately $167,000, and would be followed by an annual operation and maintenance (O&M) cost of $57,500 (including quarterly monitoring). Periodic maintenance requirements (replacements of pumps, etc.) would raise the O&M cost every five years to $70,000 and every 10 years to $99,000. A real discount rate of 2.9%, based on the current recommendation for government projects, was used to calculate the PV. The PV of the pump-and-treat costs over 30 years is estimated to be **$1,406,000**.

Based on the vendor's assessment that 15% of the total treatment cost for the ISCO plot was demonstration-related, an equivalent treatment cost for full-scale deployment of the ISCO technology would be approximately $850,000. This estimate is based on a total treatment and site preparation cost during the demonstration of approximately $1 million (from Table 7-1), less 15% of demonstration-related monitoring costs. Therefore, if the TCE remaining in the ISCO plot was allowed to attenuate naturally, the total treatment cost of ISCO would be around **$850,000**.

The economics of the ISCO technology compare favorably with the economics of an equivalent pump-and-treat system. As seen in Table H-3 in Appendix H, an investment in ISCO would be recovered in the 18th year, when the PV of a pump-and-treat system exceeds the cost of ISCO. In addition to lower PV or life-cycle costs, there may be other tangible and intangible economic benefits to using a source remediation technology that are not factored into the analysis. For example, the economic analysis in Appendix H assumes that the pump-and-treat system is operational all the time over the next 30 or more years, with most of the annual expense associated with operation and routine (scheduled) maintenance. Experience with pump-and-treat systems at several sites has shown that downtime associated with pump-and-treat systems is fairly high (as much as 50% downtime reported from some sites). This may negatively impact both maintenance requirements (tangible cost) and the integrity of plume containment (intangible cost) with the pump-and-treat alternative.

Another factor to consider is that, although the economic analysis for long-term remediation programs typically is conducted for a 30-year period, the DNAPL source (and therefore the pump-and-treat requirement) may persist for many more years or decades. This would lead to concomitantly higher remediation costs for plume containment (without source removal). Even if the limitations on the effectiveness of a source removal technology at some sites necessitate the use of pump-and-treat for the next few years, until the source (and plume) is further depleted, the cost of the pump-and-treat system and the time period over which it needs to be operated is likely to be considerably reduced.

8. Technology Applications Analysis

This section evaluates the general applicability of the ISCO technology to sites with contaminated groundwater and soil. The analysis is based on the results and lessons learned from the IDC demonstration, as well as general information available about the technology and its application at other sites.

8.1 Objectives

This section evaluates the ISCO technology against the nine evaluation criteria used for detailed analysis of remedial alternatives in feasibility studies under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Much of the discussion in this section applies to DNAPL source removal in general, and ISCO technology in particular. (For this section, "ISCO" refers to the mode in which this technology was applied at Launch Complex 34 — namely, by injection of industrial-grade potassium permanganate solution without concomitant extraction.)

8.1.1 Overall Protection of Human Health and the Environment

ISCO is protective of human health and environment in both the short and long term. At Launch Complex 34 for example, ISCO removed more than 4,000 kg of DNAPL contamination from the ISCO plot, with significant TCE mass destruction by oxidation. Because DNAPL acts as a secondary source that can contaminate an aquifer for decades or centuries, DNAPL source removal or mitigation considerably reduces the duration over which the source is active. Even if DNAPL mass removal is not 100%, the resulting long-term weakening of the plume and the reduced duration over which the DNAPL source contributes to the plume reduces the threat to potential receptors.

8.1.2 Compliance with ARARs

This section describes the technology performance versus applicable or relevant and appropriate requirements (ARARs). Compliance with chemical-, location-, and action-specific ARARs should be determined on a site-specific basis. Generally, location- and action-specific ARARs can be met with this technology, especially because of the following reasons:

- Injected oxidant solution is not reextracted or reinjected; therefore, there are no aboveground residuals that need treatment or disposal.
- When permanganate is used as the oxidant, there are no exothermic reactions that generate heat, and, therefore, no potential releases to the atmosphere.

Compliance with chemical-specific ARARs depends on the efficiency of the ISCO process at the site and the cleanup goals agreed on by various stakeholders. In general, reasonable DNAPL mass removal goals are more achievable and should lead to eventual and earlier compliance with long-term groundwater cleanup goals. Achieving short-term groundwater cleanup goals (e.g., federal or state maximum contaminant levels [MCLs]), especially in the DNAPL source zone, is more difficult because various studies (Pankow and Cherry, 1996) have shown that almost 100% DNAPL mass removal may be required before a significant change in groundwater concentrations is observed. However, removal of DNAPL, even if most of the removal takes place from the more accessible pores, probably would result in a weakened plume that may allow risk-based cleanup goals to be met in the downgradient aquifer.

The specific federal environmental regulations that are potentially impacted by remediation of a DNAPL source with ISCO are described below.

8.1.2.1 Comprehensive Environmental Response, Compensation, and Liability Act

CERCLA, as amended by the Superfund Amendments and Reauthorization Act (SARA), provides for federal authority to respond to releases or potential releases of any hazardous substance into the environment, as well as to releases of pollutants or contaminants that may present an imminent or significant danger to public health and welfare or the environment. Remedial alternatives that significantly reduce the volume, toxicity, or mobility of hazardous materials and that provide long-term protection are preferred. Selected remedies must also be cost-effective and protective of human health and the environment. The ISCO technology meets several of these criteria relating to a preferred alternative. ISCO reduces the toxicity of oxidizable contaminants by converting them into potentially nontoxic forms. For example, at Launch Complex 34, as described in Section 5.3.1, the hazardous chlorinated solvent TCE was converted to carbon dioxide, chloride, and water, without generating any aboveground residuals. This elimination of solvent hazard is permanent and leads to a considerable reduction in the time it takes for the DNAPL source to deplete fully. Although aquifer heterogeneities and technology limitations often result in less than 100% removal of the contaminant and elevated levels of dissolved solvent may persist in the groundwater over the short term, there is faster and eventual elimination of groundwater contamination in the long term. Section 7.4 shows that ISCO is cost-effective compared with the conventional alternative of long-term pump and treat.

8.1.2.2 Resource Conservation and Recovery Act

RCRA, as amended by the Hazardous and Solid Waste Amendments (HSWA) of 1984, regulates management and disposal of municipal and industrial solid wastes. The U.S. EPA and RCRA-authorized states (listed in 40 CFR Part 272) implement and enforce RCRA and state regulations. Generally, RCRA does not apply to in situ groundwater treatment because the contaminated groundwater may not be considered hazardous waste while it is still in the aquifer. The contaminated groundwater becomes regulated if it is extracted from the ground, as would happen with the conventional alternative of pump and treat. At least in the injection-only (no extraction) mode implemented at Launch Complex 34, no aboveground waste streams that may be hazardous, as defined by RCRA, are generated. At some sites, where hydraulic control requirements necessitate extraction and reinjection or treatment/disposal of injected fluids, RCRA may be invoked.

8.1.2.3 Clean Water Act

The CWA is designed to restore and maintain the chemical, physical, and biological quality of navigable surface waters by establishing federal, state, and local discharge standards. In the injection-only mode adopted at Launch Complex 34, there was no extraction of groundwater and therefore no reinjection or treatment/disposal of water; in this mode, the CWA may not be triggered. If, however, groundwater extraction is conducted in conjunction with injection, and the resulting water stream needs to be treated and discharged to a surface water body or a publicly owned treatment works (POTW), the CWA may apply. On-site discharges to a surface water body must meet National Pollutant Discharge Elimination System (NPDES) requirements, but may not require an NPDES permit. Off-site discharges to a surface water body must meet NPDES limits and require an NPDES permit. Discharge to a POTW, even if it is through an on-site sewer, is considered an off-site activity. Sometimes, soil or groundwater monitoring may lead to small amounts of purge and decontamination water wastes that may be subject to CWA requirements. Micropurging was one measure implemented at Launch Complex 34 to minimize such wastes during site characterization and technology performance assessment.

8.1.2.4 Safe Drinking Water Act

The SDWA, as amended in 1986, requires U.S. EPA to establish regulations to protect human health from contaminants in drinking water. The legislation authorizes national drinking water standards and a joint federal-state system for ensuring compliance with these standards. The SDWA also regulates underground injection of fluids through the UIC program and includes sole-source aquifer and wellhead protection programs.

The National Primary Drinking Water Standards are found at 40 CFR Parts 141 through 149. The health-based SDWA primary standards (e.g., for TCE) are more critical to meet; SDWA secondary standards (e.g., for dissolved manganese) are based on other factors, such as aesthetics (discoloration) or odor. The MCLs based on these standards generally apply as cleanup standards for water that is, or potentially could be, used for drinking water supply. In some cases, such as when multiple contaminants are present, alternative concentration limits (ACLs) may be used. CERCLA and RCRA standards and guidance are used in establishing ACLs. In addition, some states may set more stringent standards for specific contaminants. For example, the federally mandated MCL for vinyl chloride is 2 µg/L, whereas the State of Florida drinking water standard is 1 µg/L. In such instances, the more stringent standard is usually the cleanup goal.

Although the long-term goal of DNAPL source zone treatment is meeting applicable drinking water standards or other risk-based groundwater cleanup goals agreed on between site owners and regulatory authorities, the short-term objective of ISCO and source remediation is DNAPL mass removal. Because technology, site, and economic limitations may limit DNAPL mass removal to less than 100%, it may not always be possible to meet groundwater cleanup targets in the source region in the short term. Depending on other factors, such as the distance of the compliance point (e.g., property boundary, at which groundwater cleanup targets have to be met) from the source (as negotiated between the site owner and regulators), the degree of weakening of the plume due to DNAPL source treatment, and the degree of natural attenuation in the aquifer, it may be possible to meet groundwater cleanup targets at the compliance point in the short term. DNAPL mass removal will always lead to faster attainment of groundwater cleanup goals in the long term, as compared to the condition in which no source removal action is taken.

One aspect of using potassium permanganate solution as an oxidant for DNAPL source remediation is the presence of regulated trace metals in industrial-grade permanganate, the grade that is most commonly and economically available commercially. Depending on the concentration of permanganate used, levels of trace metals in the injected solution and/or the treated aquifer may temporarily exceed federal or state drinking water standards. At Launch Complex 34, injection of a 1 to 2% solution of permanganate resulted in elevated levels of some trace metals (chromium, nickel, and thallium) in the aquifer during and immediately after the demonstration (see Section 5.2.2). There is also the possibility that the strong oxidant may cause the release of other regulated metals (e.g., iron) from the aquifer formation or from other underground structures. Dissolved manganese originating from the oxidant is also subject to secondary drinking water standards. A UIC permit will be required for permanganate injection in many cases. At Launch Complex 34, a variance was obtained from the State of Florida Department of Environmental Protection to allow injection of the industrial-grade potassium permanganate for the ISCO demonstration.

Elevated levels of these metals of concern are expected to subside over time; the time period required for the metals to once again meet applicable drinking water standards will depend on the groundwater flux through the treated zone, once normal flow resumes. Many of the elevated metals are subject to secondary drinking water standards, which are somewhat less of a concern than target contamination (DNAPL) and metals subject to primary standards. One option for mitigating these concerns is to use the more expensive pharmaceutical-grade permanganate. Another option is to reduce the concentration of industrial-grade permanganate in the injected solution to a level where trace metal concentrations are compatible with regulatory standards applicable to the injected solution and/or the treated aquifer. The tradeoff between higher injected permanganate concentration (lower injection volumes and times) and lower injected permanganate (higher injection volumes and times) should be taken into consideration on a site-by-site basis.

One issue that has not been formally investigated in the field is generation and potential toxicity of organic byproducts from the incomplete oxidation of CVOCs and natural organic matter by the permanganate. This is a research need for the technology.

8.1.2.5 Clean Air Act

The CAA and the 1990 amendments establish primary and secondary ambient air quality standards for protection of public health, as well as emission limitations for certain hazardous pollutants. Permitting requirements under CAA are administered by each state as part of State Implementation Plans (SIPs) developed to bring each state in compliance with National Ambient Air Quality Standards (NAAQS).

Unlike pump-and-treat systems, which often generate air emissions (when an air stripper is used), and unlike other source removal technologies that use thermal energy (e.g., steam injection or resistive heating) or result in exothermic reactions (e.g., oxidation with Fenton’s reagent), the potential for atmospheric releases by ISCO with potassium permanganate is absent. Surface emission tests conducted in the ISCO plot during and after the demonstration did not show any TCE emissions above background levels.

8.1.2.6 Occupational Safety and Health Administration

CERCLA remedial actions and RCRA corrective actions must be carried out in accordance with OSHA requirements detailed in 20 CFR Parts 1900 through 1926, especially Part 1910.120, which provide for the health and safety of workers at hazardous waste sites. On-site construction activities at Superfund or RCRA corrective action sites must be performed in accordance with Part 1926 of RCRA, which provides safety and health regulations for construction sites. State OSHA requirements, which may be significantly stricter than federal standards, also must be met.

The health and safety aspects of ISCO are minimal, and are described in Section 3.3, which describes the operation of this technology at Launch Complex 34. Level D personal protective equipment generally is sufficient during implementation. Operation of heavy equipment and handling of a strong oxidant are the main working hazards and are dealt with by using appropriate personal protective equipment and trained workers. All operating and sampling personnel are required to have completed the 40-hour Hazardous Waste Operations training course and 8-hour refresher courses.

8.1.3 Long-Term Effectiveness and Permanence

ISCO leads to destruction of DNAPL mass and therefore permanent removal of contamination from the aquifer. Although dissolved solvent concentrations may rebound in the short term when groundwater flow redistributes through the treated source zone containing DNAPL remnants, depletion of the source through dissolution will continue in the long term, and lead to eventual and earlier compliance with groundwater cleanup goals.

8.1.4 Reduction of Toxicity, Mobility, or Volume through Treatment

ISCO effects treatment by reducing the toxicity of the contamination. Hazardous chlorinated solvents or other target contaminants are oxidized to potentially nontoxic compounds, such as chloride, carbon dioxide, and water.

8.1.5 Short-Term Effectiveness

Short-term effectiveness of the ISCO technology depends on a number of factors. If the short-term goal is to remove as much DNAPL mass as possible, this goal is likely to be met. If the short-term goal is to reduce dissolved contaminant levels in the source zone, achievement of this goal will depend on the hydrogeology and DNAPL distribution in the treated region. As seen in Section 5.2.1, TCE levels declined sharply in some monitoring wells in the ISCO plot, but rose in one of the wells. Geologic heterogeneities, preferential flowpaths taken by the oxidant, and localized permeability changes that determine flow in the treated region may lead to such variability in posttreatment groundwater levels of contamination. As discussed in Section 8.1.2.4, the chances of DNAPL mass removal resulting in reduced contaminant levels at a compliance point downgradient from the source is more likely in the short term. In the long term, DNAPL mass removal will always shorten the time period required to bring the entire affected aquifer in compliance with applicable standards.

8.1.6 Implementability

As mentioned in Section 7.2, site preparation and access requirements for implementing ISCO are minimal. Firm ground for setup of the permanganate storage and mixing equipment is required. The equipment and chemicals involved are commercially available. Setup and shakedown times are relatively small. Overhead space available at open sites is generally sufficient for housing storage and GeoProbe® equipment, if required. Accessibility to the portion of the contamination under the Engineering Support Building at Launch Complex 34 was not particularly efficient with normal injection from the outside. The use of angled injection wells/drive points or the capability of conducting injection from inside the building may be required to remediate more of the contamination under the building.

Generally, 8 to 10 hours of operator attention each day is sufficient to keep the oxidant flowing through the injection points and 24-hour presence is not required, as long as the system is automated enough that it shuts off when any backpressure is sensed in the injection lines. Strong oxidant and byproduct colors make it easier to track the progress of the oxidant in the aquifer, although confirmatory groundwater and soil sampling is required. The strong oxidant is a chemical hazard, but one that can be handled through the use of basic personal protective equipment and a common neutralizing solution.

At least in the injection-only mode used at Launch Complex 34, ISCO did not generate any significant aboveground wastes that required treatment and reinjection/disposal. If additional hydraulic control is to be achieved through the use of strategic extraction wells, then the complexity of the operation may increase to some degree and waste generation and handling requirements may become significant.

8.1.7 Cost

As described in Section 7.4, the cost of the ISCO treatment is competitive with the life-cycle cost of pump and treat (over a 30-year period of comparison). The cost comparison becomes even more favorable for source remediation in general and ISCO in particular when other tangible and intangible factors are taken into account. For example, a DNAPL source, such as the one at Launch Complex 34, is likely to persist much longer than 30 years (the normal evaluation time for long-term remedies), thus necessitating continued costs for pump and treat into the distant future (perhaps 100 years or more). Annual O&M costs also do not take into account the nonroutine maintenance costs associated with the large amount of downtime typically experienced by site owners with pump-and-treat systems.

Factors that may increase the cost of the ISCO application are:

- Operating requirements associated with any contamination under a building
- Stringent regulatory requirements on elevated levels of trace metals in the treated aquifer that necessitate operating longer with lower permanganate concentrations or moving to a higher grade of oxidant.

- Need for additional hydraulic control (e.g., with extraction wells) and any associated need to treat and dispose/reinject extracted fluids.

8.1.8 State Acceptance

The ITRC, a consortium of several states in the United States, is participating in the IDC demonstration through reports review and attendance at key meetings. The ITRC plays a key role in innovative technology transfer by helping disseminate performance information and regulatory guidance to the states.

The IDC set up a partnering team consisting of representatives from NASA and Patrick Air Force Base (site owners), U.S. EPA, State of Florida Department of Environmental Protection (FDEP), and other stakeholders early on when the demonstration was being planned. The partnering team was and is being used as the mechanism to proactively obtain regulatory input in the design and implementation of the remediation/demonstration activities at Launch Complex 34. Because of the technical limitations and costs of conventional approaches to DNAPL remediation, state environmental agencies have shown growing acceptance of innovative technologies.

8.1.9 Community Acceptance

The ISCO technology's low profile, limited space requirements, absence of air emissions, absence of waste storage, handling, and off-site transportation requirements, low noise levels, and ability to reduce short- and long-term risks posed by DNAPL contamination are expected to promote local community acceptance.

8.2 Operability

Unlike a pump-and-treat system that may involve continuous long-term operation by trained operators for the next 30 or 100 years, a source remediation technology is a short-term application. The field application of ISCO in the 75-ft × 50-ft plot at Launch Complex 34 took about seven months to complete including two interim monitoring events. The remediation generally is done as a turnkey project by multiple vendors, who will design, build, and operate the oxidant delivery system. Site characterization, site preparation (utilities, etc.), monitoring, and any waste disposal often are done by the site owner. Although various organization has patented some aspects of the process, ISCO of dissolved contamination, in general, has been known for a long time and is commercially available through several vendors.

The chemical (permanganate) oxidation process is relatively easy to set up and operate using off-the-shelf equipment and generally proficient operators. Potassium permanganate handling requires moderate health and safety measures; however, other oxidants, such as Fenton's reagent or ozone, may require additional precautions.

8.3 Applicable Wastes

ISCO has primarily been applied to remediation of aquifers contaminated with chlorinated solvents. Source zones consisting of PCE and TCE in DNAPL form, as well as dissolved *cis*-1,2-DCE and vinyl chloride can be addressed. However, oxidation has a range of other potential applications. Permanganate, for example, is able to oxidize source zones containing naphthalene, phenanthrene, pyrene, and phenols. ISCO can be implemented in source zones present in saturated or vadose zones. The technology also has been contemplated for treating dissolved contaminant plumes of these compounds. Oxidants, such as Fenton's reagent, have been found to be capable of treating methyl-*tert*-butyl ether (MTBE) hot spots. In general, any contaminant that exists in a relatively reduced form that can be oxidized into potentially nontoxic products is amenable for treatment by ISCO.

8.4 Key Features

The following are some of the key features of chemical (permanganate) oxidation that makes it attractive for DNAPL source zone and groundwater treatment:

- In situ application
- Potential for injection-only mode at some sites that prevents the generation of aboveground wastes, which would need additional treatment or handling
- Potentially nontoxic products
- Uses relatively simple, commercially available equipment
- Relatively fast field application time
- Longer-lived oxidant (potassium permanganate) distributes in the aquifer through both advection and diffusion, thus achieving better contact with contaminants
- At many sites, a one-time application has the potential to reduce a DNAPL source to the point where either natural attenuation is sufficient to address a weakened plume or pump and treat needs to be applied for over a shorter duration in the future.

8.5 Availability/Transportability

ISCO is commercially available from multiple vendors or consulting organizations as a service on a contract basis.

In addition, potassium permanganate or sodium permanganate suppliers are familiar enough with the application that they can help design some of the front-end permanganate storage and delivery equipment. No stand-alone mobile ISCO plant has been built, but components are readily available and oxidant delivery systems can be assembled or disassembled on site relatively quickly.

8.6 Materials Handling Requirements

Potassium permanganate is typically available as a solid and requires solids handling and mixing equipment; however, sodium permanganate is available as a solution that can be diluted on site before the in situ application.

8.7 Ranges of Suitable Site Characteristics

The following factors should be considered when determining the suitability of a site for ISCO application:

- **Type of contaminants.** Contaminants should be amenable to oxidation with commonly available oxidants.
- **Site geology.** Oxidant can be distributed more effectively in sandy soils. Silts or clays can make the application more difficult. Aquifer heterogeneities and preferential flowpaths can make contact between the oxidant and the contaminants more difficult. DNAPL source zones in fractured bedrock also may pose a challenge.
- **Soil characteristics.** Soils with low organic carbon content require less oxidant and application is relatively quicker. Soils with higher organic content consume more oxidant and slow down the spread of the oxidation front.
- **Regulatory acceptance.** Although ISCO has long-term benefits in terms of a diminished DNAPL source, at least in the short term, use of industrial-grade permanganate can elevate the levels of trace metals in the treated aquifer. Regulatory acceptance is important for this application, and a UIC permit or variance may be required. In addition, hydraulic control requirements and economics at some sites may necessitate extraction, treatment, and reinjection of the oxidant solution. A reinjection permit will be required.
- **Site accessibility.** Sites that have no aboveground structures and fewer utilities are easier to remediate with ISCO. Presence of buildings or a network of utilities can make the application more difficult.

None of the factors mentioned above necessarily eliminate ISCO from consideration. Rather, these are factors that may make the application less or more economical.

8.8 Limitations

The ISCO technology has the following limitations:

- Not all types of contaminants are amenable to oxidative transformation. In addition, some cocontaminants, such as heavy metals, could be mobilized by oxidation.
- Byproducts of oxidation may make it unsuitable for application in a region very close to a receptor, even though some of these byproducts are subject to secondary (nonhealth-based) drinking water standards. Byproducts, such as manganese, chloride, and trace metals, require sufficient time and distance to dissipate (around 100 ft at Cape Canaveral).
- Aquifer heterogeneities can make the application more difficult, necessitating more complex application schemes, greater amounts of oxidant, and/or longer injection times.
- Some sites may require greater hydraulic control to minimize the spread of contaminants. This may necessitate the use of extraction, aboveground treatment, and disposal/reinjection.

9. References

Appelo, C.A.J and D. Postma. 1994. *Geochemistry, Groundwater, and Pollution.* A.A. Balkema: Rotterdam. 536 pp.

Battelle. 1999a. *Hydrogeologic and Chemical Data Compilation, Interagency DNAPL Consortium Remediation Demonstration Project, Launch Complex 34, Cape Canaveral Air Station, Florida*. Prepared for Interagency DNAPL Consortium.

Battelle. 1999b. *Interim Report: Performance Assessment Site Characterization for the Interagency DNAPL Consortium, Launch Complex 34, Cape Canaveral Air Station, Florida*. Prepared for Interagency DNAPL Consortium.

Battelle. 1999c. *Pre-Demonstration Assessment of the Treatment Plots at Launch Complex 34, Cape Canaveral, Florida*. Prepared for Air Force Research Laboratory and Interagency DNAPL Consortium. September 13.

Battelle. 1999d. *Quality Assurance Project Plan: Performance Evaluation of In-Situ Oxidation for DNAPL Destruction at Launch Complex 34, Cape Canaveral, Florida*. Prepared for the Air Force Research Laboratory, Tyndall AFB, FL. September 3.

Battelle. 1999e. *First Interim Report for Performance Assessment of Six-Phase Heating™ and In-Situ Oxidation Technologies at LC34*. Prepared for the Interagency DNAPL Consortium, November 2.

Battelle. 1999f. *Second Interim Report for Performance Assessment of Six-Phase Heating™ and In-Situ Oxidation Technologies at LC34*. Prepared for the Interagency DNAPL Consortium, December 2.

Battelle. 2000a. *Third Interim Report for Performance Assessment of Six-Phase Heating™ and In-Situ Oxidation Technologies at LC34*. Prepared for the Interagency DNAPL Consortium, May 11.

Battelle. 2000b. *Fourth Interim Report for Performance Assessment of Six-Phase Heating™ and In-Situ Oxidation Technologies at LC34*. Prepared for the Interagency DNAPL Consortium, June 30.

Battelle. 2000c. *Fifth Interim Report for Performance Assessment of Six-Phase Heating™ and In-Situ Oxidation Technologies at LC34*. Prepared for the Interagency DNAPL Consortium, November 2.

Battelle. 2000d. *Sixth Interim Report: IDC's Demonstration of Three Remediation Technologies at LC34, Cape Canaveral Air Station*. Prepared for the Interagency DNAPL Consortium, February 12.

Battelle. 2001. *Seventh Interim Report on the IDC Demonstration at Launch Complex 34, Cape Canaveral Air Station*. Prepared for the Interagency DNAPL Consortium. August 15.

Eddy-Dilek, C., B. Riha, D. Jackson, and J. Consort. 1998. *DNAPL Source Zone Characterization of Launch Complex 34, Cape Canaveral Air Station, Florida*. Prepared for Interagency DNAPL Consortium by Westinghouse Savannah River Company and MSE Technology Applications, Inc.

G&E Engineering, Inc. 1996. *RCRA RFI Work Plan for Launch Complex 34, Cape Canaveral Air Station, Brevard County, Florida.* Prepared for NASA Environmental Program Office.

Gates, D., R. Siegrist, and S. Cline. 1995. "ISCO of Contaminants in Clay or Sandy Soil." *Proceedings of ASCE National Conference on Environmental Engineering*. American Society of Civil Engineering, Pittsburgh, PA.

Hazen, T.C., G. Sewell, and A. Gavaskar. 2000. *Biological Sampling and Analysis Work Plan: The Effect of Source Remediation Methods on the Presence and Activity of Indigenous Subsurface Bacteria at Launch Complex 34, Cape Canaveral Air Station, Florida.* Letter Report to the IDC. May 17.

IT Corporation. 2000. *In Situ Oxidation System Demonstration Test, Final Report: Treatment Cell C, Launch Complex 34 DNAPL Source Zone Project, Cape Canaveral, FL*. Prepared for MSE Technology Applications, Inc., Butte, MT. October 20.

Lowe, K.S., F.G. Gardner, and R.L. Siegrist. 2002. Field Pilot Test of In Situ Chemical Oxidation through Recirculation using Vertical Wells. *Ground Water Monitoring and Remediation*. Winter issue. pp. 106-115.

MSE Technology Applications, Inc. 2002. *Comparative Cost Analysis of Technologies Demonstrated for the Interagency DNAPL Consortium Launch Complex 34, Cape Canaveral Air Station, Florida.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory. June.

Pankow, J., and J. Cherry. 1996. *Dense Chlorinated Solvents and Other DNAPLs in Groundwater: History, Behavior, and Remediation.* Waterloo Press, Portland, OR.

Resolution Resources. 2000. *Location of Well Below Confining Unit on LC34 Seismic Data.* Letter memo to NASA. September 11.

Schmalzer, P.A., and G.A. Hinkle. 1990. *Geology, Geohydrology and Soils of the Kennedy Space Center: A Review*. NASA Kennedy Space Center, FL.

Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe. 2001. *Principles and Practices of In Situ ISCO Using Permanganate.* Battelle Press, Columbus, Ohio. July.

Vella, P., G. Deshinsky, J. Boll, J. Munder, and W. Joyce. 1990. Treatment of Low Level Phenols with Potassium Permanganate. *Research Journal Water Pollution Control Federation*, *62*(7): 907-914.

Watts, R., P. Rausch, S, Leung, and M. Udell. 1990. “Treatment of Pentachlorophenol Contaminated Soils Using Fenton’s Reagent.” *Hazardous Waste and Hazardous Materials 7*: 335-345.