Demonstration of Steam Injection/Extraction Treatment of a DNAPL Source Zone at Launch Complex 34 in Cape Canaveral Air Force Station

Final Innovative Technology Evaluation Report

Appendix A: Performance Assessment Methods

A.1 Statistical Design and Data Analysis Methods
A.2 Sample Collection and Extraction Methods
A.3 Standard Sample Collection and Analytical Methods

A.1 Statistical Design and Data Analysis Methods

Estimating TCE/DNAPL mass removal due to the steam injection technology application was a critical objective of the IDC demonstration at Launch Complex 34. Analysis of TCE in soil samples collected in the steam injection plot before and after the demonstration was the main tool used to determine TCE mass distribution and removal. Two data evaluation methods were used for estimating TCE/DNAPL masses in the steam injection plot before and after the demonstration:

- ☐ Linear interpolation (contouring)
- ☐ Kriging

Section 4.1 of the report contains a general description of these methods. Section 5.1 of this report) summarizes the results obtained from using contouring and kriging to estimate TCE/DNAPL masses. Both methods are linear interpolation methods that predict the TCE concentration between two sampling points whose actual TCE concentrations are known. Both methods assume that the TCE concentrations are linearly distributed between sampling points. The contouring method estimates the TCE concentration between the two sample points by averaging the known TCE concentrations. Both the predicted and actual concentration values then are used to create a three-dimensional contour plot of the TCE concentrations in the targeted stratigraphic unit. 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.

The contour plot consists of iso-concentration shells for TCE. The TCE concentration of each shell is multiplied by the volume of the shell (as estimated by the software) and the bulk density of the soil (estimated as 1.59 g/cm^3 during site characterization) to estimate a TCE mass for each shell. The total sum of the mass estimates from the individual shells is quantified as the estimated total TCE mass in the targeted unit. The DNAPL mass is obtained by adding up the portion of the shells that have TCE concentrations above 300 mg/kg. 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. By collecting approximately 300 samples in the plot during the pre- and postdemonstration sampling events, sufficient coverage of the plot was obtained to make a reliable determination of the true TCE mass in the region of interest. However, linear interpolation by contouring does not minimize the errors associated with the predicted values of TCE concentrations. Section A.1.1 of this appendix describes how the number of samples and appropriate sampling locations were determined to obtain good coverage of the 75 ft × 50 ft plot.

Kriging also uses the known TCE concentrations from sampling points to predict the TCE concentrations between those points. Kriging uses spatial correlations among the TCE data and makes 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 at unsampled points in an entire region of interest (i.e., the entire test plot or a single stratigraphic unit).

Kriging accounts for the uncertainty in each point estimate by calculating a standard error for the estimate. Therefore, a range of TCE concentration 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 average value and standard error for the range of TCE concentrations is then used to calculate an average value and standard error for the TCE mass in the targeted region. 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 targeted for the data evaluation. The sampling design sought to ensure a level of significance of 80% and a power of 75% for the statistical tests used to analyze TCE removal. Section A.1.2 of this appendix describes the kriging method further.

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

Both contouring and kriging were used to estimate the total TCE mass in the targeted unit before and after the steam injection treatment. Kriging was the preferred method for handling spatially correlated data because kriging minimized the errors associated with the predicted TCE concentration values. The TCE mass estimate from the kriging and contouring methods were compared to each other. The TCE mass estimate from the contouring method fell within the range of the kriging TCE mass estimates. The contouring method was used to estimate the DNAPL mass in the targeted unit before and after treatment by examining the data for those regions of the plot that exceed the TCE saturation threshold. Kriging was not used for estimating the DNAPL mass in the targeted unit because the site characterization data indicated that too few soil samples had TCE concentrations above the DNAPL threshold value.

The TCE mass removal percentage range was determined after the confidence intervals for the pre- and posttreatment total TCE masses were calculated by kriging at the 80% confidence level. In general, the statistical evaluation was adjusted as more information about the actual TCE distribution inside the test plot before and after treatment was gathered. The combined methods of contouring and kriging for total TCE mass and contouring for DNAPL mass have been found the most suitable for evaluating the technology effectiveness during previous demonstrations at this site (Battelle, 2001b; Battelle, 2001c). The proposed methodology also has been found to be superior to the statistical paired comparison method mentioned in previous QAPPs for this site (Battelle, 1999a, b).

Although the primary objective of this demonstration is to evaluate TCE destruction, the soil samples also will be analyzed for DCE and VC concentrations. This data will be used to determine general trends in the TCE degradation byproducts that may have formed during treatment. Kriging and contouring will not be used to estimate the mass of the DCE and VC data.

A.1.1 Sampling Design to Obtain Sufficient Coverage of the Steam Injection Plot

Selection of the sampling plan for this particular test plot was based, in part, on the objectives of the study for which the samples were being collected. In this study, the objectives were:

- **Primary objective:** To determine the magnitude of the reduction in the levels of TCE across the entire test plot.
- **Secondary objectives:**
    - To determine whether remediation effectiveness differs by depth (or stratigraphic unit such as the upper sand unit [USU], middle fine-grained unit [MFGU], or lower sand unit [LSU]).
    - To determine whether the three remediation technologies demonstrated differ in their effectiveness at removing chlorinated volatile organic compounds (CVOCs).

Four alternative plans for selecting the number and location of sampling in the test plot were examined. These four plans were designated as simple random sampling (SRS), paired sampling, stratified sampling, and systematic sampling. Systematic sampling was chosen as the best approach for sampling soil in the steam injection plot. Each of the four plans, including the advantages and limitations, are discussed in brief detail below.

Simple Random Sampling

The most basic statistical sampling plan is SRS, in which all locations within a given sampling region are equally likely to be chosen for sampling. For this study, using SRS would require developing separate SRS plans for each of the three test plots. In addition, because two sampling events were planned for the test plot, using SRS would involve determining two sets of unrelated sampling locations for the test plot.

The main benefit of using SRS is that the appropriate sample size can be determined easily based on the required power to detect a specific decrease in contaminant levels. In addition, SRS usually involves a reasonable number of samples. However, a key disadvantage of using SRS is that it would not guarantee complete coverage of the test plot; also, if contaminant levels are spatially correlated, SRS is not the most efficient sampling design available.

Paired Sampling

Paired sampling builds on SRS methods to generate one set of paired sampling locations for a given test plot rather than two separate sets. Instead of sampling from each of two separate random sample locations for pre- and post-remediation sampling, paired sampling involves the positioning of post-remediation sample locations near the locations of pre-remediation sampling. The number of samples required to meet specific power and difference requirements when using this design would be similar to the number of locations involved using SRS; the exact sample size cannot be determined because information is required about contaminant levels at collocated sites before and after remediation.

Paired sampling offers three significant benefits to this particular study. First, the work of determining the sampling locations is reduced in half. Second, the comparison of contaminant levels before and after remediation is based on the differences in levels at collocated sites. Third, the variability of the difference should be less than the variability associated with the SRS, which would result in a more accurate test. The disadvantages of this sampling procedure are the same as with the SRS: there is no guarantee of complete coverage of the test plot, and the plan is inefficient for spatially correlated data.

Stratified Sampling

Stratified sampling guarantees better coverage of the plot than either SRS or paired sampling: to ensure complete coverage of a given test plot, it is divided into a regular grid of cells, and random samples are drawn from each of the grid cells. Samples then are selected within each grid cell either using SRS or paired sampling. The number of samples required to meet specific power and difference requirements would be slightly greater than that for SRS, although the difference would not be great. For this study, which involves test plots 50 × 75 ft in size, the most effective grid size would be 25 × 25 ft, which results in six grid cells per test plot.

Again, the main benefit of stratified sampling is that it guarantees more complete coverage of the test plot than SRS or paired sampling. Also, if any systematic differences in contaminant levels exist across the site, stratified sampling allows for separate inferences by sub-plot (i.e., grid cell). Disadvantages of stratified sampling are that the method requires a slightly larger number of samples than SRS or paired sampling methods, and that stratified sampling performs poorly when contaminant levels are spatially correlated.

Systematic Sampling

The samples for the steam injection demonstration were collected using a systematic sampling plan. Systematic sampling is the term applied to plans where samples are located in a regular pattern. In geographic applications such as this study, the systematic sampling method involves the positioning of sampling locations at the nodes of a regular grid. The grid need not be square or rectangular; in fact, a grid of equilateral triangles is the most efficient grid design. (Regular hexagonal grids also have been used regularly and are nearly as efficient as triangles and squares.) The number of samples and the size of the area to be sampled determine the dimensions of the grid to be used. With systematic sampling, the selection of initial (e.g., pre-remediation) set of sampling locations requires the random location of only one grid node, because all other grid nodes will be determined based on the required size of the grid and the position of that first node. A second (e.g., post-remediation) set of sampling locations can be either chosen using a different random placement of the grid or collocated with the initial set of sampling locations.

One variation of the systematic sampling method worth consideration is *unaligned* sampling. Under this method, a given test plot is divided into a grid with an equal number of rows and columns. One sample per grid cell then is selected by:

- ☐ Assigning random horizontal coordinates for each row of the grid;
- ☐ Assigning random vertical coordinates for each column of the grid;
- ☐ Determining the sampling locations for a cell by using the horizontal and vertical coordinates selected for the corresponding row and column.

In other words, every cell in a row shares a horizontal coordinate, and every cell in a column shares a vertical coordinate. Figure A.1-1 illustrates the locations generated using unaligned systematic sampling with a 3 × 3 grid.

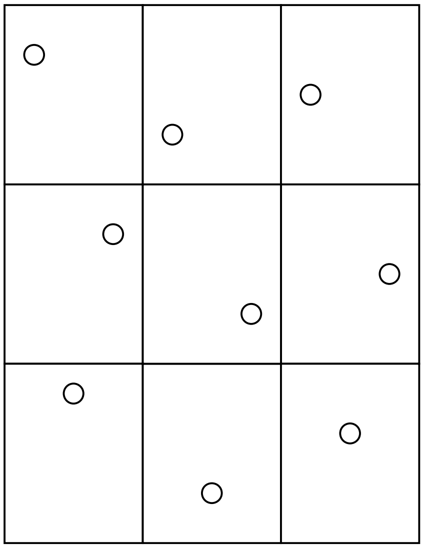

Figure A.1-1. Unaligned Systematic Sampling Design for a 3 × 3 Grid

The major benefit of systematic sampling was that it is the most efficient design for spatially correlated data. In addition, coverage of the entire plot was guaranteed. One disadvantage of systematic sampling was that determining the required sample size was more difficult than the other three methods discussed in this appendix.

A.1.2 Kriging Methods and Results

The geostatistical analysis approach was to utilize kriging, a statistical spatial interpolation procedure, to estimate the overall average TCE concentration in soil before and after remediation, and then determine if those concentrations were significantly different.

To meet the objectives of this study, it was sufficient to estimate the overall mean TCE concentration across an entire test plot, rather than estimating TCE concentrations at various spatial locations within a test plot. In geostatistical terms, this is known as global estimation. One approach for calculating a global mean estimate is to calculate the simple arithmetic average (i.e., the equally weighted average) across all available TCE concentrations measured within the plot. However, this approach is appropriate only in cases where no correlation is present in the measured data. Unfortunately, this is a rare situation in the environmental sciences.

A second approach, and the approach taken in this analysis, is to use a spatial statistical procedure called kriging to take account of spatial correlation when calculating the global average. Kriging is a statistical interpolation method for analyzing spatially varying data. It is used to estimate TCE concentrations (or any other important parameter) on a dense grid of spatial locations covering the region of interest, or as a global average across the entire region. At each location, two values are calculated with the kriging procedure: the estimate of TCE concentration (mg/kg), and the standard error of the estimate (also in mg/kg). The standard error can be used to calculate confidence intervals or confidence bounds for the estimates. It should be noted that this calculation of confidence intervals and bounds also requires a serious distributional assumption, such as a normality assumption, which is typically more reasonable for global estimates than for local estimates.

The kriging approach includes two primary analysis steps:

1. Estimate and model spatial correlations in the available monitoring data using a semivariogram analysis.
2. Use the resulting semivariogram model and the available monitoring data to interpolate (i.e., estimate) TCE values at unsampled locations; calculate the statistical standard error associated with each estimated value.

A.1.2.1 Spatial Correlation Analysis

The objective of the spatial correlation analysis is to statistically determine the extent to which measurements taken at different locations are similar or different. Generally, the degree to which TCE measurements taken at two locations are different is a function of the distance and direction between the two sampling locations. Also, for the same separation distance between two sampling locations, the spatial correlation may vary as a function of the direction between the sampling locations. For example, values measured at each of two locations, a certain distance apart, are often more similar when the locations are at the same depth, than when they are at the same distance apart but at very different depths.

Spatial correlation is statistically assessed with the semivariogram function, $((\underline{h})$, which is defined as follows (Journel and Huijbregts, 1981):

$$2\gamma(\underline{h}) = E\,\{[Z(\underline{x}) - Z(\underline{x} + \underline{h})]^2\}$$

where $Z(\underline{x})$ is the TCE measured at location $\underline{x}$, $\underline{h}$ is the vector of separation between locations $\underline{x}$ and $\underline{x} + \underline{h}$, and E represents the expected value or average over the region of interest. Note that the location $\underline{x}$ is typically defined by an easting, northing, and depth coordinate. The vector of separation is typically defined as a three-dimensional shift in space. The semivariogram is a measure of spatial differences, so that small semivariogram values correspond to high spatial correlation, and large semivariogram values correspond to low correlation.

As an initial hypothesis, it is always wise to assume that the strength of spatial correlation is a function of both distance and direction between the sampling locations. When the spatial correlation is found to depend on both separation distance and direction, it is said to be anisotropic. In contrast, when the spatial correlation is the same in all directions, and therefore depends only on separation distance, it is said to be isotropic.

The spatial correlation analysis is conducted in the following steps using the available measured TCE data:

- Experimental semivariogram curves are generated by organizing all pairs of data locations into various separation distance and direction classes (e.g., all pairs separated by 20-25 ft in the east-west direction ±22.5º), and then calculating within each class the average squared-difference between the TCE measurements taken at each pair of locations. The results of these calculations are plotted against separation distance and by separation direction.

- To help fully understand the spatial correlation structure, a variety of experimental semivariogram curves may be generated by subsetting the data into discrete zones, such as different depth horizons. If significant differences are found in the semivariograms they are modeled separately; if not, the data are pooled together into a single semivariogram.

- After the data have been pooled or subsetted accordingly, and the associated experimental semivariograms have been calculated and plotted, a positive-definite analytical model is fitted to each experimental curve. The fitted semivariogram model is then used to input the spatial correlation structure into the subsequent kriging interpolation step.

A.1.2.2 Interpolation Using Ordinary Kriging

Ordinary kriging is a linear geostatistical estimation method which uses the semivariogram function to determine the optimal weighting of the measured TCE values to be used for the required estimates, and to calculate the estimation standard error associated with the estimates (Journel and Huijbregts, 1981). In a sense, kriging is no different from other classical interpolation and contouring algorithms. However, kriging is different in that it produces statistically optimal estimates and associated precision measures. It should be noted that the ordinary kriging variance, while easy to calculate and readily available from most standard geostatistical software packages, may have limited usefulness in cases where local estimates are to be calculated, and the data probability distribution is highly skewed or non-gaussian. The ordinary kriging variance is more appropriately used for global estimates and symmetric or gaussian data distributions. The ordinary kriging variance provides a standard error measure associated with the data density and spatial data arrangement relative to the point or block being kriged. However, the ordinary kriging variance is independent of the data values themselves, and therefore may not provide an accurate measure of local estimation precision.

A.1.2.3 TCE Data Summary

Semivariogram and kriging analyses were conducted on data collected from the steam injection plot. The plot was approximately 50 by 75 feet in size, and was sampled via 26 boreholes, half before and half after remediation. The location of each drill hole was recorded by measuring the distance in the northing and easting directions from a designated point on the Cape Canaveral Air Station.

Pre- and post-remediation TCE measurements were collected in order to analyze the effectiveness of the contaminant removal methods. The sampling borehole locations were predetermined spatially based on the aforementioned unaligned systematic sampling design in a 12-grid of the steam injection plot for both pre- and postdemonstration characterization. In addition, one duplicate borehole was drilled approximately 2 feet away from the corresponding primary borehole during each pre- and post-remediation sampling event. Because the approach for the kriging analysis considered the pre- and post-remediation data as independent data sets (see Section 1.0), the duplicate samples were included in the analyses, even though the pre-remediation duplicate borehole did not correspond to the same location as the post-remediation duplicate borehole.

The cores were drilled at least 44 feet deep; and the largest drill hole extends 46 feet. Except in instances where no core was recovered, every 2 feet of the borehole soil samples were collected and analyzed for TCE concentration levels. Thus, approximately 20 to 25 2-foot core sections were analyzed from each borehole. The vertical location of each core section was identified by the elevation of the midpoint of the section above sea level. At the time of data collection, the surface elevation at the location of the drill hole, as well as the top and bottom depths of each core section (rounded to the nearest half of a foot), were recorded. Hence, the elevation of each sample was calculated by the subtracting the average of the top and bottom depths from the surface elevation. For example, if a sample was collected from a core section that started and ended at 20 and 22 feet below a ground surface elevation of 5.2 feet, then the sample elevation equaled $5.2 - (20+22)/2=15.8$ feet above sea level.

In some cases, field duplicate samples were collected by splitting an individual two-foot core section. In order to optimize the additional data, all measurements were used when evaluating spatial correlation with the semivariogram analysis, and when conducting the kriging analysis. However, to remain compatible with the kriging software, it was necessary to shift the location of the duplicate data slightly, by adding one-tenth of a foot to the easting coordinate. Table A.1-1 summarizes the number of samples and duplicate samples collected from the soil cores. The duplicate soil core that was collected during each pre- and postdemonstration sampling event is counted in the “Total # of Duplicate Samples” column.

Table A.1-1. Number of Field Duplicate Measurements Taken from the Steam Injection Plot

Plot	Event	Number of 2-Foot Sections from Which 1 Sample was Drawn	Total # of Duplicate Samples	Total
Steam Injection	Pre-demo	267	35	302
	Post-demo	275	37	312

There were also cases where the observed TCE concentration for a particular sample occurred below the analytical method detection limit (MDL). In such cases, the measurement that was included in our analyses equaled one-half of the given MDL. Table A.1-2 summarizes the number of observations that were below the MDL.

Table A.1-2. Number of Measurements (Including Duplicates) Below the Minimum Detection Limit

Plot	Event	Number of Samples			Total
		Below MDL	Above MDL	No Sample Recovery	
Steam Injection	Pre-Demo	58	243	1	302
	Post-Demo	29	274	9	312

When a two-foot section was removed from the core, the sample was identified by the easting, northing, and elevation coordinates. In addition, the geologic stratum, or soil type of the sample, was also documented. These strata and soil types included the vadose zone, Upper Sand Unit (USU), Middle Fine-Grained Unit (MFGU), and Lower Sand Unit (LSU). Note that the stratum of the sample was not solely determined by depth, but also by inspection by a geologist.

A.1.2.4 Semivariogram Results

In this study, the computer software used to perform the geostatistical calculations was Battelle's BATGAM software, which is based on the GSLIB Software written by the Department of Applied Earth Sciences at Stanford University, and documented and released by Prof. Andre Journel and Dr. Clayton Deutsch (Deutsch and Journel, 1998). The primary subroutine used to calculate experimental semivariograms was GAMV3, which is used for three-dimensional irregularly spaced data.

The data were considered vertically and separately by layer (i.e., USU, MFGU and LSU layers). Semivariogram and kriging analyses were not performed with the vadose data since the pre-remediation TCE concentrations were already relatively low and insignificant. In all cases, the experimental semivariograms are relatively variable due to high data variability and modest sample sizes. As a result, the semivariogram model fitting is relatively uncertain, meaning that a relatively wide range of semivariogram models could adequately fit the experimental semivariogram points. This probably does not affect the TCE estimates (especially the global estimates), but could significantly affect the associated confidence bounds.

A.1.2.5 Kriging Results

The kriging analysis was performed using the BATGAM software and GSLIB subroutine KT3D. To conduct this analysis, each plot was defined as a set of vertical layers and sub-layers. Estimated mean TCE concentrations were then calculated via kriging for each sub-layer separately, as well as across the sub-layers. The vertical layering for kriging was consistent with the semivariogram modeling:

(a) Kriging the steam injection plot was performed separately for the USU, MFGU and LSU layers. The thickness of the USU unit is set to be 28 ft., with a vertical midpoint of –3 ft (i.e., 3 ft below MSL). The thickness of the MFGU unit is 8 ft, with a vertical midpoint of –21 ft below MSL. The thickness of the LSU unit is to be 10 ft., with a vertical midpoint of –30 ft. (i.e., 30 ft below MSL).

(b) For kriging of each layer (i.e., USU or MFGU or LSU separately), the data search considered all available data at all elevations. Note that by extending the data search radius to include all data within a plot, an implicit assumption is made that the semivariogram model holds true for distances up to about 100 ft., which are distances beyond those observable with this dataset in the experimental semivariograms. This assumption seems reasonable given the relatively short dimensions of the steam injection plot.

Results from the kriging analysis are presented in Tables A.1-3 and A.1-4 for the steam injection pre- and post-remediation data, and for each of USU, MFGU and LSU layers, as well as by sub-layer within each layer. Because of the shortcomings of using the ordinary kriging variance (discussed in Section 1.0) for local estimates, confidence bounds are only presented in Table A.1-3 for the global layer estimates. In cases where the upper confidence bound for the post-remediation average TCE concentration falls below the lower confidence bound for the pre-remediation average TCE concentration, the post-remediation TCE concentrations are statistically significantly lower than the pre-remediation TCE concentrations. For the steam injection technology demonstration, this case did not occur in any of each stratigraphic unit or the entire plot. Following are the kriging summary of TCE in the three units.

USU Results. These vertical dimensions were kept constant for both the Pre-demo and Post-demo calculations. The estimated (two-sided, 80% confidence interval) Pre-demo TCE concentration is 247.1 ±80.3 mg/kg. The estimated (two-sided, 80% confidence interval) Post-demo TCE concentration is 82.6 ±82.2 mg/kg.

MFGU Results. These vertical dimensions were kept constant for both the Pre-demo and Post-demo calculations. The estimated (two-sided, 80% confidence interval) Pre-demo TCE concentration is 2967.8 ±582.0 mg/kg. The estimated (two-sided, 80% confidence interval) Post-demo TCE concentration is 438.5 ±338.9 mg/kg.

LSU Results. These vertical dimensions were kept constant for both the Pre-demo and Post-demo calculations. The estimated (two-sided, 80% confidence interval) Pre-demo TCE concentration is 3,993.2 ±632.2 mg/kg. The estimated (two-sided, 80% confidence interval) Post-demo TCE concentration is 497.0 ±145.9 mg/kg.

Table A.1-3. Kriging Summary Statistics for TCE Concentrations

Stragraphy	Thickness (ft)	Volume (ft^3)	Pre-Demo (mg/kg) Avg . Conc,	Var.	Lower Bound	Upper Bound	Post-Demo (mg/kg) Avg. Conc.	Var.	Lower Bound	Upper Bound
USU	28	96,061.8	247.1	3,922.6	166.8	327.4	82.6	4,115.7	0.35	164.8
MFGU	8	24,196.9	2,967.8	2,06,079.3	2,385.8	3,549.8	438.5	69,865.9	99.6	777.4
LSU	10	47,260.8	3,993.2	24,3201.8	3,360.9	4,625.4	497	12,952.1	351.1	642.9
Total	46	167,519.5	1,696.9	24,946.4	1,494.5	1,899.4	250.9	3,841.9	171.5	330.4

The estimated total TCE mass and reductions (expressed on a percentage basis) are shown in Tables A.1-4 and A.1-5. The total TCE masses are calculated by multiplying the concentration estimates in the three stratigraphic units by the soil bulk density (1.590 g/cm^3) and the mass of dry soil in each stratigraphic unit.

Table A.1-4. Kriging Estimates for Total TCE Mass in the Steam Demonstration

Stratigraphic Unit	Pre-Demonstration TCE *			Post-Demonstration TCE *			TCE Mass Removal *		
	Avg (kg)	Lower Bound (kg)	Upper Bound (kg)	Avg (kg)	Lower Bound (kg)	Upper Bound (kg)	Average	Lower Bound	Upper Bound
USU	1,069	722	1,416	357	2	713	67%	32%	100%
MFGU	3,234	2,600	3,868	478	109	847	85%	73%	97%
LSU	8,349	7,028	9,671	1,099	776	1,422	88%	83%	92%
TOTAL	**12,652**	**11,145**	**14,159**	**1,934**	**1,328**	**2,540**	**85%**	**80%**	**90%**

USU Results. The reduction of TCE in the USU is estimated to be 67 ±35%. To test whether the TCE reduction is significant, an 80% lower confidence bound was calculated on the difference of the pre-demo minus post-demo TCE concentrations. If this lower concentration bound (LCB) is greater than 0 (zero), then the reduction is significant at the 20% significance level. The estimated average TCE concentration reduction is 712 kg (i.e., 67% of the TCE was removed), with an 80% LCB of 89.2 mg/kg, which is significant at the 20% significance level. In fact, this reduction is significant up to about the 3% level of significance.

MFGU Results. The reduction of TCE in the MFGU is estimated to be 85 ±12%. The estimated TCE concentration reduction is 2,529.3 mg/kg (i.e., 85% of the TCE was removed), with an 80% LCB of 2,088.0 mg/kg, which is significant at the 20% significance level. In fact, this reduction is significant up to the 1% level of significance and higher.

LSU Results. The reduction of TCE in the LSU is estimated to be 85±5%. The estimated (two-sided, 80% confidence interval) post-demo TCE concentration is 497.0 (±) 145.9 mg/kg. The estimated TCE concentration reduction is 3496.2 mg/kg (i.e., 88% of the TCE was removed), with an 80% LCB of 3071.1 mg/kg, which is significant at the 20% significance level. In fact, this reduction is significant up to the 1% level of significance and higher.

In summary, the reduction in TCE for the entire plot is estimated to be 85.2% ±5% (i.e., an interval of 80.2-90.2%). The confidence bounds by recognizing that the % reduction is the ratio of two estimated quantities, and using a Taylor Series expansion to estimate the uncertainty in the ratio.

Table A.1-5. Calculations of Total TCE Mass

Pre-demo				Conc	var(conc)	Lower	Upper	Mass	Var(mass)	BEB low	BEB upper
	Depth	Area	Volume	mg/kg		mg/kg	mg/kg	kg		kg	kg
USU	28	3750	96061.8	247.1	3922.6	166.8075	327.3925	37741.62	91510244	25477.89	50005.36
MFGU	8	3750	24196.95	2967.8	206079.3	2385.824	3549.776	114180.6	3.05E+08	91790.16	136571.1
LSU	10	3750	47260.76	3993.2	243201.8	3360.975	4625.425	300067.5	1.37E+09	252559.2	347575.7
TOTAL	46	3750	167519.5	1696.938	24946.41	1494.454	1899.423	451989.7	1.77E+09	398056.7	505922.7

Soil density=1590 kg/m^3

Post-demo				Conc	var(conc)	Lower	Upper	Mass	Var(mass)	BEB low	BEB upper
	Depth	Area	Volume	mg/kg		mg/kg	mg/kg	kg		kg	kg
USU	28	3750	96061.8	82.6	4115.7	0.354929	164.8451	12616.18	96015069	54.21122	25178.15
MFGU	8	3750	24196.95	438.5	69865.9	99.63973	777.3603	16870.48	1.03E+08	3833.454	29907.5
LSU	10	3750	47260.76	497	12952.1	351.0991	642.9009	37346.87	73136781	26383.2	48310.54
TOTAL	46	3750	167519.5	250.918	3841.908	171.4557	330.3804	66833.53	2.73E+08	45668.25	87998.81

Soil density=1590 kg/m^3

Difference				Conc	var(conc)	Lower	Upper	Mass	Var(mass)	BEB low	BEB upper
	Depth	Area	Volume	mg/kg		mg/kg	mg/kg	kg		kg	kg
USU	28	3750	96061.8	164.5	8038.3	49.56028	279.4397	25125.44	1.88E+08	7569.751	42681.14
MFGU	8	3750	24196.95	2529.3	275945.2	1855.859	3202.741	97310.14	4.08E+08	71400.75	123219.5
LSU	10	3750	47260.76	3496.2	256153.9	2847.359	4145.041	262720.6	1.45E+09	213963.7	311477.5
TOTAL	46	3750	167519.5	1446.02	28788.31	1228.502	1663.539	385156.2	2.04E+09	327218.8	443093.5

	% Reduction	Test stat	80% LCB
USU	66.57224	1.834779	89.18848
MFGU	85.22475	4.814918	2088.044
LSU	87.55384	6.907896	3071.062
TOTAL	85.21348	8.522485	1303.496

% Reduction				Remain	Var	LCB	UCB	Reduc	LCB	UCB
	Depth	Area	Volume				mg/kg			
USU	28	3750	96061.8	0.334278	0.074585	-0.015839	0.684394	66.57224	31.56058	101.5839
MFGU	8	3750	24196.95	0.147753	0.008443	0.029955	0.26555	85.22475	73.44497	97.00452
LSU	10	3750	47260.76	0.124462	0.001049	0.082949	0.165974	87.55384	83.4026	91.70508
TOTAL	46	3750	167519.5	0.147865	0.001524	0.097825	0.197906	85.21348	80.20942	90.21755

A.2 Sample Collection and Extraction Methods

This section describes the modification made to the EPA standard methods to address the lithologic heterogeneities and extreme variability of the contaminant distribution expected in the DNAPL source region at Launch Complex 34. Horizontal variability was addressed by collecting a statistically determined number (12) of soil cores in the steam injection plot. The vertical variability at each soil coring location was addressed with this modified sampling and extraction procedure, which involved extraction of much larger quantities of soil in each extracted sample, as well as allowed collection and extraction of around 300 samples in the field per event. This extraction allowed the extraction and analysis of the entire vertical column of soil at a given coring location.

A.2.1 Soil Sample Collection (Modified ASTM D4547-98) (1997c)

A.2.1.1 Predemonstration Sampling Procedure

The soil samples collected before and after the demonstration were sampled using a stainless steel core barrel driven into the subsurface by a Vibra-Push® drilling rig. After the core barrel was driven the required distance, it was brought to the surface and the soil sample was examined and characterized for lithology. One quarter of the sample was sliced from the core and placed into a pre-weighed 500-mL polyethylene container. At locations where a field duplicate sample was collected, a second one-quarter sample was split from the core and placed into another pre-weighed 500-mL polyethylene container. The remaining portion of the core was placed into a 55-gallon drum and disposed of as waste. The samples were labeled with the date, time, and sample identification code, and stored on ice at 4°C until they were brought inside to the on-site laboratory for the extraction procedure.

After receiving the samples from the drilling activities, personnel staffing the field laboratory performed the methanol extraction procedure as outlined in Section A.2.2 of this appendix. The extraction procedure was performed on all of the primary samples collected during drilling activities and on all of the field duplicate samples collected for quality assurance (5% of the primary samples, or approximately one duplicate sample per borehole). Samples were stored at 4°C until extraction procedures were performed. After the extraction procedure was finished, the soil samples were dried in an oven at 105°C and the dry weight of each sample was determined. The samples were then disposed of as waste. The remaining three-quarter section of each core previously stored in a separate 500-mL polyethylene bottle were archived until the off-site laboratory had completed the analysis of the methanol extract. The samples were then disposed of in an appropriate manner.

A.2.1.2 Postdemonstration Soil Sampling Procedure

Modifications were made to the soil sampling procedure during the postdemonstration sampling event in an effort to minimize any VOC loss associated with the elevated soil temperatures. The following procedure was used during postdemonstration soil sampling:

- ☐ Soil samples were collected in a butyrate sleeve located inside the stainless steel core barrel of the Vibra-Push® drilling rig. After the core barrel was driven the required distance, the barrel was brought to the surface and the butyrate sleeve containing the soil was removed from the stainless steel core barrel. The butyrate sleeve was immediately capped on both ends using flexible polymer sheets to minimize VOC losses. The temperature of the soil was monitored by placing a thermometer into one end of the sleeve. The entire sleeve was placed in an ice bath for approximately 30 minutes to cool the soil below 20ºC before collecting samples.

- ❑ After the soil had cooled, the sleeve was removed from the ice bath and opened. Multiple subsamples of soil were scooped from the two-foot section of core designated for sampling into a pre-weighed, 500-mL polyethylene bottle containing approximately 250 mL of reagent-grade methanol. Approximately 125 g of soil were added to the bottle. In contrast to the predemonstration sampling procedure, the soil was added directly to a methanol-filled bottle in the field in an attempt to minimize and capture any VOCs that might have collected in the headspace of the bottle. At depths were a duplicate soil sample was collected, the soil was collected into a second methanol-filled bottle. One duplicate sample was collected per borehole (5%) for quality control. The bottles were stored at 4ºC until the methanol extraction could be performed in the on-site field lab.

- ❑ After the soil samples had been collected, the core was characterized for lithology and then discarded in an appropriate manner. Lithological characterization was performed last because of the need to collect the soil samples as quickly as possible to minimize VOC losses.

- ❑ All field personnel exercised caution while handling and sampling soil cores with elevated temperatures. The drilling crew and Battelle field personnel used special heat-resistant gloves in instances where the cores were too hot to handle with the standard nitrile gloves.

- ❑ After the extraction procedure was finished, the soil samples were dried in an oven at 105°C and the dry weight of each sample was determined. The samples were then disposed of as waste.

A.2.2 Soil Extraction Procedure (Modified EPA SW846-Method 5035)

Extreme care was taken to minimize the disturbance of the soil sample so that loss of volatile components was minimal. Nitrile gloves were worn by field personnel whenever handling sample cores or pre-weighed sample containers. A modification of EPA SW846-Method 5035 was used to procure the cored samples in the field. Method 5035 lists different procedures for processing samples that are expected to contain low concentrations (0.5 to 200 μg/kg) or high concentrations (>200 μg/kg) of volatile organic compounds (VOCs). Procedures for high levels of VOCs were used in the field because those procedures facilitated the processing of large-volume sample cores collected during soil sampling activities.

Two sample collection options and corresponding sample purging procedures are described in Method 5035; however, the procedure chosen for this study was based on collecting approximately 150 to 200 g of wet soil sample in a pre-weighed bottle that contains 250 mL of methanol. A modification of this method was used in the study, as described by the following procedure:

- ❑ After soil samples were brought in from the field, the bottles were reweighed and then stored in a refrigerator at 4ºC until the extraction procedure was performed. Extractions were performed on all soil samples collected. During the postdemonstration sampling event, a surrogate spike of 1,1,1 trichloroethane (1,1,1-TCA) was added to the soil sample collected from 2 ft bgs. The purpose of the surrogate spike was to test the efficiency of the extraction procedure, and the 2-ft depth was chosen because the soil at that depth contained relatively little TCE that would interfere with the TCA analysis. The soil samples spiked with TCA were handled in the same manner as all other samples during the extraction procedure.

- ❑ The bottles containing methanol and soil were placed on an orbital shaker table and agitated for approximately 30 min.

- ❑ Containers were removed from the shaker table and reweighed to ensure that no methanol was lost during the agitation period. The containers were placed upright and suspended soil matter was allowed to settle for approximately 15 min.
- ❑ The 500 mL containers were then placed in a floor-mounted centrifuge. The centrifuge speed was set at 2,800-3,000 rpm and the samples were centrifuged for 10 min.
- ❑ Methanol extract was then pipetted into disposable 20-mL glass volatile organic analysis (VOA) vials using 10-mL disposable borosilicate pipettes. The 20-mL glass VOA vials containing the extract then were capped, labeled, and stored in a refrigerator at 4°C until they were shipped on ice to the off-site analytical laboratory.
- ❑ Methanol samples in VOA vials were placed in coolers and maintained at approximately 4°C with ice. Samples were shipped overnight via air to the subcontracted off-site laboratory with properly completed chain-of-custody forms and custody seals.
- ❑ The dry weight of each of the soil samples was determined gravimetrically after decanting the remaining solvent and drying the soil in an oven at 105°C. Final concentrations of VOCs were calculated per dry weight of soil.

Three potential concerns existed with the modified solvent extraction method. The first concern was that the United States Environmental Protection Agency (U.S. EPA) had not formally evaluated the use of methanol as a preservative for VOCs. However, methanol extraction often is used in site characterization studies, so the uncertainty in using this approach was reasonable. The second concern was that the extraction procedure itself would introduce a significant dilution factor that could raise the method quantitation limit beyond that of a direct purge-and-trap procedure. The third concern was that excess methanol used in the extractions would likely fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste. During characterization activities, the used methanol extract was disposed of as hazardous waste into a 55-gallon drum. The suitability of using the modified soil extraction procedure was confirmed through experiments involving a surrogate compound spiked into soil samples. TCE recoveries in samples ranged from 72 to 86% based on the results of the spiking experiments (Battelle 1999).

The analytical portion of Method 5035 describes a closed-system purge-and-trap process for use on solid media such as soils, sediments, and solid waste. The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards to a vial containing the sample. Then the process purges the VOCs using an inert gas stream while agitating the contents of the vial, and finally traps the released VOCs for subsequent desorption into a gas chromatograph (GC). STL Environmental Services analyzed the solvent extraction samples collected for the predemonstration, April 2001, and August 2001 sampling events. DHL Analytical Laboratory was contracted to analyze all subsequent extraction samples. Soil samples were analyzed for organic constituents according to the parameters summarized in Table A.2-1. Laboratory instruments were calibrated for VOCs according to EPA Method 8260B. Samples were analyzed as soon as was practical and within the designated holding time from collection (14 days). No samples were analyzed outside of the designated 14-day holding time.

Table A.2-1. Soil Sampling and Analytical Parameters

Analytes	Extraction Method	Analytical Method	Sample Holding Time	Matrix
VOCs	SW846-5035	SW846-8260B	14 days	Methanol

A.3 List of Standard Sample Collection and Analytical Methods

Table A.3-1 contains a list of collection methods and equipment used during sampling activities conducted as part of the steam injection technology demonstration. Table A.3-2 contains a list of the sample handling procedures and analytical methods used for determining the parameter of interest. The references to methods may be found in Section A.4 of this appendix.

Table A.3-1. Sample Collection Procedures

Measurements	Task/Sample Collection Method	Equipment Used
Primary Measurements		
CVOCs	Soil sampling/ Mod.$^{(a)}$ ASTM D4547-98 (1997c)	Stainless steel sleeve 500-mL plastic bottle
CVOCs	Groundwater sampling/ Mod.$^{(a)}$ ASTM D4448-01 (1997a)	Peristaltic pump Teflon™ tubing
Secondary Measurements		
TOC	Soil sampling/ Mod.$^{(a)}$ ASTM D4547-98 (1997c)	Stainless steel sleeve
Field parameters$^{(b)}$ TOC BOD Inorganics–cations Inorganics–anions TDS Alkalinity	Groundwater sampling/ Mod.$^{(a)}$ ASTM D4448-01 (1997a)	Peristaltic pump Teflon™ tubing
Hydraulic conductivity	Hydraulic conductivity/ ASTM D4044-96 (1997d)	Winsitu® troll Laptop computer
Groundwater level	Water levels	Water level indicator
CVOCs	Vapor Sampling/Tedlar Bag, TO-14	Vacuum Pump

(a) Modifications to ASTM are detailed in Appendix B.

(b) Field parameters include pH, ORP, temperature, DO, and conductivity. A flowthrough cell will be attached to the peristaltic pump when measuring field parameters.

ASTM = American Society for Testing and Materials.

Table A.3-2. Sample Handling and Analytical Procedures

Measurements	Matrix	Amount Collected	Analytical Method	Maximum Holding Time(a)	Sample Preservation(b)	Sample Container	Sample Type
Primary Measurements							
CVOCs	Soil	250 g	Mod. EPA 8260B(c)	14 days	4°C	Plastic	Grab
CVOCs	Groundwater	40-mL × 3	EPA 8260B	14 days	4°C, pH < 2 HCl	Glass	Grab
Secondary Measurements							
CVOCs	Groundwater	40-mL × 3	EPA 8260B	14 days	4°C, pH < 2 HCl	Glass	Grab
CVOCs	Vapor	1 L	EPA TO-14	14 days	NA	Tedlar™ Bag	Grab
pH	Soil	50 g	Mod. EPA 9040b	7 days	None	Plastic	Grab
pH	Groundwater	50 mL	EPA 150.1	1 hour	None	Plastic	Grab
TOC	Soil	20 g	Based on SW 9060	28 days	None	Plastic	Grab
TOC	Groundwater	125 mL	EPA 415.1	28 days	4°C, pH < 2 H_2SO_4	Plastic	Grab
BOD	Groundwater	1,000 mL	EPA 405.1	48 hours	4°C	Plastic	Grab
Hydraulic conductivity	Aquifer	NA	ASTM D4044-96 (1997d)	NA	NA	NA	NA
Inorganics–cations(d)	Groundwater	100 mL	SW 6020	28 days	4°C, pH<2, HNO_3	Plastic	Grab
Inorganics–anions(d)	Groundwater	50 mL	SW9056	28 days	4°C	Plastic	Grab
TDS	Groundwater	500 mL	EPA 160.1	7 days	4°C	Plastic	Grab
Alkalinity	Groundwater	200 mL	EPA 310.1	14 days	4°C	Plastic	Grab
Water levels	Aquifer	NA	Water level from the top of well casing	NA	NA	NA	NA

(a) Samples will be analyzed as soon as possible after collection. The times listed are the maximum holding times which samples will be held before analysis and still be considered valid. All data obtained beyond the maximum holding times will be flagged.

(b) Samples will be preserved immediately upon sample collection, if required.

(c) Samples will be extracted using methanol on site. For the detailed extraction procedure see Appendix B.

(d) Cations include Ca, Mg, Fe, Mn, Na, and K. Anions include Cl, SO_4, and NO_3/ NO_2.

HCl = Hydrochloric acid.

NA = Not applicable.

A.4 References

American Society for Testing and Materials. 1997a. *Standard Guide for Sampling Groundwater Monitoring Wells*. Designation: D 4448-01.

American Society for Testing and Materials. 1997b. *Standard Guide for the Decontamination of Field Sampling Equipment*. Designation: D 5088-90.

American Society for Testing and Materials. 1997c. *Standard Practice for Waste and Soils for Volatile Organics*. Designation: D 4547-98.

American Society for Testing and Materials. 1997d. *Standard Test Method (Field Procedure) for Instantaneous Change in Head (Slug) Tests for Determining Hydraulic Properties of Aquifers*. Designation: D 4044-96.

ASTM, see American Society for Testing and Materials.

Battelle. 1999. *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.

Deutsch, C.V. and Journel, A.G. 1998. *GSLIB Geostatistical Software Library and User's Guide, second edition*. Oxford University Press, New York.

Journel, A. G., and C. J. Huijbregts. 1981. *Mining Geostatistics (with revisions)*. Academic Press, Inc.