

Rapid Optical ScreenTool (ROST™)

Innovative Technology Evaluation Report

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Notice

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Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems ; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

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Abstract

In August 1994, a demonstration of cone penetrometer-mounted sensor technologies took place to evaluate their effectiveness in sampling and analyzing the physical and chemical characteristics of subsurface soil at hazardous waste sites. The effectiveness of each technology was evaluated by comparing each technology's results to the results obtained using conventional reference method technologies. The demonstration was developed under the Environmental Protection Agency's Superfund Innovative Technology Evaluation Program.

Three technologies were evaluated: the rapid optical screening tool (**ROST™**) developed by Loral Corporation and Dakota Technologies, Inc., the site characterization and analysis penetrometer system (SCAPS) laser induced fluorescence sensor developed by the Tri-Services (Army, Navy, and Air Force), and the conductivity sensor developed by Geoprobe Systems. These technologies were designed to provide rapid sampling and real-time, relatively low cost analysis of the physical and chemical characteristics of subsurface soil to quickly distinguish contaminated areas from noncontaminated areas.

Three sites were selected for the demonstration, each contained varying concentrations of coal tar waste and petroleum fuels, and wide ranges in soil texture.

This demonstration found that the **ROST™** technology produced screening level data. Specifically, the qualitative assessment showed that the stratigraphic and chemical cross sections were comparable to the reference methods. The quantitative assessment showed that during the 1994 demonstration, the **ROST™**'s data could not be used as a reliable predictor of actual contaminant concentration. Based on this study, the **ROST™** appears to be capable of rapidly and reliably mapping the relative magnitude of the vertical and horizontal extent of subsurface contamination when that contamination is fluorescent. This type of contamination includes petroleum fuels and polynuclear aromatic hydrocarbons. The design of the **ROST™**'s fluorescence detection system also allows this technology to identify specific waste types, such as jet petroleum (JP-4), diesel fuel, or coal tar. This chemical mapping capability, when combined with the stratigraphic data produced by the cone penetrometer creates a powerful tool for site characterization.

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List of Abbreviations and Acronyms

ASTM	American Society for Testing and Materials
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylene
CCAL	continuing calibration
cm	centimeter
cm/s	centimeter per second
DQO	data quality objective
DSO	digital storage oscilloscope
DTI	Dakota Technologies, Inc.
EPA	Environmental Protection Agency
ERA	Environmental Resource Associates
ETS	Environmental Technical Services
FID	flame ionization detector
FMGP	Former Manufactured Gas Plant
FVD	fluorescence versus depth
GC	gas chromatograph
HPLC	high performance liquid chromatography
Hz	pulses per second
ICAL	initial calibration
ITER	innovative technology evaluation report
LCS	laboratory control samples
LIF	laser induced fluorescence
MDL	method detection limit
Method OA-1	University of Iowa Hygienics Laboratory Method
$\mu\text{g/kg}$	micrograms per kilogram
$\mu\text{g/L}$	microgram per liter
mg/L	milligram per liter
mg/kg	milligram per kilogram
mg/mL	milligram per milliliter
Mj	millijoules
mL	milliliter
mm	millimeter
MMTP	Measurement and Monitoring Technologies Program
MS	matrix spike
MSD	matrix spike duplicate
NDSU	North Dakota State University
Nd:YAG	neodymium-doped yttrium aluminum garnet
NRML	National Risk Management Research Laboratory
NERL-CRD	National Exposure Research Laboratory-Characterization Research Division
nm	nanometer
ns	nanosecond
%D	percent difference
%RSD	percent relative standard deviation
PAH	polynuclear aromatic hydrocarbon
PE	performance evaluation

List of Abbreviations and Acronyms (Continued)

PID	photoionization detector
PMT	photomultiplier tube
POL	petroleum, oils, and lubricants
ppb	parts per billion
ppm	parts per million
PRC	PRC Environmental Management, Inc.
PRL	PACE reporting limit
PTI	Photon Technology, Inc.
QA	quality assurance
QAPJP	quality assurance project plan
QC	quality control
ROST™	Rapid Optical Screening Tool
RPD	relative percent difference
SCAPS	Site Characterization and Analysis Penetrometer System
SITE	Superfund Innovative Technology Evaluation
TER	technology evaluation record
TOC	total organic carbon
TPH	total petroleum hydrocarbon
TPM	technical project manager
USCS	Unified Soil Classification System
USDA	United States Department of Agriculture
VOC	volatile organic compound
VPH	volatile petroleum hydrocarbon
WTM	wavelength-time matrix

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Section 1 Executive Summary

Recent changes in environmental site characterization have resulted in the application of cone penetrometer technologies to site characterization. With a variety of in situ physical and chemical sensors, this technology is seeing an increased frequency of use in environmental site characterization. Cone penetrometer technologies employ a wide array of sampling tools and produce limited investigation-derived waste.

The Environmental Protection Agency's (EPA) Monitoring and Measurement Technologies Program (MMTP) at the National Exposure Research Laboratory, Las Vegas, Nevada, selected cone penetrometer sensors as a technology class to be evaluated under the Superfund Innovative Technology Evaluation (SITE) Program. In August 1994, a demonstration of cone penetrometer-mounted sensor technologies took place to evaluate how effective they were in analyzing the physical and chemical characteristics of subsurface soil at hazardous waste sites. Prior to this demonstration, two separate predemonstration sampling efforts were conducted to provide the developers with site-specific samples. These samples were intended to provide data for site-specific calibration of the technologies and matrix interferences.

The main objective of this demonstration was to examine technology performance by comparing each technology's results relative to physical and chemical characterization techniques obtained using conventional reference methods. The primary focus of the demonstration was to evaluate the ability of the technologies to detect the relative magnitude of fluorescing subsurface contaminants. This evaluation is described in this report as the qualitative evaluation. A subordinate focus was to evaluate the possible correlations or comparability of the technologies chemical data with reference method data. This evaluation is described in this report as the quantitative evaluation. All of the technologies were designed and marketed to produce only qualitative screening data. The reference methods for evaluating the physical

characterization capabilities were stratigraphic logs created by a geologist from soil samples collected by a drill rig equipped with hollow stem augers, and soil samples analyzed by a geotechnical laboratory. The reference methods for evaluating the chemical characterization capabilities were EPA Method 418.1 and SW-846 Methods 8310 and 8020, and University of Iowa Hygienics Laboratory Method OA-1. In addition, the effect of total organic carbon (TOC) on technology performance was evaluated.

Three technologies were evaluated: the rapid optical screening tool (**ROST™**) developed by Loral Corporation and Dakota Technologies, Inc. (DTI), the site characterization and analysis penetrometer system (SCAPS) developed by the Tri-Services (Army, Navy, and Air Force), and the conductivity sensor developed by **Geoprobe®** Systems. Results of the demonstration are summarized by technology and by data type (chemical or physical) in individual innovative technology evaluation reports (ITER). In addition to the three technology-specific ITERs, a general ITER that examines cone penetrometry, hydraulic probe samplers, and hollow stem auger drilling in greater detail has been prepared.

The purpose of this ITER is to chronicle the development of the **ROST™**, its capabilities, associated equipment, and accessories. The report concludes with an evaluation of how closely the results obtained using the technology compare to the results obtained using the reference methods.

The **ROST™** evolved from U.S. Government Department of Defense funded research performed at North Dakota State University (NDSU). The funding was sponsored by the U.S. Department of Defense Tri-Services SCAPS committee. The technology is being commercialized and marketed by a consortium of government and industry led by the Loral Corporation. Loral Corporation owns the marketing rights to **ROST™** with development assistance provided by DTI, Tri-

Services, and the U.S. Advanced Research Projects Agency. The technology was generally designed to provide rapid sampling and real-time, relatively low cost screening level analysis of the physical and chemical characteristics (primarily petroleum fuels and coal tars) of subsurface soil to quickly distinguish contaminated areas from noncontaminated areas. The **ROST™** measures fluorescence and is attached to a standard cone penetrometer tool, which provides a continuous reading of subsurface physical characteristics. This is translated by software into various soil classifications. This capability will allow investigation and remediation decisions to be made more efficiently on site and will reduce the number of samples that need to be submitted for costly confirmatory analyses.

One hazardous waste site each was selected in Iowa, Nebraska, and Kansas to demonstrate the technologies. The sites were selected because of their varying concentrations of coal tar waste and petroleum fuels, and because of their ranges in soil textures.

This demonstration found that the **ROST™** produces screening level data. Specifically, the qualitative assessment showed that the stratigraphic and the chemical cross sections were comparable to the reference methods. The **ROST™** showed advantages relative to the reference methods in that the technology does not require the collection of samples for analysis because analysis occurs in situ. This capability helps the technology avoid the problems with sample recovery encountered with the reference methods during this demonstration. The relatively continuous data output from the **ROST™** eliminated the data interpolation required for the reference methods, and it provided greater resolution. The **ROST™** can also be used to identify changes in waste type during a site characterization. Through the use of a wavelength-time-matrix (WTM), the **ROST™** can identify classes of contaminants, such as gasoline, diesel, jet petroleum (JP-4), and coal tar. The qualitative assessment showed that relative to the degree of contamination; for example, low, medium, and high, the technology's data and the reference data were well correlated. Changes in TOC concentration did not appear to affect the technology's performance.

The in situ nature of the **ROST™** minimized the altering of soil samples, a possibility inherent with conventional sampling, transport, and analysis. Furthermore, the cone penetrometer rods are steam cleaned directly upon removal from the ground, reducing potential contamination hazards to field personnel. In addition, the continuous data output for both the chemical and physical properties of soil produced by the

ROST™ appears to be a valuable tool for qualitative site characterization.

The quantitative assessment found that the **ROST™** data exhibited little correlation to any of the reference data concentrations of the target analytes. The lack of correlation for the quantitative evaluation cannot be solely attributed to the technology. Rather, it is likely due to the combined effect of matrix heterogeneity, lack of technology calibration, uncertainties regarding the exact contaminants being measured, and the age and constituents in the waste. Based on the data from this demonstration, it is not possible to conclude that the technology can or cannot be quantitative in its current configuration. Based on the effects listed above, a high degree of correlation should not be expected in comparisons with conventional technologies.

Verification of this technology's performance should be done only on a qualitative level. Even though it cannot quantify levels of contamination or identify individual compounds, it can produce qualitative contaminant distribution data very similar to corresponding data produced by conventional reference methods, such as drilling and laboratory sample analysis. The general magnitude of the technology's data is directly correlated to the general magnitude of contamination detected by the reference methods. The performance of the **ROST™** during this demonstration showed that it could generate site characterization data faster than the reference methods and with little to no waste generation relative to the reference methods. The cost associated with using this technology to produce the qualitative data used in this demonstration was approximately \$41,000 which included the cone penetrometer truck and cone penetrometer sensor, and the **ROST™**. Due to the increased quality control and visitor distractions, it is likely that the actual "production mode" cost of the **ROST™** operation would be less than that exhibited during this demonstration. This can be compared to the approximate \$55,000 used to produce the reference method cross sections, which were not available until 30 days after the demonstration. The **ROST™** cost less than the reference methods, it produced almost 1,200 more data points (continuously), and provided data in a real-time fashion.

The question that this demonstration can not answer is whether or not it is better to have fewer data points at the highest data quality level or more data points at a lower data quality level. Issues such as matrix heterogeneity may greatly reduce the need for definitive level data in an initial site characterization. Sampling and analysis must always be done to effectively use the **ROST™** and critical samples will always require definitive analysis.

Section 2 Introduction

The purpose of this ITER is to present information on the demonstration of the **ROST™**, a technology designed to analyze the chemical characteristics of subsurface soil. Since the **ROST™** must currently be used in conjunction with a cone penetrometer truck, the geological data collection abilities of the cone penetrometer truck also were evaluated during this demonstration.

This technology was demonstrated in conjunction with two other sensor technologies: (1) the SCAPS sensor designed by the Tri-Services (the U.S. Army, the U.S. Air Force, and the U.S. Navy), and (2) the conductivity sensor developed by **Geoprobe®** Systems. The results of the demonstration of the other two technologies are presented in individual ITERs similar to this document. An additional general ITER was prepared which discusses the history, sampling, and other capabilities of cone penetrometry, hydraulic probe samplers, and hollow stem auger drilling. Complete details of the demonstration, descriptions of the sites, and the experimental design are provided in the final demonstration plan for geoprobe- and cone penetrometer-mounted sensors (PRC 1994). This information is briefly summarized for this document.

This section summarizes general information about the demonstration, such as the purpose, objectives, and design. Section 3 presents and discusses the validity of the data produced by the reference methods in the evaluation of the **ROST™** technology. Section 4 discusses the **ROST™** technology, its capabilities, equipment and accessories, and costs. Section 5 evaluates how closely the results obtained using the **ROST™** compare to the results obtained using the reference methods. Section 6 discusses the potential applications of the technology. Section 7 presents the developer's comments on this ITER as well as an update on the current application of the technology. Section 8 provides complete references for the documents cited in this report.

Demonstration Background, Purpose, and Objectives

The demonstration was developed under the MMTP. The MMTP is a component of the EPA's SITE Program. The goal of the MMTP is to identify and demonstrate new, viable technologies that can identify, quantify, or monitor changes in contaminants at hazardous waste sites or that can be used to characterize a site less expensively, better, faster, and/or safer than reference methods.

The **ROST™** uses laser induced fluorescence (LIF) to detect the presence and absence of fluorescing compounds, such as petroleum fuels and coal tar wastes. The technology is incorporated into a standard CP sensor and advanced into the soil with a standard cone penetrometer truck.

The **ROST™** was designed to provide rapid sampling and real-time, relatively low cost screening level analysis of the physical and chemical characteristics of subsurface soil. The **ROST™** was designed to analyze the chemical characteristics of the subsurface soil by quickly identifying the presence or absence of contamination, and possibly, approximate concentrations. Since the **ROST™** can be deployed with a CP sensor, it also is possible to obtain physical properties of subsurface soils as the **ROST™** sensor is advanced. These capabilities allow investigation and remediation decisions to be made more efficiently and quickly, reducing overall project costs such as the number of samples that need to be submitted for confirmatory analyses and the need for multiple mobilizations.

The primary focus of the demonstration was to evaluate the ability of the technologies to detect the relative magnitude of fluorescing subsurface contaminants, and in some cases their ability to measure subsurface stratigraphy. This evaluation is described in this

report as the qualitative evaluation. A secondary focus was to evaluate the possible correlations or comparability of the technologies chemical data with reference method data. This evaluation is described in this report as the quantitative evaluation. All of the technologies were designed and marketed to produce qualitative screening data.

There were three objectives for the qualitative evaluations, and one objective for the quantitative evaluations conducted during this demonstration. The first qualitative objective evaluated for the **ROST™** was its ability to vertically delineate subsurface soil contamination and physical properties of the soil. Cross sections of subsurface contaminant plumes and soil stratigraphy produced by **ROST™** were visually compared to corresponding cross sections produced by the reference methods. The second qualitative objective evaluated the ability of the **ROST™** to characterize physical properties of subsurface soils. The third qualitative objective was to evaluate reliability, ruggedness, cost, and range of application of the **ROST™**. The **ROST™** was quantitatively evaluated on how its data compared to the reference methods, and an attempt was made to identify its threshold detection limits.

Demonstration Design

The experimental design of this demonstration was created to meet the specific quantitative and qualitative objectives described above. The experimental design was approved by all demonstration participants prior to the start of the demonstration. This experimental design is detailed in the final demonstration plan (PRC 1994).

Sample results from the **ROST™** were compared to results from the reference methods. The reference methods are commonly used means of obtaining the same data as that produced by an innovative technology. For this demonstration, the reference methods included standard SW-846 methods for measuring petroleum hydrocarbons and polynuclear aromatic hydrocarbons (PAH), and borehole logging and sampling by a geologist using continuous samples from hollow stem auger drilling. These comparisons were used to determine the quality of data produced by the technology. Two data quality levels were considered during this evaluation: definitive and screening data. These data quality levels are described in the EPA's "Data Quality Objectives Process for Superfund - Interim Final Guidance" (1993).

Definitive data are generated using rigorous analytical methods, such as approved EPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce tangible raw data (e.g., chromatograms, spectra, digital values)

in the form of paper printouts or computer-generated electronic files. Data may be generated at the site or at an off-site location, as long as the quality assurance/quality control (QA/QC) requirements are satisfied. For the data to be definitive, either analytical or total measurement error must be determined.

Screening data are generated by rapid, less precise methods of analysis with less rigorous sample preparation. Sample preparation steps may be restricted to simple procedures, such as dilution with a solvent, instead of elaborate extraction/digestion and cleanup. Screening data provide analyte identification and quantification, although the quantification may be relatively imprecise. At least 10 percent of the screening data are confirmed using analytical methods and QA/QC procedures and criteria associated with definitive data. Screening data without associated confirmation data are not considered to be of known quality.

Since this technology is new and innovative, approved EPA methods for in situ LIF analysis do not exist. For the purpose of this demonstration, the lack of approved EPA methods did not preclude **ROST™** from being considered a definitive level technology. The evaluation of this technology as to its quantitative capabilities was included to provide potential users a complete picture of the technology's capabilities in its present configuration during the demonstration. In the configuration demonstrated, the developer never claimed the technology was quantitative. Recent developer advances in data interpretation may increase the likelihood that the technology can be quantitative. The main criteria for data quality level assignment was based on the comparability of the technology's data to data produced by the reference methods. Table 2-1 defines the statistical parameters used to define the data quality levels produced by **ROST™**.

The sampling and analysis methods used to collect the baseline data for this demonstration are currently accepted by EPA as providing legally defensible data. This data is defined as definitive level data by Superfund guidance. Therefore, for the purpose of this demonstration, these technologies and analytical methods were considered reference methods.

Qualitative Evaluation

Qualitative evaluations were made through observations and by comparing stratigraphic and chemical cross sections from the technology to cross sections produced from the reference methods. The reference methods for the stratigraphic cross sections were continuous sampling with a hollow stem auger advanced by a drill rig and

TABLE 2-1. CRITERIA FOR DATA QUALITY CHARACTERIZATION

Data Quality Level	Statistical Parameter
Definitive	$r^2 = 0.80$ to 1.0 , and the slope ^a and y-intercept are statistically similar to 1.0 and 0.0 , respectively, the precision is less than or equal to 20 percent and inferential statistics indicate the two data sets are statistically similar.
Screening	$r^2 = 0.80$ to 1.0 , the precision RSD is greater than 20 percent, and the technology meets its developers performance specifications, normal deviate test statistics on the two regression parameters indicate the two data sets are statistically not similar; or in the case where the regression analysis indicates the data is of definitive quality, but the inferential statistics indicate the data sets are statistically different.

Notes:

r^2 Coefficient of determination.

RSD Relative standard deviation.

^a Since the **ROST™** did not produce data in equivalent units to the reference methods, the slope cannot be used to assess accuracy, however, comparability can still be evaluated.

borehole logs created by a geologist. In addition, the technology’s ability to determine subsurface soil texture at discrete intervals was further compared to data produced by an off-site geotechnical laboratory. The reference methods for the chemical cross sections were subsurface sampling using a drill rig and off-site sample analysis by EPA Method 418.1 and SW-846 Method 8310. EPA Method 418.1 produces data on total petroleum hydrocarbon (TPH) concentrations. EPA Method 8310 produces data on PAH concentrations. These reference methods were selected for the qualitative evaluations based on recommendations made by the developer, consideration of the types of fluorescing target analytes, and the project objectives. In addition, soil samples were analyzed for (TOC) using the 90-3 Walkley-Black Method; and soil texture analysis was performed by American Society of Testing Materials (ASTM) Method D-422.

To qualitatively assess the ability of the **ROST™** to identify the presence or absence of contamination and produce contaminant distribution cross sections, the technology was required to continuously sample at five points located along a transect line at each of the demonstration sites (Figure 2-1). These points were called sample nodes. The transect line was placed across an area of known subsurface contamination identified during predemonstration sampling activities and previous investigative sampling at these sites. A 6-foot by 6-foot area was marked around each sample node. This area was subdivided into nine sections of equal size, identified as Sections A through I. At least one sample node per site was placed outside the area of contamination.

Once each 6-foot by 6-foot area was marked, sampling points for each technology and the reference methods were assigned randomly at each node. This

produced a stratified random sampling design. This design does not result in a predictable or fixed sampling pattern for the technologies or the reference methods. Sections for sampling at each node were only used once.

The stratified random sampling design was used since the distribution of target analyte information was believed to be heterogeneous throughout a given sampling interval, and since the information’s distribution was not controlled by the demonstration.

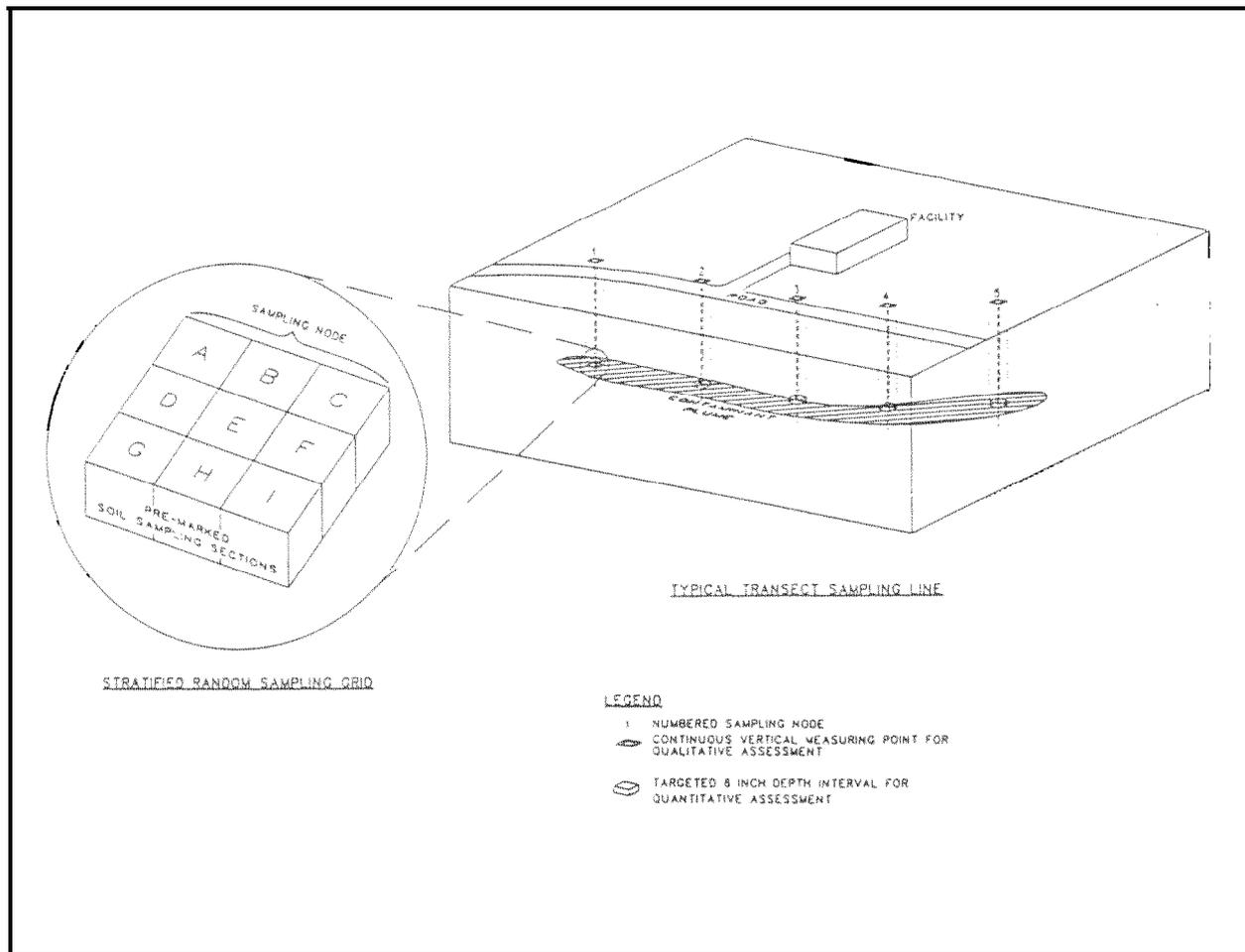
The potential effect of organic matter was evaluated qualitatively by TOC analysis of soil samples. This geotechnical evaluation was intended to examine potential interferences from TOC on fluorescence response.

The chemical and geotechnical data generated by the **ROST™** in conjunction with its CP advancement platform was used to produce qualitative data regarding contaminant and stratigraphic cross sections along each transect line. These cross sections were compared to cross sections generated by the reference methods results from soil samples collected with a drill rig. The comparison of contaminant cross sections involved visual comparisons with overlays, and minimum and maximum depths of contamination at each location along a transect line.

Other factors that underwent qualitative evaluation were technology costs, ease of operation, ruggedness, instrument reliability, environmental sampling capability, and production rates. PRC assigned an observer to work with the developer to become knowledgeable in the use and application of the **ROST™**. With this training, PRC was able to assess these operational factors.

During the demonstration, a total of 78 soil samples were collected and analyzed by the reference methods,

FIGURE 2-1. TYPICAL TRANSECT SAMPLING LINE AND STRATIFIED RANDOM SAMPLING GRID



and used in the qualitative data evaluations. These samples were distributed as follows: 28 from the Atlantic site, 26 from the York site, and 24 from the Fort Riley site. Only sample data reported as positive values were used in the evaluation. Sample data reported as “not detected” was not used.

Quantitative Evaluation

The **ROST™** was evaluated quantitatively on its ability to chemically characterize subsurface soil contamination relative to classes of contaminants and specific contaminants. This evaluation consisted of comparing data generated using the technology to data obtained using reference analytical methods over a wide range of concentrations. The reference method for the chemical cross sections sampling was hollow stem drilling. The University of Iowa Hygienics Laboratory Method OA-1 volatile petroleum hydrocarbon (VPH), SW-846 Method 8310 (PAH), SW-846 Method 8020 benzene, toluene, ethylbenzene, and xylene (BTEX), and EPA Method 418.1 (TPH) were used as the reference analytical methods. This allowed technology evaluation

relative to VPH, TPH, PAH, and BTEX concentrations. This demonstration attempted to determine if the results from the **ROST™** could be correlated to results from the reference methods, and if the technology was able to differentiate between different types of contamination, such as PAHs and BTEX. In addition, PRC attempted to determine the detection thresholds of the technology for these classes of contaminants.

To quantitatively assess the comparability of the data produced by the **ROST™** technology to the reference methods' data, the final demonstration plan (PRC 1994) required each technology to conduct its most accurate and precise measurements at discrete depths at each sampling node. These depths represented zones of initial contaminant detection, medium, and high fluorescence. However, at the start of the demonstration, the developers of both **ROST™** and SCAPS technologies informed PRC that the data produced during their standard dynamic push modes was the most accurate data they could produce. Therefore, the technologies' data for qualitative evaluation was the same as that used in the quantitative evaluations.

The locations for the reference method sampling for the quantitative evaluation were selected after reviewing both the **ROST™** and SCAPS data for a site. Sample intervals that showed similar data from both technologies were selected as reference method sampling intervals. Reference method sampling intervals represented zones of initial contaminant detection, medium, and high fluorescence. The data produced at these intervals was used to quantify contamination, identify contaminants, establish a technology's precision and resolution, and establish a technology's contamination detection thresholds.

For the quantitative evaluation, data produced by the **ROST™** was averaged over a 12-inch push interval corresponding to intervals sampled for reference method analysis. This data was used to determine a mean fluorescence over that interval. This data was compared to corresponding mean reference method concentrations for any given interval. To create these mean reference method concentrations, PRC collected five replicate samples from the 12-inch intervals identified as reference method sampling intervals based on the **ROST™** and SCAPS data. Each replicate sample was collected from a randomly assigned section at each sample node. The mean fluorescence for the **ROST™** was compared to the mean constituent concentration for the same interval, as generated by the reference method analysis and the replicate sampling.

The data developed by the **ROST™** was compared to reference method data for the following compounds or classes of compounds: TPH, total BTEX, VPH, total PAH, total naphthalene (naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene) and individual compounds (BTEX, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, fluoranthene, pyrene, benzoapyrene, and anthracene). These comparisons were described in the August 1994 final demonstration plan.

Method precision also was examined during the demonstration. The **ROST™** was required to produce 10 separate readings or measurements at given depths without moving the sensor between readings. From these 10 measurements at each discrete depth, precision control limits were established. This data also allowed an examination of technology resolution and precision.

For the quantitative evaluation, a total of 103 soil samples were collected and analyzed by the reference methods. The distribution of these samples was as follows: 8 replicate sampling intervals producing 38 samples at the Atlantic site, 7 replicate sampling intervals producing 35 samples at the York site, and

30 samples from 6 replicate sampling intervals at the Fort Riley site. Only sample data reported as positive values were used in the evaluation. Sample data reported as "not detected" was not used.

Deviations from the Approved Demonstration Plan

The primary deviation from the demonstration plan (PRC 1994) dealt with the statistical analysis for the quantitative evaluation.

Since the technology did not produce data directly representing the concentration of contaminants, or data in the same units as the reference method analysis, the **Wilcoxon Rank Sum Test** could not be used, and the comparison of the technology's data to 99 percent confidence intervals was not made. In addition, the effect of soil moisture was not examined due to the fact that the bulk of the contaminated zones at each site were at or near saturation. Finally, the demonstration plan identified a hydraulic probe sampler as the reference method for collecting the soil samples used in the quantitative evaluations. However, due to sample matrix effects (running sands), the hydraulic probe samples could not meet the soil sampling objectives regarding sample volume. The inability of this method to produce full sample recovery was caused by the saturated fine sands encountered at many of the target sampling depths. To allow for adequate sample volume, PRC changed the reference method for this soil sampling to hollow stem augering and split spoon sampling.

Site Descriptions

The demonstration took place at three sites within EPA Region 7. The three sites are the (1) Atlantic-Poplar Street Former Manufactured Gas Plant (FMGP) site (Atlantic site), (2) York FMGP site (York site), and (3) the Fort Riley Building 1245 site (Fort Riley site). Brief summaries for each site are given below. Complete details are located in the August 1994 final demonstration plan.

The Atlantic site is located in Atlantic, Iowa. The site is surrounded by gas stations, grain elevators, a seed supply company, and a railroad right-of-way. All structures associated with the FMGP have been demolished. A gas station now operates on the location of the FMGP.

The Atlantic Coal Gas Company operated the FMGP from 1905 to 1925. During that time, an unknown quantity of coal tar was disposed of on site. In

addition to the coal tar waste, more recent releases of petroleum from two nearby gas stations also have occurred. An investigation conducted at the site from 1990 to 1992 identified the following primary contaminants: BTEX and PAHs. The local groundwater contains free petroleum product and pure coal tar.

The York site is located in York, Nebraska. The site encompasses nearly a half acre in an industrial section of the city. The site is bordered by a former railroad right-of-way, a concrete company, a seed company, and a farm supply store. The site is nearly level, and one building occupied by the FMGP is still present. The York Gas and Electric company operated

the FMGP from 1899 to 1930. Coal tar waste was disposed of at the site. Current information on the site suggests that coal tar waste and its constituents should be the only waste encountered.

The Fort Riley site is located at Building 1245 on the east side of the Camp Funston area at Fort Riley, Kansas. Between 1942 and 1990, five 12,000-gallon steel underground storage tanks were located at this site. The tanks were used to store leaded and unleaded gasoline, diesel fuel, and military operations' gasoline. Soil at the site is contaminated with gasoline and diesel believed to be the result of past petroleum fuel releases from the underground storage tanks.

Section 3 Reference Method Results

All soil samples collected during this demonstration were submitted to PACE, Inc. (PACE), for chemical and geotechnical analysis. The PACE laboratory in Lenexa, Kansas, performed the methods 418.1, 8020, and OA-1 analyses, while the PACE laboratory in St. Paul, Minnesota, performed the Method 8310 analyses. PACE subsequently subcontracted the geotechnical analyses to Environmental Technical Services (ETS), Petaluma, California. The chemical data supplied by the reference laboratory, the geotechnical data supplied by the geotechnical laboratory, and the data produced by the on-site professional geologist are discussed in this section.

Reference Laboratory Procedures

Samples collected during this demonstration were homogenized and split for the following analyses:

- * TPH by EPA Method 418.1 (EPA 1986)
- * PAH by EPA SW-846 Method 8310 (EPA 1986)
- * BTEX by EPA SW-846 Method 8020 (EPA 1986)
- * Total VPH as gasoline by University of Iowa Hygienic Laboratory Method OA-1 (University Hygienic Laboratory 1991)
- * Soil texture and TOC by the 90-3 Walkley-Black Method (Page 1982)

The results of these analyses are summarized in Appendix A, Tables A-1 and A-9. The results are reported as wet-weight values as required in the demonstration plan (PRC 1994). The data is grouped by analytical method, site, and whether the data is intended for qualitative or quantitative data evaluation. The chemical cross sections produced by the qualitative data are presented and discussed later in this section.

The data from the PACE laboratory was internally reviewed by PACE personnel before the data was delivered to PRC. PRC personnel conducted a data review on the results provided by PACE following EPA guidelines (1991). PRC reviewed the raw data and checked the calculated sample values.

The following sections discuss specific procedures used to identify and quantitate TPHs, VPHs, PAHs, BTEX, and TOC. Most of these procedures involved requirements that were mandatory to guarantee the quality of the data generated.

In addition to being generally discussed in this section, all of the reference method results used to assess the **ROST™** are presented in Appendix A, Tables A-1 through A-9.

Sample Holding Times

The required holding times from the date of sample receipt for each analytical method used to analyze the soil samples were as follows: University of Iowa Hygienics Laboratory Method OA-1 (Method OA-1), 14 days for extraction and analysis; EPA SW-846 Method 8020 (BTEX), 14 days for extraction and analysis; EPA Method 418.1 (TPH), 14 days for extraction and 40 days for analysis; EPA SW-846 Method 8310 (PAH), 14 days for extraction and 40 days for analysis; and 90-3 Walkley-Black Method (TOC), 28 days for extraction and analysis.

All holding times for the samples were met during this demonstration.

Sample Preparation

Preparation of soils for TPH analysis was performed following EPA Method 418.1. This method uses a Soxhlet extraction as stated in SW-846 Method 9071. The soil sample extracts were analyzed for TPH using SW-846 Method 418.1.

Extracts for VPH analysis were prepared following Method OA-1. The BTEX sample preparation requirements were carried out as specified in that method.

The preparation of soil samples for TOC analysis were carried out as specified in the 90-3 Walkley-Black Method.

Sonication extraction, Method SW-846 3550, was used for the preparation of soil samples for SW-846 Method 8310 analysis. The preparation of samples for PAH analysis by SW-846 Method 8310 were carried out according to the method requirements.

Initial and Continuing Calibrations

Initial calibrations (ICAL) were performed before sample analysis began. ICALs for SW-846 Methods 8020, 8310, and 418.1 consisted of the analysis of five concentrations of standards. Method OA-1 required the analysis of three concentrations of standards for the ICAL. Linearity for these ICALs was evaluated by calculating the percent relative standard deviation (%RSD) of the calibration factors. The %RSD QC limit for SW-846 Methods 8020 and 8310 and Method OA-1 was 20 percent. The calibration factors were calculated by dividing the response (measured as the area under the peak or peak height) by the amount of compound injected on the gas chromatograph (GC) column. The 90-3 Walkley-Black Method for TOC required a daily calibration to a reference sulfate solution. This ICAL was performed in duplicate. All initial calibrations met the respective method requirements.

Continuing calibrations (CCAL) were performed on a daily basis to check the response of the detector by analyzing a mid-concentration standard and comparing the calibration factor to that of the mean calibration factor from the ICAL.

Calibration factors were monitored in accordance with the SW-846 and OA-1 Methods. No CCAL was performed for the 90-3 Walkley-Black Method. Six CCALs exceeded the 15 percent difference (%D) criteria for various BTEX compounds. This resulted in sample results being qualified as estimated (J) and usable for limited purposes. Various PAH compounds in six SW-846 Method 8310 CCALs exceeded 15 %D for one of the two detectors. Sample results for the compounds exceeding 15 %D were qualified as estimated (J) and usable for limited purposes. SW-846 Method 8310 uses two detectors, an ultraviolet detector and a fluorescence detector. Since one detector's CCAL response was within QC guidelines, this data is considered useable.

Retention times of the single analytes were monitored through the amount of retention time shift from the CCAL standard as compared to the ICAL standard. The retention time windows for SW-846 Method 8310 were set by taking three times the standard deviation of the retention times that were calculated from the ICAL and CCAL standards. The retention time windows for SW-846 Method 8020 were set by PACE at plus or minus 0.07 minutes for benzene, ethylbenzene, m-xylene, and plus or minus 0.10 minutes for toluene. No CCAL retention times for the individual PAH analytes were outside the retention time windows. CCAL retention times for the individual BTEX analytes were observed outside the retention time windows as set by the ICAL. No samples were qualified based on this QC criteria because the retention time shifts were adjusted appropriately by PACE for sample identification and quantitation.

Following the ICAL, a method blank was analyzed to verify that the instrument met the method requirements. Following this, sample analysis may continue for 24 hours. As stated in SW-846 Method 8000, a CCAL must be analyzed and the calibration factor verified on each working day. Sample analysis may continue as long as CCAL standards meet the method requirements.

Sample Analysis

Specific PAH and BTEX compounds were identified in a sample by matching retention times of peaks found after analyzing the sample with those compounds found in PAH and BTEX standards. VPH was identified in a sample by matching peak patterns found after analyzing the sample with those compounds found in VPH standards. Peak patterns may not always match exactly because of the way the VPHs were manufactured or because of the effects of weathering. When peak patterns do not match, the analyst must decide the validity of the identification of VPHs. For this reason, peak pattern identification is highly dependent on the experience and interpretation of the analyst.

Quantitation of PAHs, BTEX compounds, TPHs, and VPHs was performed by measuring the response of the peaks in the sample to those same peaks identified in the ICAL standard. The reported results of this calculation were based on wet weights (except for PAHs), as required by PRC. PAH data was reported on a dry-weight basis. PRC converted this data to wet-weight based results dividing the dry-weight result by the percent moisture of the original wet sample. Quantitation of TOC was performed by measuring the volume of potassium dichloride ($K_2Cr_2O_7$) titrated and calculating the milliequivalents of $K_2Cr_2O_7$ titrated.

This value was then multiplied by conversion factors defined in the method and subsequently divided by the grams of sample. TOC results were reported on a wet-weight basis.

Sample extracts can frequently exceed the calibration range determined during the ICAL. When this occurred, the extracts were diluted to obtain peaks that fall within the linear range of the detector. For BTEX compounds and VPHs, this linear range was defined as the highest standard concentration response of the analytes of interest analyzed during the ICAL. The linear range for TPHs was defined as an absorbance maximum of 0.8. For PAHs, as defined in SW-846 Method 8310, the linear range was from 8 times the method detection limit (MDL) to 800 times the MDL with the following exception: benzo(ghi)perylene recovery at 80 times and 800 times the MDL are low. Once a sample was diluted to within the linear range, it was analyzed again. Dilutions were performed when appropriate on the samples for this demonstration.

Detection Limits

The PACE reporting limit (PRL) for PAHs was calculated by multiplying the calibration correction factor based on dry weight, times the MDL for each specific PAH. PRLs for BTEX compounds were determined by the lowest concentration standard of the ICAL. The BTEX ICAL concentration range was from 10 micrograms per liter (ug/L) to 100 $\mu\text{g/L}$. The PBL for benzene, toluene, and ethyl benzene was 50 micrograms per kilogram ($\mu\text{g/kg}$) and 100 $\mu\text{g/kg}$ for total xylene. The three levels of standard concentrations for the VPH ICAL ranged from 2 milligrams per milliliter (mg/mL) to 8 mg/mL. The PRL for VPH was 5 milligrams per kilograms (mg/kg). For TPH, the calibration range was calculated by calibrating the infrared detector using a series of working standards. A plot was then prepared of absorbance versus milligram petroleum hydrocarbons per 100 milliliter (mL) solution. The PRL for TPH was 10 mg/kg. The MDL for TOC analysis was 10 mg/kg wet weight.

Quality Control Procedures

A number of QC measures were used by PACE as required by SW-846 Methods 8310 and 8020, EPA Method 418.1, Method OA-1, and the 90-3 Walkley-Black Method. These QC measures included the analyses of method blanks, instrument blanks, laboratory control samples (LCS), matrix spike (MS) and matrix spike duplicates (MSD), and the use of sample surrogate recoveries.

All method and instrument blanks met the appropriate QC criteria, except for two method blanks analyzed by Method 418.1. TPH was reported as slightly above the PRL of 10 mg/kg in two method blanks. Due to the low values reported in the two method blanks, the sample results were not qualified.

Surrogate standards were added to all samples, method blanks, MSs, and LCSs for the SW-846 Methods 8310 and 8020, and Method OA-1. All surrogate recoveries for SW-846 Method 8020 were within the QC acceptance criteria of 42 to 140 percent for soil. Seven samples were qualified as estimated (J) and usable for limited purposes based on surrogate recoveries for the Method OA-1. The QC acceptance criteria for surrogate recovery for Method OA-1 was 67 to 127 percent. Thirty soil samples for SW-846 Method 8310 analysis were qualified as estimated (J) and usable for limited purposes based on surrogate recoveries observed outside the QC limits of 58 to 140 percent. Two surrogates were used for Method 8310. Samples were qualified only when both surrogates were outside the QC limits and no dilution analysis was performed. Numerous soil samples required dilution for the Method 8310 analysis because of petroleum interference. Dilution of these samples resulted in corresponding reductions in surrogate concentrations. When this occurred, the resultant concentration of surrogate was below its MDL. In cases where dilution resulted in failure to detect the surrogate, no coding of the data was implemented.

MS samples are samples to which a known amount of the target analytes are added. There were 10 MSs performed during the analysis by Method 418.1. Eight of the MS samples were affected by high concentrations of target analytes in the spiked samples. No samples were qualified. Eleven MSs were performed during the analysis of samples by Method 8310. All but three MSs and MSDs were outside the QC limits for percent recovery and relative percent difference (RPD). These QC exceedences were due to petroleum matrix interference. The data associated with the QC samples was not qualified because EPA guidelines state that samples cannot be qualified based on MS and MSD results alone (1991). There were seven MS and MSD samples analyzed by Method 8020 and five by Method OA-1. The MSs and MSDs analyzed by Method 8020 did not meet QC acceptance criteria for percent recoveries or RPDs. No samples were qualified based on these MS and MSD results due to the reasons stated above. All MS and MSDs analyzed by Method OA-1 and 90-3 Walkley-Black Method met all QC acceptance criteria and were considered acceptable.

All LCSs met QC acceptance criteria and were considered acceptable for all soil samples analyzed by SW-846 Method 8310, Method OA-1, 90-3 Walkley-Black Method, and Method 418.1. One soil LCS analyzed by Method 8020 was outside the QC control limits. The soil LCS percent recovery for toluene was below the QC limit. Twenty soil samples were qualified as estimated (J) and usable for limited purposes.

Also, three equipment rinsate blanks and one trip blank were analyzed to assess the efficiency of field decontamination and shipping methods, respectively. There was no contamination found above PRLs in any of these blanks, indicating decontamination procedures were adequate.

Confirmation of Analytical Results

Confirmation of positive results was not required by any of the analytical methods performed except SW-846 Method 8310. Confirmation of positive PAH results by Method 8310 was performed by the use of two types of detectors. Both an ultraviolet detector and a fluorescence detector were used in the analysis of PAHs. The only requirement for using either detector for quantitation was that they meet the QC criteria for linearity (ICAL) and %D (CCAL). If either detector failed either of these criteria, it could not be used for quantitation, but it could be used for confirmation of positive results.

Data Reporting

The results reported and qualified by the reference method contained two types of qualifier codes. Some data was coded with a "J," which is defined by PACE as detected but below the PRL; therefore, the result is an estimated concentration. The second code, "MI," was defined as matrix interference. Generally, the effect of a matrix interference is to reduce or enhance sample extraction efficiency.

Quality Assessment of Reference Laboratory Data

This section discusses the accuracy, precision, and completeness of the reference method data.

Accuracy

Accuracy of the reference methods were independently assessed through the use of performance evaluation (PE) samples purchased from Environmental Resource Associates (ERA) located in Arvada, Colorado, containing a known quantity of TPH. In addition, LCSs and past PE audits of the reference

laboratory were used to verify analytical accuracy. Based on a review of this data, the accuracy of the reference methods were considered acceptable.

Precision

Precision for the reference method results was determined by evaluating field duplicates, laboratory duplicate, and MS and MSD sample results. Precision was evaluated by determining the RPDs for sample results and their respective duplicate sample results.

The MS and MSD RPD results for the PAH compounds averaged 25 percent for all of the 11 MS and MSD sample pairs. However, there was one MS and MSD sample pair that had a RPD of 99.9 for 1-methyl-naphthalene. If this point was removed, the overall average would decrease to 20 percent. The average RPD for the seven BTEX MS and MSD sample pairs was less than 25 percent. Only four BTEX RPDs were outside advisory QC guidelines defined by the reference laboratory's control charts. All five VPH MS and MSD sample RPDs met advisory QC guidelines set by the reference laboratory's control charts. The 10 TPH MS and MSD sample pairs were considered acceptable.

Laboratory duplicate samples are two separate analyses performed on the sample. During the analysis of demonstration samples, 10 TPH laboratory duplicate samples were prepared and analyzed. All TPH laboratory duplicate RPD result values were less than 25 percent. This was considered to be acceptable.

Completeness

Results were obtained for all of the soil samples. PACE J-coded values that were detected below the PRL, but above the MDL. As previously discussed, samples were J-coded based on one or more of the advisory QC guidelines not being met (i.e., surrogate and spike recoveries). Also, some samples were J-coded based on BTEX CCALs not meeting QC guidelines. PRC did not consider this serious enough to preclude the use of this data because the %Ds for the CCALS did not exceed the QC guidelines by more than 10 percent. The analytes with %Ds outside the QC guidelines were not detected in most of the samples associated with the CCALS. The J-coded data is valid and usable for statistical analysis because the QC guidelines were based on advisory control limits set by either the reference analytical methods or by PACE. This data set should be considered representative of data produced by conventional technologies. For this reason, the actual completeness of data used was 100 percent.

Use of Qualified Data for Statistical Analysis

One hundred percent of the reference laboratory results were reported and validated by approved QC procedures. The data review indicated that J-coded data was acceptable for meeting the demonstration objective of providing baseline data to compare against the demonstrated technologies.

None of the QA/QC problems was considered serious enough to preclude the use of J-coded data for this demonstration. The surrogate and spike recovery control limits were for advisory purposes only, and no corrective action was required for the surrogate recoveries that were outside of this range. RPD results for MSs and MSDs that did not meet advisory QC control limits were common when the matrix contained a high concentration of petroleum. Again, these were advisory limits and no corrective action was required. These same general results would be seen by any laboratory using the reference analytical methods on such highly contaminated samples.

Also, rejection of a large percentage of data would increase the apparent variation between the reference laboratory data and the data from the technology. This apparent variation would probably be of similar magnitude to that introduced by using the data. For these reasons, the J-coded data was used.

Chemical Cross Sections

Chemical cross sections were created from the reference analytical data produced for the qualitative data evaluation (see Appendix A, Tables A-1 through A-6). These samples were collected by a professional geologist on site during the logging of boreholes. The cross sections were hand contoured. The contour intervals were selected to best represent a conventional approach to the delineation of subsurface contamination. The cross sections are presented on Figures 3-1 to 3-6. A written interpretation of these cross sections is presented below.

Atlantic Site

The five sampling nodes formed a northwest to southeast trending transect across the site (Figure 3-1). Node 1 on the far northwestern edge of the cross section represented an area that was not impacted by the contamination from the Atlantic site. Just southeast of this location at Node 2, two distinct layers of contamination were identified. The upper zone extended from approximately 1 foot to 5 feet below ground surface (bgs). This zone was characterized by TPH contamination ranging from 100 to 10,000 parts per

million ppm). The lower zone of contamination extended from approximately 22 feet to 28 feet bgs. The TPH concentrations in this zone ranged from 100 to greater than 10,000 ppm. These two zones expanded and blended together as Node 3 was approached. Around Nodes 3 and 4, the thickness of the TPH plume remained fairly constant, extending from approximately 1 foot to 31 feet bgs. The central portion of this zone exhibited TPH contamination greater than 1,000 ppm. The remainder of this zone exhibited TPH contamination in the range of 100 to 1,000 ppm. As the far southeastern edge of the transect was approached at Node 5, the highest concentrations in the center of the plume pinched out, leaving a contamination zone that extended from just below the ground surface to approximately 27 feet bgs. This zone exhibited contamination in the range of 100 to 1,000 ppm.

The total PAH cross section along this same transect exhibited a slightly different distribution (Figure 3-2). As with the TPH cross section, the total PAH cross section began at Node 1 in the area exhibiting no signs of contamination. At Node 2, again two zones of contamination were detected. The upper zone extended from the ground surface to approximately 7 feet bgs. This zone deepened toward the east. The concentrations of total PAHs in this zone ranged from 10 to greater than 100 ppm. The lower zone extended from approximately 14 to 30 feet bgs. The concentrations of total PAHs in this zone ranged from 10 to greater than 100 ppm. Concentrations greater than 100 ppm were not exhibited at this depth in the nodes occurring further east. The distribution of the 10 to 100 ppm dipped below the ground surface at progressive depths farther east of Node 2. At Node 5, this upper zone began at approximately 7 feet bgs. This zone also reached its maximum depth around Nodes 3 and 4, approximately 30 feet bgs. Around Nodes 3 and 4 were two lenses of total PAH contamination in excess of 100 ppm. The largest of these zones appeared to be thickest around Node 3, extending from approximately 7 to 16 feet bgs. This zone thinned to the east and pinched out between Nodes 4 and 5. A smaller lens of greater than 100 ppm total PAH contamination was exhibited at Node 4. This zone extended between 7 to 9 feet bgs. This zone was not detected in Nodes 3 or 5.

York Site

The five sampling nodes formed a north to south trending transect. The TPH and total PAH distributions appeared to be similar, except at Node 5, at the York site (Figures 3-3 and 3-4). At Node 5, the TPH contamination was more extensive, extending from 1 to 25 feet bgs. At this same locations, the PAH contamination extended from 13 to 21 feet bgs.

FIGURE 3-1. TPH REFERENCE METHOD CHEMICAL CROSS SECTION -ATLANTIC SITE

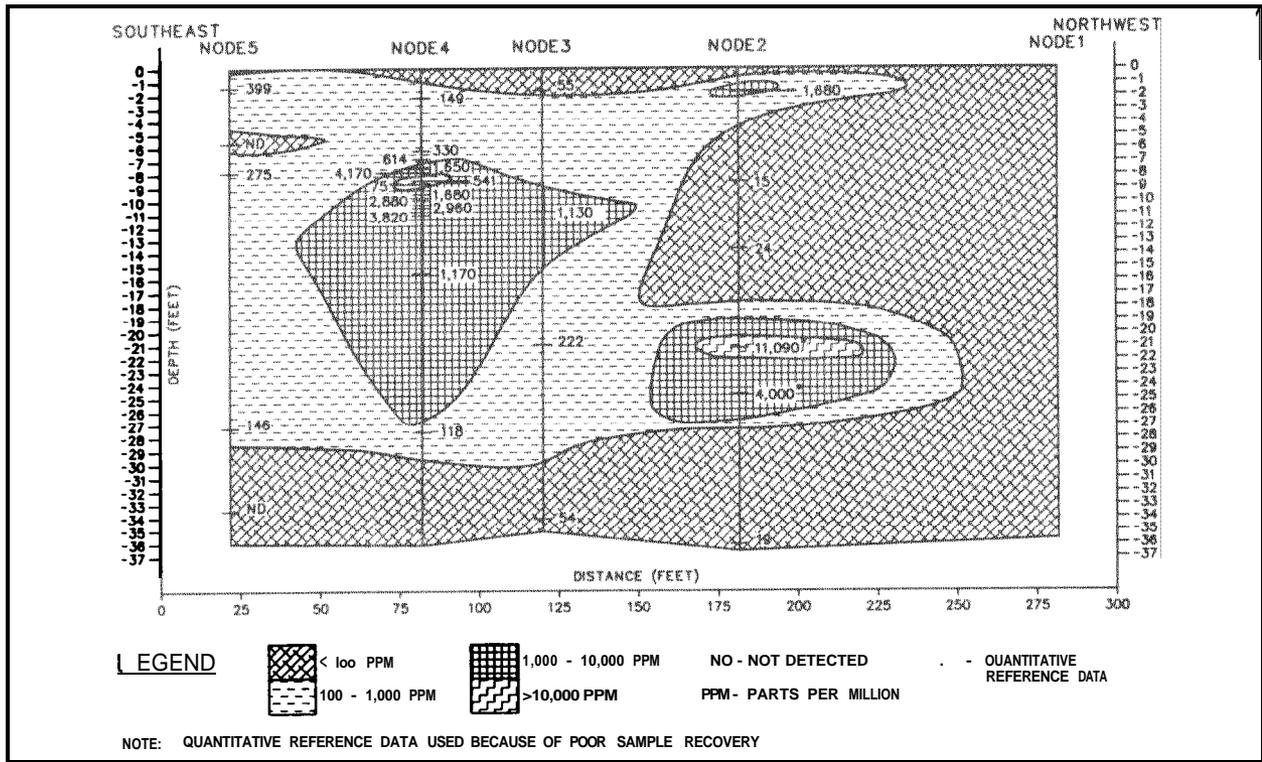


FIGURE 3-2. PAH REFERENCE METHOD CHEMICAL CROSS SECTION -ATLANTIC SITE

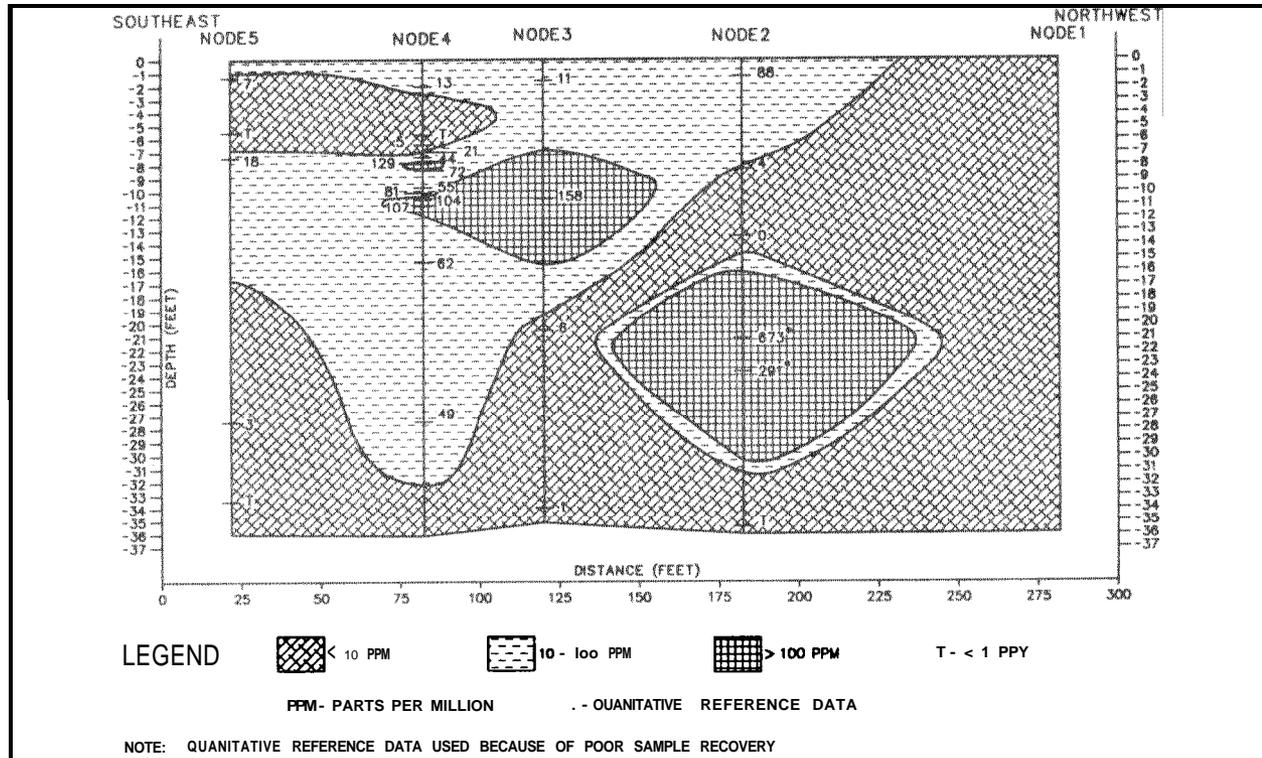


FIGURE 3-3. TPH REFERENCE METHOD CHEMICAL CROSS SECTION - YORK SITE

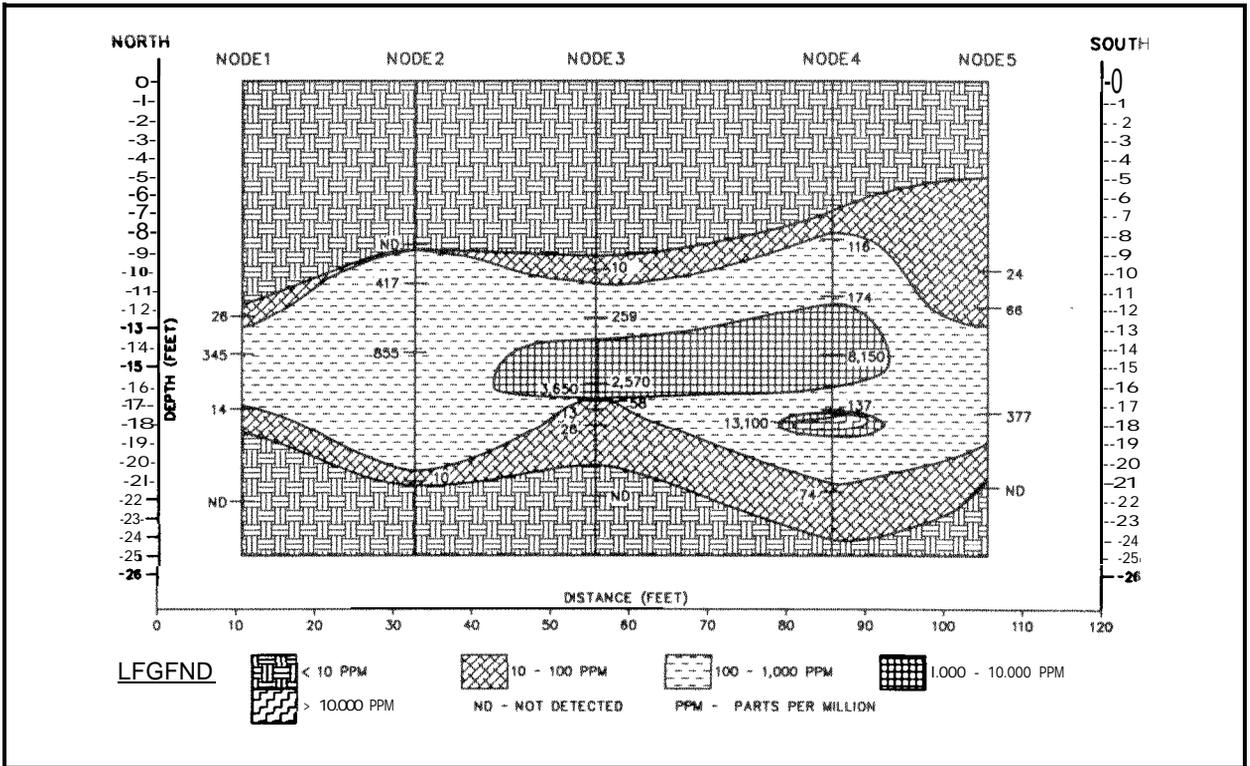


FIGURE 34. PAH REFERENCE METHOD CHEMICAL CROSS SECTION - YORK SITE

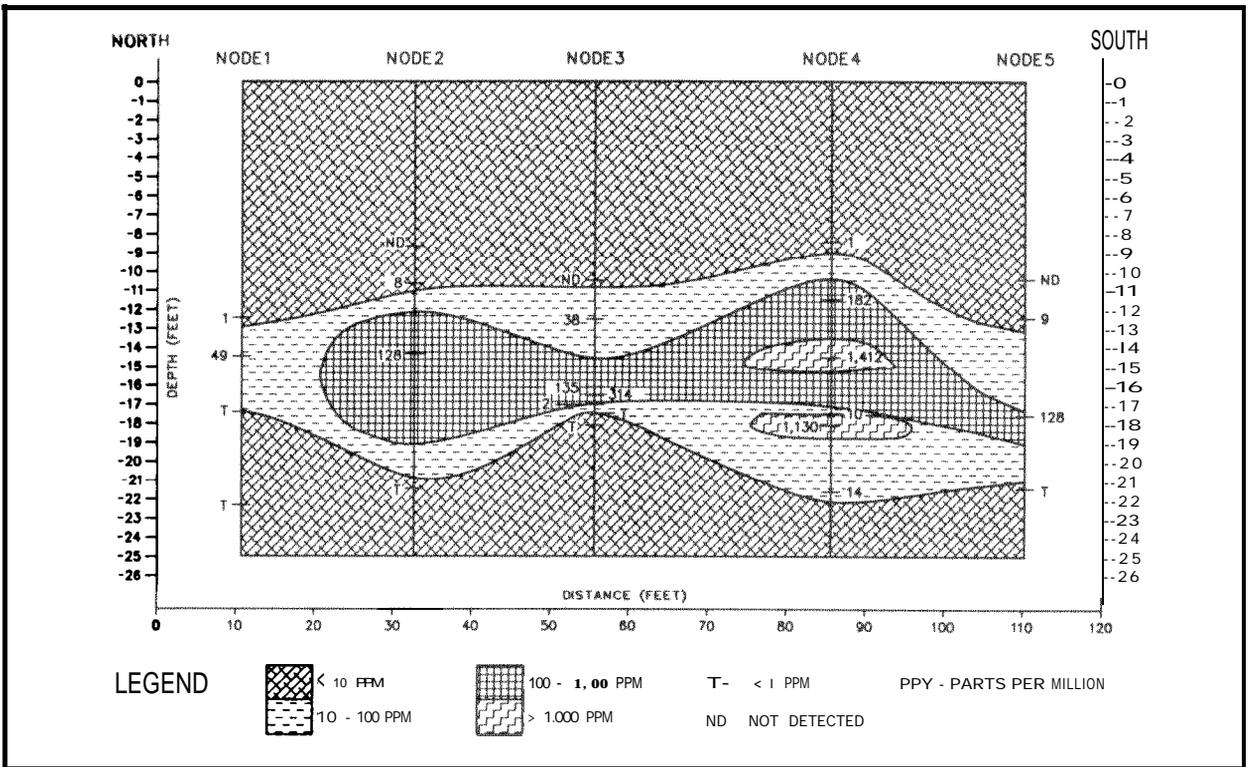


FIGURE 3-5. TPH REFERENCE METHOD CHEMICAL CROSS SECTION - FORT RILEY SITE

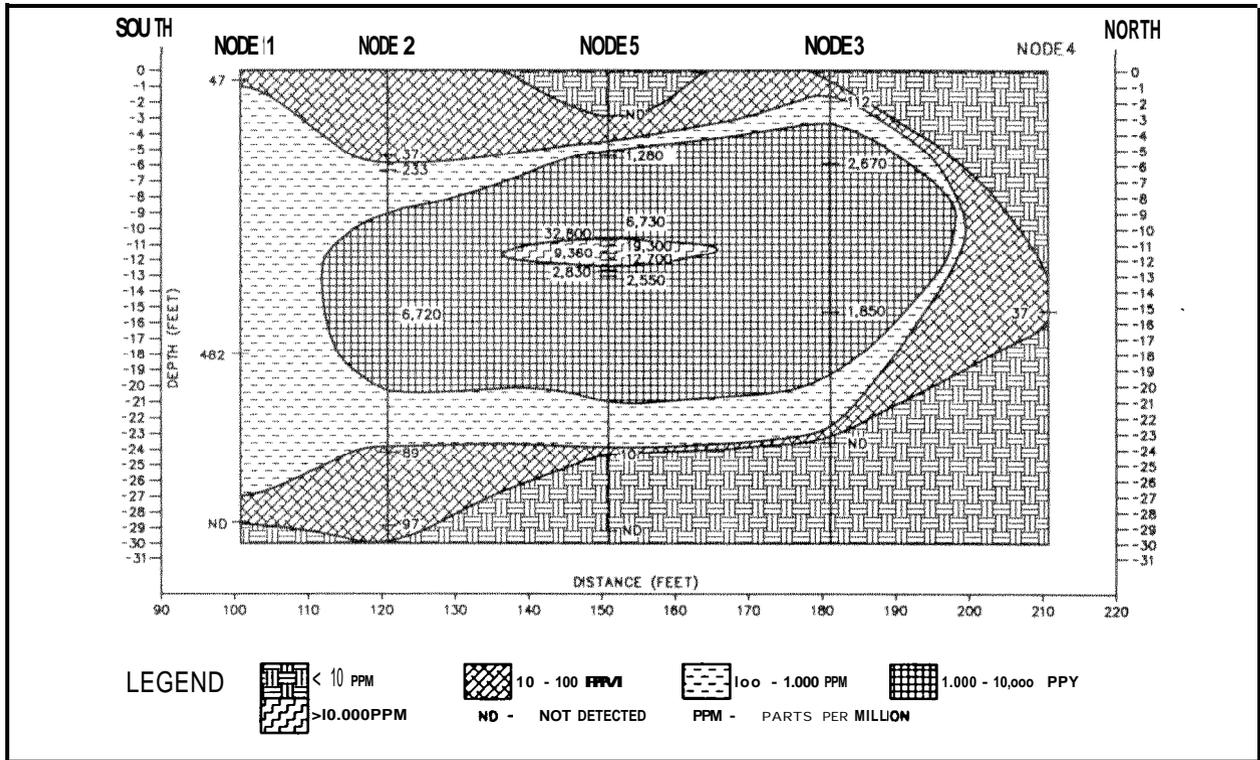
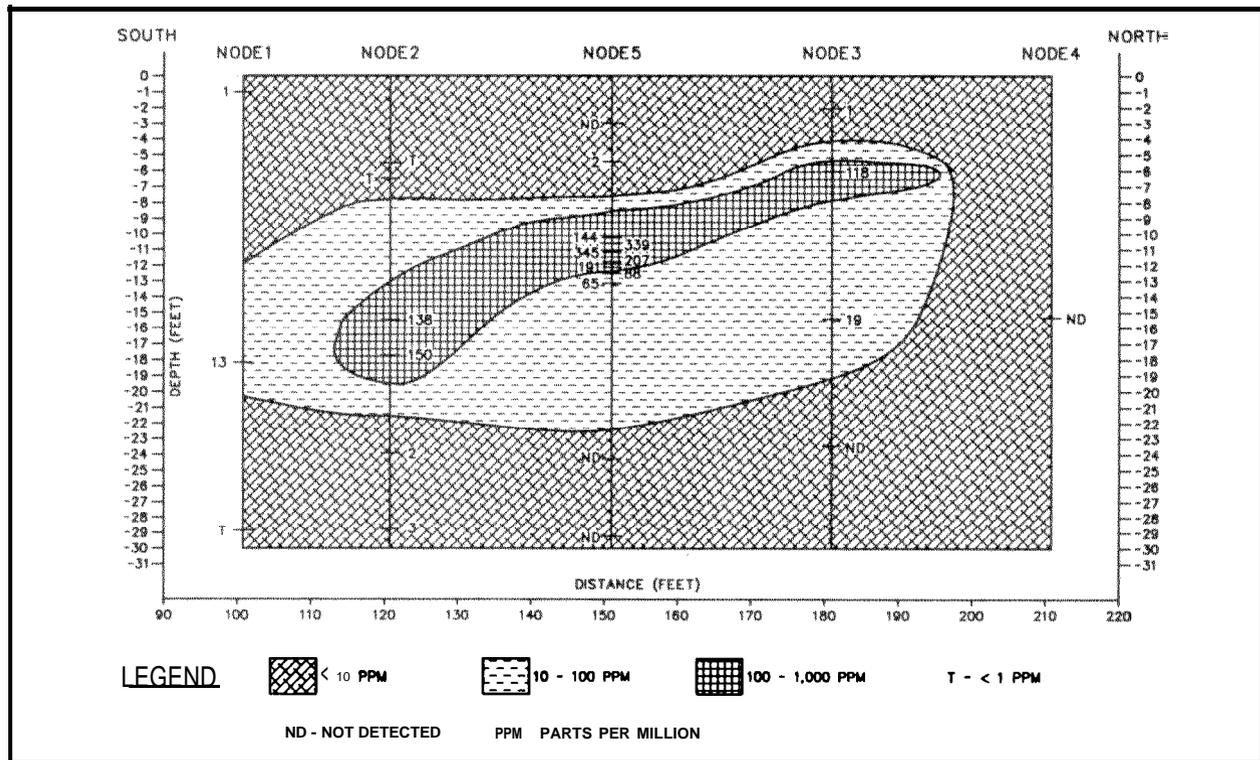


FIGURE 3-6. PAH REFERENCE METHOD CHEMICAL CROSS SECTION - FORT RILEY SITE



All of the nodes for this transect occurred in areas that were impacted by the contamination associated with this site. The contamination at this site appeared to occur in a single band extending from approximately 10 to 22 feet bgs for total PAH and 2 to 25 feet bgs for TPH contamination. This band of contamination thinned from south to north across the transect. At the north end of the transect, the TPH contamination thinned to a zone extending from 12 to 19 feet bgs. Concentrations of TPH in this zone ranged from 10 to 10,000 ppm, and the concentrations of total PAH contamination range from 10 to 1,000 ppm. TPH contamination exhibited its maximum concentrations in a lens around Nodes 3 and 4. This lens extended from approximately 12 to 16 feet bgs, and exhibited TPH concentrations greater than 1,000 ppm. This lens tended to thin and deepen from south to north. Node 4 exhibited the greatest TPH and total PAH contamination. Two narrow lenses of total PAH concentrations greater than 1,000 ppm existed at approximately 14 to 16 feet bgs and 18 to 20 feet bgs. A narrow lens of TPH contamination greater than 10,000 ppm was detected at approximately 18 to 19 feet bgs at Node 4.

Fort Riley Site

The five sampling nodes formed a south to north trending transect. The TPH and total PAH distributions appeared to be similar at the Fort Riley site (Figures 3-5 and 3-6). Node 4, situated at the far north end of the transect, was not affected by contamination. All of the remaining nodes for this transect occurred in areas that were impacted by the contamination associated with this site. The contamination at this site appeared to occur in a single zone extending from approximately 1 to 25 feet bgs for total PAH and 0 to 30 feet bgs for TPH contamination. This zone of contamination exhibited relatively constant thickness across Nodes 2, 3, and 5. Concentrations of TPH in this zone ranged from 100 to greater than 10,000 ppm, and the concentrations of total PAH contamination ranged from 10 to 300 ppm. Total PAH contamination exhibited its maximum concentrations in a lens around Nodes 2, 3, and 5. This lens extended from approximately 5 to 8 feet bgs at Node 3, becoming thicker and deeper at Node 2 where it extended from 10 to 20 feet bgs. The TPH concentrations exhibited two lenses of concentration at greater than 10,000 ppm. These lenses did not appear to be extensive and their occurrence was limited to the areas around single nodes. Node 5 in the center of the transect exhibited one of these lenses of highest TPH contamination extending from 10 to 13 feet bgs. Node 2 has the other such lens which extended from 17 to 19 feet bgs.

Quality Assessment of Geotechnical Laboratory Data

This section discusses the data quality of the geotechnical laboratory results, the data quality of the borehole logging conducted by the on-site professional geologist, and the soil sampling depth control. The stratigraphic cross sections resulting from this logging are presented and discussed later in this section.

Geotechnical Laboratory

Soil samples submitted for textural determination were analyzed by ASTM Method D-422 (1990). ETS, Petaluma, California, conducted these analyses. ASTM Method D-422 does not define specific QA/QC criteria, however, it specifies the use of certified sieves, and calibrated thermometers and hydrometers. ETS followed the approved method and complied with all the equipment certification and calibration requirements of the method. Based on this, the geotechnical data was determined acceptable.

Borehole Logging

The data quality of the on-site professional geologist's borehole logs was checked through on-site audits by a soil scientist, and by comparison of the geologist's descriptions for intervals corresponding to samples analyzed by ASTM Method D-422. This comparison is discussed later in this section.

Sampling Depth Control

At each site, random checks of the reference sampling intervals were made. These checks consisted of stopping drilling operations just before inserting the split spoon sampler into the hollow stem auger to collect samples. At this time, a weighted tape measure was used to measure the top of the sampling interval. The measurement was checked against the intended sampling depth. If the difference between the intended and actual sampling depth had varied by more than 1 inch, the borehole would have been redrilled. Depth checks were made at a minimum of once per sampling day. None of these depth checks resulted in data exhibiting a greater than 1 inch difference between intended and actual sampling depth. Based on this, the reported sample intervals were considered accurate.

Stratigraphic Cross Sections

Stratigraphic cross sections were based on the data produced by a professional geologist during the logging

FIGURE 3-7. REFERENCE METHOD STRATIGRAPHIC CROSS SECTION - ATLANTIC SITE

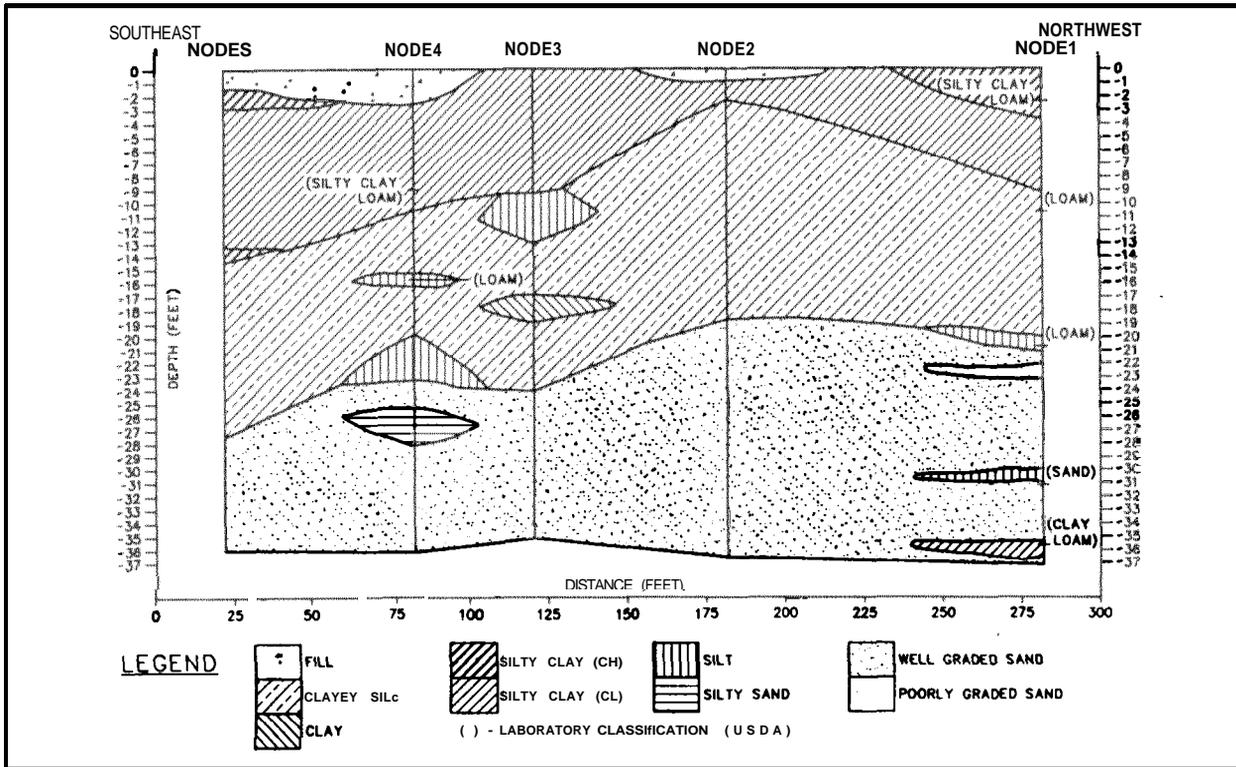


FIGURE 3-8. REFERENCE METHOD STRATIGRAPHIC CROSS SECTION - YORK SITE

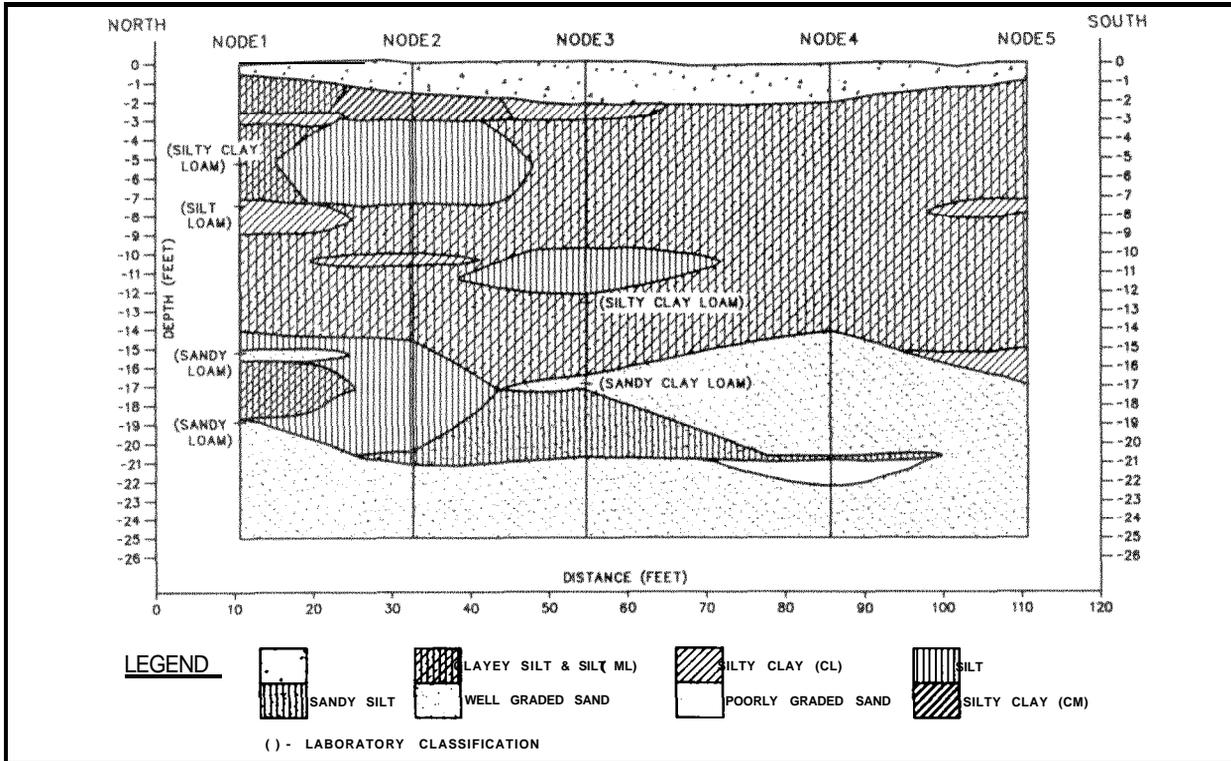
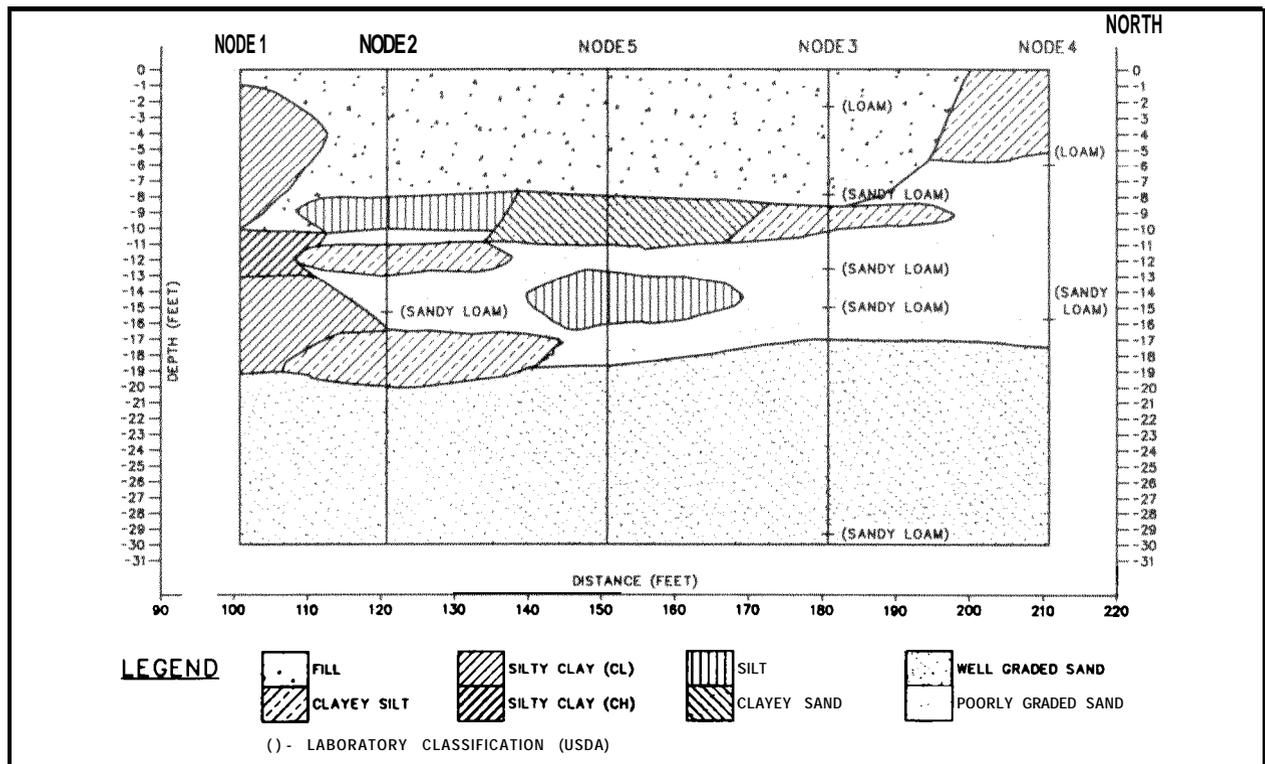


FIGURE 3-9. REFERENCE METHOD STRATIGRAPHIC CROSS SECTION - FORT RILEY SITE



of boreholes during the demonstration. The cross sections were intended to represent a conventional approach to the delineation of subsurface stratigraphy. The cross sections are presented on Figures 3-7 to 3-9. A verbal interpretation of these cross sections is presented below by site. QA/QC consisted of the collection of samples for textural analysis by a geotechnical laboratory (see Appendix A, Tables A-1 through A-9). These samples are discussed at the end of each site-specific discussion.

Atlantic Site

The Atlantic site is located on the flood plain of the Nislmabotna River, which is located about 0.7 mile west of the site. The flood plain is nearly level. The surface soil at the site is a silty clay. These soils have most likely formed from alluvium. Stratigraphic cross sections produced during the demonstration from soil borings indicated that the subsurface soil at the site consisted of silts and clays and silty clay interlingered with each other to a depth of approximately 21 feet bgs on the northwest end (Node 1) and to 28 feet bgs on the southeast (Node 5). See Figure 3-7 for a graphical representation of the cross section. A layer of sand was present from 18 to 36 feet bgs at Node 2. This zone remained relatively uniform from Node 2 to Node 5.

Seven soil samples were collected to verify the geologist's borehole logging at the Atlantic site. The geologist's classification of soils matched the geotechnical laboratory's classifications six out of seven times (Table 3-1). This one point of disagreement was sample DR16 from the 2- to 3-foot interval at Node 1. In this sample, the geologist identified silt as the predominant size fraction of the sample, while the geotechnical laboratory identified clay as the predominant size fraction. This is a common point of variance between field soil classification and laboratory classification. These common differences are magnified in grossly contaminated soils, and when the geologist is forced to wear plastic gloves during classification. This difference was noted, and geologist's stratigraphic borehole logs meet the demonstration data quality objectives (DQO) for screening level data.

York Site

The York site is located on the flood plain of Beaver Creek, which is located 0.1 mile southwest of the site. The site is situated on a nearly flat lying terrace above the river. The surface soils is a silt loam. These soils most likely formed in alluvium on stream terraces. A stratigraphic cross section based on soil borings during the demonstration was prepared (Figure 3-8). The top

TABLE 3-1. COMPARISON OF GEOLOGIST'S DATA AND GEOTECHNICAL LABORATORY DATA - ALL SITES

Site	Geologist Classification	Geotechnical Laboratory Classification	Match
Atlantic	Silty Clay (ML)	Sandy Lean Clay (CL)	No^a
	Clayey Silt (CL)	Clay or Silt (CL or ML)	Yes
	Silt (ML)	Silt or Clay (ML or CL)	Yes
	Well Graded Sand (SW)	Well or Poorly Graded Sand (SW or SP)	Yes
	Clay (CL)	Sandy Lean Clay or Sandy Silt (CL or ML)	Yes
	Silty Clay (CL)	Sandy Lean Clay or Sandy Silt (CL or ML)	Yes
	Silty Clay (CL)	Silt or Clay (ML or CL)	Yes
York	Clayey Silt (ML)	Silt or Clay (ML or CL)	Yes
	Silty Clay (CL)	Silt or Clay (ML or CL)	Yes
	Well Graded Sand (SW)	Silty to Clayey Sand (SM or SC)	No^a
	Poorly Graded Sand (SP)	Poorly Graded Sand with Silt or Clay (SW-SC or SP-SC)	Yes
	Clayey Silt (ML)	Silt or Lean Clay (CL or ML)	Yes
	Sand (SW)	Silty or Clayey Sand (SM or SC)	No^a
Fort Riley	Poorly Graded Sand (SP)	Silty or Clayey Sand (SM or SC)	No
	Fill	Silty or Clayey Sand (SM or SC)	Yes
	Poorly Graded Sand (SP)	Silty or Clayey Sand (SM or SC)	No
	Clayey Silt (ML)	Silty or Clayey Sand with Gravel (SC or SM)	No^a
	Poorly Graded Sand (SP)	Silty or Clayey Sand (SM or SC)	No^a
	Poorly Graded Sand (SP)	Silty or Clayey Sand (SM or SC)	No^a
	Poorly Graded Sand (SP)	Silty or Clayey Sand (SM or SC)	No^a
	Well Graded Sand (SW)	Silty or Clayey Sand (SM or SC)	No^a

Notes:

- ^a These failures to match were due to the geologist underestimating the percentage of fines in the sample.
 () Unified Soil Classification System two-letter code

1 to 2 feet of the cross section was fill. From 2 to 14 feet bgs, the cross section consisted of clayey silt with some lenses of silty clay and silt. At approximately 14 feet bgs, there were thick lenses of silt, sandy silt, and sand. These lenses were approximately 7 feet thick and were interfingered with each other. At approximately 21 feet bgs, the material became primarily well graded sand to the bottom of the section at 25 feet bgs.

Six soil samples were collected to verify the geologist's borehole logging at the York site. The geologist's classification of soils matched the

geotechnical laboratory's classifications four out of six times (Table 3-1). The two points of disagreement were samples DR27 (Node 1, 15 to 15.5 feet bgs) and DR 29 (Node 3, 12 to 13 feet bgs). In both cases, the geologist underestimated the percentage of silt and clay size particles in the samples. This is a common point of variance between field soil classification and laboratory classification. These differences are magnified in grossly contaminated soils, and when the geologist is forced to wear plastic gloves during classification activities. The variances described above are not uncommon in environmental studies, and thus, the geologist's stratigraphic borehole logs, while exhibiting

some disagreement with the laboratory data, are considered to meet the demonstration DQOs for screening level data.

Fort Riley Site

The Fort Riley site is located on the flood plain of the Kansas River, which is located 0.1 mile southeast of the site. The site is situated on a nearly flat lying terrace above the river. The surface soil is a silt loam. This soil is most likely formed from deep alluvium. A stratigraphic cross section based on soil borings conducted during the demonstration is presented on Figure 3-9. This cross section showed typical deposition in an alluvial setting with interfingered beds of clay, silt, silty clay, clayey silt and sand. In the center of the cross section, the top 8 feet was fill. The northern and southern edges of the cross section were silt or silty clay at the surface. In the northern half of the cross section, poorly graded sand was present from 5 to 17 feet bgs. In the southern half of the cross section from 8 to approximately 18 feet bgs, the cross section consisted of

interfingered lenses of clay, silty sand, and sand. Below 20 feet bgs, the cross section became primarily sand with silt and clay lenses of various thickness intermixed to the terminal depth of the cross section.

Eight soil samples were collected to verify the geologist's borehole logging at the Fort Riley site. The geologist's classification of soils matched the geotechnical laboratory's classifications one out of eight times (Table 3-1). Both classifications did correctly identify the dominant particle size fraction. In all of the cases of disagreement, the geologist underestimated the percentage of silt and clay size particles. Small shifts in the estimation of these particles can alter the descriptive modifier used in classification. The variances described above affect the accuracy of the reference stratigraphic cross sections as far as the secondary classification modifiers are concerned. The baseline classification as to the dominant particle size is accurate. This data met the demonstration's DQOs, however, decisions based solely on differences in classification modifiers should be qualified as semiquantitative Table 3-1.

Section 4 Rapid Optical Screening Tool

This section describes the **ROST™** technology evaluated under this demonstration. The description provided is based on information provided by the developer, on information PRC obtained from reports and journal articles written about the technology, and on observations made during the demonstration. The description includes background information on the technology and its components. General operating procedures, training and maintenance requirements, and cost of the technology also are discussed.

Background Information

The Department of Defense, through the U.S. Air Force's Armstrong Laboratory, has supported research at NDSU to develop tunable dye laser systems for field environmental analysis since 1989. A prototype tunable system built at NDSU was integrated with a cone penetrometer truck and demonstrated at Tinker Air Force Base in 1992. Follow-up demonstrations of the tunable dye laser systems for optical cone penetrometry were carried out in late 1993 and 1994 at the following air force bases: Plattsburgh, Patrick, and Dover. This second round of demonstrations used an improved prototype built by DTI. DTI is a small business formed by two individuals who developed the original tunable dye laser system at NDSU.

In 1993, a consortium comprised of Unisys Corporation, DTI, NDSU, and the U.S. Air Force Armstrong Laboratory received a Technology Reinvestment Project award from the Advance Research Projects Agency, which led to the development of the **ROST™**. Loral Corporation acquired the portion of Unisys responsible for the **ROST™** development and services on May 5, 1995. For this demonstration, **ROST™** was temporarily installed on a cone penetrometer truck supplied by a subcontractor to PRC. The subcontractor selected was Fugro Geosciences, Inc. (Fugro); however, the developer stated that **ROST™** is compatible with almost any standard cone penetrometer truck.

Components

This subsection describes the components of **ROST™** and the cone penetrometer truck system.

Cone Penetrometer Truck System

A complete cone penetrometer truck system consists of a truck, hydraulic rams and associated controllers, and the CP itself. The weight of the truck provides a static reaction force, typically 20 tons, to advance the CP. The hydraulic system working against the static reaction on force advances 1-meter-long segments of 3.57-centimeter-diameter threaded push rod into the ground. The CP, which is mounted on the end of the series of push rods, contains sensors that continuously log tip stress and sleeve friction. The **ROST™** technology's fiber optic cables, mirrors, supports, and sapphire window are built into a "sub" which is fitted to a standard CP. This CP is fitted with tip stress and sleeve friction sensors. The data from CP sensors are used to map subsurface stratigraphy. Conductivity or pore pressure sensors can be driven into the ground simultaneously with the modified CP. Soil, groundwater, and soil gas sampling tools can also be used with the cone penetrometer truck. These capabilities are discussed in greater detail in the general ITER. Generally, sampling tools and sensors are not used concurrently due to the necessity for sampler retrieval after each sample is collected.

In favorable stratigraphies, push depths of 50 meters or greater have been achieved. The CP can be pushed through asphalt, but concrete must be cored prior to advancing the CP. Advancing sensors and sampling tools with the cone penetrometer truck may be difficult or impossible in the following subsurface environments:

- Gravel units
- Cemented sands and clays
- Buried debris
- Boulders
- Bedrock

The cone penetrometer truck used with the **ROST™** during this demonstration was fitted with a steam cleaner to decontaminate the push rods as they were withdrawn from the ground. The decontamination water is contained in the decontamination apparatus and it can be directly discharged into a storage container. The clean water, pressure sprayer, and grouting pump are mounted in a trailer that is towed by a support vehicle.

ROST™ Technology

The main **ROST™** system components are:

- Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) primary laser
- Tunable dye laser pumped by the Nd:YAG laser
- Fiber optic cable and CP “sub”
- Detection system comprised of a monochromator, photomultiplier tube (PMT), and digital storage oscilloscope (DSO)
- Control computer

In the prototypes that preceded **ROST™**, the components of the tunable dye laser were arranged on a 122-centimeter (cm) by 61-cm optical breadboard, which sat on top of a cart in which the other components were placed. The **ROST™** technology used in this demonstration is more compact and integrated. The **ROST™** components are assembled into two half-height instrumentation racks. Each rack is approximately 66-cm high by 51-cm wide by 61-cm deep. A diagram that shows how the **ROST™** system components are arranged in the racks is shown on Figure 4-1. The main **ROST™** components are discussed in more detail below. All of the electronic components are powered by a gasoline generator, independent of the cone penetrometer truck power system.

Nd:YAG Laser

The primary laser is a Nd:YAG laser with a second harmonic generation option manufactured by Big Sky Laser Technologies. It generates 532 nanometers (nm) of light at a repetition rate of 50 pulses per second (Hz). The near-Gaussian output beam is approximately 6.35 cm in diameter. The primary laser is rated at a pulse energy of 50 millijoules per pulse (MJ). It requires standard 110-volt line voltage; a dedicated 20-amp circuit is recommended. Because water to cool the Nd:YAG rod is supplied by an internal circulator in the power supply, no external source of cooling water is required. The light from the primary laser pumps the dye laser.

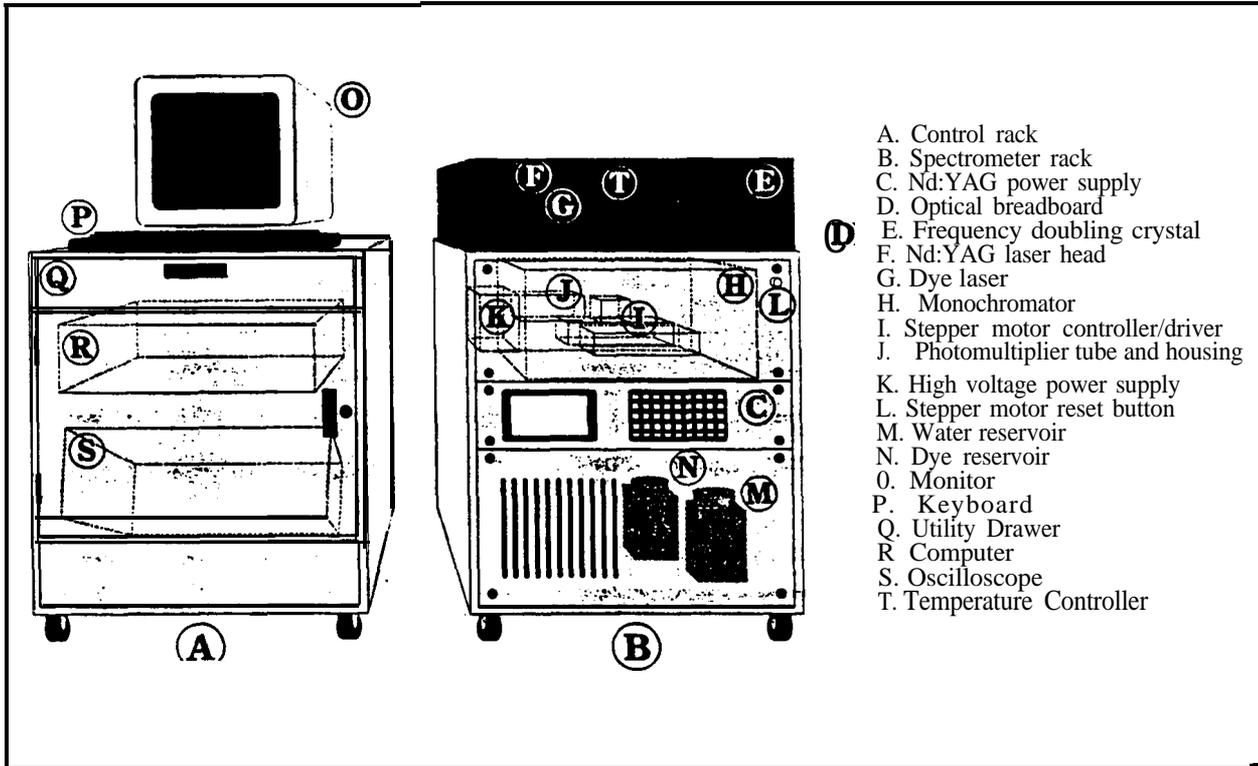
Tunable Dye Laser

The dye laser converts the fixed wavelength light of the Nd:YAG laser into wavelengths that can be optimized for the contaminant(s) of interest. The dye laser is pumped by the Nd:YAG laser output. The output wavelength range of the dye laser depends on which dye is used. The dye was Rhodamine 6G for this demonstration. The wavelength range that can be generated from Rhodamine 6G is approximately 560 to 600nm.

The dye laser uses Bethune prism dye cells, which are right angle prisms with a narrow bore through which the dye flows. The collimated light from the Nd:YAG laser enters the hypotenuse face of the prism. After undergoing total internal reflection at the other two faces, the light creates a highly uniform illumination of the dye solution that is flowing through the Bethune cells. The developer states that a major advantage of the Bethune cells is that the Nd:YAG laser light does not have to be focused into the dye cell. Collimated light (or nearly so) is sufficient to maintain the total internal reflection condition.

The wavelength of the monochromatic laser light, which is produced in the oscillator of the dye laser, is selected to be optimal for the detection of specific compounds. The oscillator consists of the Bethune cell, cavity mirrors, and a wavelength dispersing element (a diffraction grating in this case). The broad Rhodamine 6G fluorescence (560 to 600 nm) that exits the bore of the Bethune prism cell hits a feedback element that reflects a portion of the light back through the Bethune cell bore. The feedback element, which can be a wedged piece of fused silica, also serves as the output coupler of the dye laser. On this second passage, the light is amplified by stimulated emission into a narrow pencil of light. On the other side of the prism cell, the pencil of light grazes the surface of a diffraction grating. The diffraction grating disperses the light. That is, it spatially separates light into its wavelength components in the same fashion as a prism. A tuning mirror returns the diffracted light back to the grating at which point the return beam is rediffracted. Only a narrow range of wavelengths within the rediffracted beam follow the proper path to pass back through the Bethune cell. This monochromatic light is further intensified by stimulated emission as it passes back through the dye cell. It exits the laser cavity through the feedback element. By varying the angle of the tuning mirror, one may select the wavelength of light which finally exits the dye laser cavity, which is why the dye laser is referred to as tunable.

FIGURE 4-I. SYSTEM COMPONENTS



- A. Control rack
- B. Spectrometer rack
- C. Nd:YAG power supply
- D. Optical breadboard
- E. Frequency doubling crystal
- F. Nd:YAG laser head
- G. Dye laser
- H. Monochromator
- I. Stepper motor controller/driver
- J. Photomultiplier tube and housing
- K. High voltage power supply
- L. Stepper motor reset button
- M. Water reservoir
- N. Dye reservoir
- O. Monitor
- P. Keyboard
- Q. Utility Drawer
- R. Computer
- S. Oscilloscope
- T. Temperature Controller

The monochromatic laser light emerging from the oscillator of the dye laser is amplified as it passes through a second Bethune cell, which is also energized from the Nd:YAG laser. The amplified beam then passes through a frequency doubling crystal, which converts a portion of the incoming light into photons of half the wavelength, in this case in the range 280 to 300 nm. The unconverted visible light is removed by a blocking filter and the remaining light is focused onto the launch end of the fiber optic cable.

Fiber Optic Cable

The fiber optic cable delivers excitation light from the dye laser through the sapphire window in the modified CP and returns any fluorescence emission arising from aromatics contamination in the soil back to the PMT, which is a component of the detection system. The sapphire window is typically 2 to 3 millimeters (mm) thick and 6.35 mm in diameter. This window is mounted flush with the outside of the standard CP sensor casing. The window is located about 20 to 25 centimeters above the terminal end of the CP sensor casing. This window allows laser light to pass from the **ROST™** and into the soil. The window also transmits LIF from the soil back into a return fiber optic cable. Sapphire is used due to its good optical transmission characteristics and due to its abrasion resistance. The fiber that transmits the laser light to the

sapphire window is referred to as the delivery fiber. The return fiber (or fibers) is referred to as a collection fiber (or fibers). The delivery and collection fibers run from the dye laser through the center of the series of push rods to which the CP is attached.

The fibers have three concentric layers. The light travels through the innermost zone known as the core. The middle layer is a cladding material that has a higher reflective index than the core fiber. This difference in reflective index causes internal reflection as light to move through the core. In effect, the cladding traps light within the core. The outer layer is a protective abrasion-resistant buffer. For additional protection, the fibers are inserted into furcation tubing.

For this demonstration, the developer used a single delivery fiber and a single collection fiber. Sensitivity could be increased with additional collection fibers.

Detection System

The detection system consists of a monochromator, PMT, and a DSO. The monochromator incorporates entrance and exit slits, a diffraction grating, and several mirrors. The monochromator acts as a variable wavelength narrow bandpass filter. By acquiring fluorescence data at a series of wavelengths, the fluorescence technician can determine the wavelength of

maximum intensity in the fluorescence spectrum. The light passing through the monochromator at this wavelength is converted to an electrical signal by the PMT. The signal from the PMT is fed to the DSO, which displays the waveform (fluorescence intensity as a function of time following the excitation laser pulse). Typically, the data are acquired over a window of 100 to 500 nanoseconds (ns). The DSO also averages the signal from several consecutive laser shots. After the selected number of laser shots have been averaged, the waveform is downloaded to the control computer for permanent storage and post-processing of the data.

Control Computer

The **ROST™** technology is controlled by a personal computer, which also is used for off-line data analysis. Several **ROST™** technology motors are controlled by the computer: one to drive the tuning mirror of the dye laser oscillator, one to position the frequency doubling crystal, and one to drive the monochromator wavelength selection. The control computer also sets the high voltage on the PMT and provides communication with the DSO via a GPIB bus.

General Operating Procedures

The sapphire window is located in a “sub” that is fitted to a standard CP. These push rods are approximately 1 meter long and must be continuously added as the CP is advanced using a hydraulic ram. The standard penetration rate is approximately 2 centimeters per second (cm/s). The maximum depth of a push is determined by soil matrix conditions and the static reaction force of the cone penetrometer truck. A standard 20-ton cone penetrometer truck was used for this demonstration.

The CP also provides continuous monitoring of tip stress and sleeve friction. These data are downloaded onto a computer with software that classifies the soil type.

When sensors are not attached to the push rods, conventional soil, soil gas, and groundwater sampling tools can be fitted to the push rods for environmental sampling. In addition, cone penetrometer trucks can be used to install small diameter piezometers.

Before collecting data at a site, the **ROST™** is calibrated. The **ROST™** operator attaches a sealed vial containing 10,000 ppm solution of gasoline to the sapphire window. The emission wavelength of the laser is set and multiple laser shots are fired at the solution and the resultant fluorescence is measured. The data

system is then calibrated to read 100 percent fluorescence based on the fluorescence of the standard at the predetermined emission monitoring wavelength. All subsequent data is reported as a percent fluorescence relative to the standard.

The **ROST™** technology can be operated in both dynamic (push) and static modes. In the dynamic mode, the modified CP equipped with the sapphire window and fiber optics is advanced at a rate between 1.5 and 2.5 cm/s. In this mode, which the developer refers to as FVD (fluorescence versus depth), the excitation laser wavelength and fluorescence emission monitoring wavelength are held constant. The fluorescence emission intensity is plotted as a function of depth bgs. The developer selected an excitation wavelength in the range 280 to 295 nm for this demonstration. This wavelength range was selected because naphthalene, a major PAH constituent of coal tar and diesel fuel, fluoresces strongly under these conditions. The emission monochromator was set at a wavelength determined during the laboratory analysis of the predemonstration samples. It was set at 400 nm for the Atlantic and York sites, and at 360 nm at the Fort Riley site. With these laser and detector settings, the **ROST™** was configured to detect the presence or absence of primary fluorescing compounds associated with the petroleum fuel and coal tar contamination expected during this demonstration.

For this demonstration, the laser repetition rate was 50 Hz. The DSO in the current **ROST™** system configuration averages the time-integrated signal from these 50 pulses to produce a fluorescence datum for that depth. The spatial resolution was, therefore, 2 cm. The complete averaged fluorescence intensity versus depth profile was archived for post-processing.

Once areas of significant contamination have been identified in the dynamic mode, **ROST™** can be operated in the static mode to identify the general class of contamination present. In this mode, the CP is held at a fixed depth. The fluorescence technician, who is observing the fluorescence signal visually, can simply signal the hydraulic operator to halt the push. **ROST™** also can operate in the static mode when additional push rods are added to the string.

During the static mode, **ROST™** can obtain multidimensional data representations, called wavelength-time-matrices (WTM). These differ from the two dimensional FVDs that are plots of relative fluorescence intensity versus depth. A WTM represents a 3-dimensional plot of relative fluorescence intensity versus fluorescence lifetimes versus wavelength. produce contaminant class specific three-dimensional figures. Preliminary research indicates that this

characteristic image can be used in a fashion similar to fingerprinting to identify contamination. This data can be used to identify contaminants present, for example, the type of fuel that is present. For WTM acquisition, either the excitation or the fluorescence emission wavelength can be varied. Normally the excitation wavelength is held constant and the emission monitoring wavelength is varied. This was the procedure used during the demonstration. For a WTM, the data from 100 to 200 laser pulses are averaged at each of a series of return emission wavelengths separated by 10 nm, between 50 and 300 nm. The acquisition of a WTM takes about 5 minutes longer than the time required to add an additional probe rod for continued probe advancement.

Training and Maintenance Requirements

One person is needed to operate the **ROST™** technology and two are needed to operate the cone penetrometer truck. A crew chief operates the hydraulics of the cone penetrometer truck and monitors the push depth, cone tip resistance, sleeve friction, and pore pressure or conductivity measurements if taken. The rod person screws on additional push rods after completing each 1-meter push. The fluorescence technician operates the **ROST™** technology.

The technology is presently offered only as a service from Loral Corporation. Their operators are fully trained in the operation and maintenance of the equipment and the interpretation of the data. The typical operator has a bachelor's degree in a science or engineering discipline, plus any prerequisite environmental field training. Typically the **ROST™** operators have 30 days of training in the use of the technology. This training consists of classroom and on-the-job training.

Cost

Because the **ROST™** technology is still in the developmental stage, a specific sales cost for the technology has not been established. Currently, use of the **ROST™** technology is contracted out on a job-by-job basis. The developer envisions **ROST™** being sold as a complete unit eventually. Training would likely be incorporated into the sale price.

The developer estimates that the daily rate for use of a cone penetrometer truck and **ROST™** would be between \$5,000 and \$5,500. Mobilization and operator per diem costs are not included. The **ROST™** technology and one operator costs \$2,800 per day if a cone penetrometer truck is already being supplied. These costs also do not include mobilization or per diem. The

ROST™ technology was used with a Fugro cone penetrometer truck. The cone penetrometer truck costs incurred during the demonstration were \$2,350 per day, which included mobilization for the Fugro cone penetrometer truck and two operators. If the cost of subcontracting the cone penetrometer truck is added to the daily use charge of the **ROST™** technology, a daily use rate for a complete **ROST™** rig, as used in this demonstration, would be approximately \$5,150 per day. The total cost of the three site characterizations performed using **ROST™** would have been approximately \$41,200. For comparison, the predemonstration activities produced similar data at the three sites, however, it required more personnel and on-site analytical capabilities at an approximate cost of \$43,000. The predemonstration resulted in fewer data points, relative to the continuous data output of the **ROST™** and CP. In addition, the predemonstration activities only produced one borehole log at each site. Another cost comparison can be made relative to the costs accrued producing the reference cross sections for this demonstration. Data acquisition and production costs of the reference cross sections cost approximately \$55,000, including approximately \$30,000 for drilling services, approximately \$8,000 for the on-site geologist and sampler, approximately \$12,000 for off-site analytical services, and approximately \$5,000 for handling and disposal of investigation derived waste.

Observations

An observer was assigned to the **ROST™** technology demonstration to assess the following operational factors:

- cost
- Ease of operation, ruggedness, and reliability
- Sampling capabilities and production rates

A summary of the observations made during the **ROST™** demonstration is included in the following paragraphs. The developers' corrective actions and responses to some of these observations are presented in Section 7.

The cone penetrometer truck equipment, as previously stated, was supplied by Fugro Geosciences, Inc., Houston, Texas. The cone penetrometer truck consisted of a driver's cab and an enclosed 15- by 8-foot rear compartment, which housed the cone penetrometer truck pushing equipment and tools, and the electronic equipment used by both the cone penetrometer truck and **ROST™**. The technology's components were supplied by the developer and included the equipment previously identified in this section of this report. In addition, the **ROST™** system used a printer to allow in-the-field printouts of push data.

Major consumables for the **ROST™** demonstration were water, grout, bentonite, cement, diesel fuel, kerosene, and gasoline. Repair parts for the **ROST™** or the CP could be stored in the cone penetrometer truck or sent by the manufacturer by overnight carrier.

Use of the **ROST™** technology is limited mainly by physical factors relating directly to the cone penetrometer truck. These include terrain, both above ground (clearance from overhead hazards), and below ground (presence of gravel or rock fragments and buried utilities). While attempting to push through the coarse and fine sands, the overlying clay and silt layers provided little lateral support to the cone penetrometer truck rod, increasing the possibility of bending or breaking the rod. This caused the operator to terminate pushes in most cases at approximately 30 feet below ground surface. The cone penetrometer truck operator can overcome this problem by placing casing through the clay and silt layer. The casing provides adequate lateral support to the rod to allow the cone penetrometer truck to push through the deeper sand layers.

The developer of **ROST™** claims it is capable of performing 300 feet of cone penetrometer truck pushes per lo-hour work day. The demonstration showed that this claim was accurate. Initial setup of the **ROST™** technology required 4 hours for this demonstration, and takedown and stowage time between site mobilizations was approximately 2 hours for this demonstration.

Specific problems that occurred during the demonstration included:

- Moisture fogging the sapphire window was experienced during three pushes, twice at the Atlantic site, and once at the York site. The push rod was dismantled and the window was cleaned with methanol. When the rod was reassembled, great care was taken to avoid introduction of moisture from ambient air into the rod. The O-ring seals were also replaced to ensure that the rod was leak-tight. Each time this corrective action was taken, it required approximately 3 hours of down time.
- The fiber optic cable broke during a push at the Atlantic site. This may have been due to stress applied to the cable during storage and push rod handling. The fiber optic cable was replaced and the system was recalibrated. This repair and recalibration required approximately 4 hours of down time. A portion of the cable lies on the floor of the cone penetrometer truck during pushes and is always susceptible to

breakage from falling tools or from being stepped on.

- The self-contained decontamination unit frequently leaked during usage. This was due to physical abrasion of the rubber gaskets used to scrape soil and provide a water tight seal around the push rods. This is a potential route for contaminant migration down the probe hole. The leaking water tended to migrate into the push rod hole along the outside of the push rods. Based on the performance, to prevent leakage, the operator (Fugro) suggested that these gaskets be replaced after every cone penetrometer truck push, and checked for leak-tightness before each cone penetrometer truck push. Replacement of these gaskets required approximately 0.5 hour of down time.
- The depth-gauge cable for the push rods broke during a push at the Atlantic site. Parts were acquired from a local hardware store to fix the device. This repair required approximately 2 hours of down time.
- The independent depth-gauge and recording device used by the **ROST™** technology did not correspond with the cone penetrometer truck depth gauge after the initial two pushes at the Atlantic site. Because accurate measurements from the cone penetrometer truck push rod depth gauge were available, depth corrections were made. The failure of the depth recording device was caused by slippage of the ROW device's depth measuring wheel during the push. The depth recording wheel is made of a smooth hard plastic. **ROST™** technicians are considering replacing the hard plastic with a more slip resistant material.
- The depth of penetration of the CP was limited to 30 to 35 feet bgs at the Atlantic and York sites. This limitation was imposed by the cone operator in an attempt to prevent damaging the equipment. This decision was based on the subsurface stratigraphy. During the pushes at these sites, soft clay or silt layers were logged by the CP as occurring above a harder sand or stiff clay zone at the terminal end of the pushes. Since the overlying soft clays and silts do not provide lateral support for the push rods, pushes were terminated as soon as any hard zone, relative to overlying zones, were encountered. Even with the relatively shallow push depths, the **ROST™** technology was able to

apparently map the vertical extent of elevated fluorescence at all three sites.

Data Presentation

To qualitatively assess the abilities of the **ROST™** technology to identify the subsurface physical properties of a site, it was necessary to collect soil physical data at each of the five sample nodes at each site. The nodes were arranged in a transect line across a known area of subsurface soil contamination, which was identified during predemonstration sampling and previous investigations conducted at each site.

The soil texture data generated by the technology was used to produce soil texture cross sections along each transect line. A comparison of its data to that of the reference methods is discussed in Section 5. The following sections present chemical and physical data for the **ROST™** technology by site.

Chemical Data

The **ROST™** sensor and CP sensors data is presented and discussed as cross sections. The comparative evaluation of this data against the reference methods is discussed in Section 5. The **ROST™** data used for the quantitative evaluation in Section 5 is presented in Tables 4-1, 4-2, and 4-3.

The **ROST™** LIF logs are plotted as relative FVD and are used to describe the relative distribution of subsurface contaminants. The WTM's are used to identify changes in contaminant type. The **ROST™** did not produce its own cross sections, therefore, PRC prepared **ROST™** LIF cross sections based on the FVD data, and on scales that matched the ones used for the reference methods. The contour intervals for the cross sections were based on order of magnitude ranges. The **ROST™** technology's standard graphical outputs are panel plots of relative fluorescent intensity versus depth and WTM's. The written data evaluation of these cross sections is presented below.

The **ROST™** LIF data is reported as fluorescence intensity relative to the fluorescence intensity of a 20,000 ppm gasoline standard. Theoretically, changes in intensity relative to the standard can be used to assess relative changes in concentrations of subsurface fluorescing materials, such as the PAHs associated with coal tars and petroleum fuels. In practice, as the LIF intensity increases, the concentration of fluorescing contaminants also may increase. One objective of this demonstration was to directly evaluate the relationship between changes in the **ROST™** LIF intensity data and changes in contaminant concentrations.

The following data summary was provided by the **ROST™** personnel, and represents a typical narrative data evaluation provided by **ROST™**. PRC edited this evaluation and removed text that was not directly related to cross section definition.

Atlantic Site

The **ROST™** LIF and CP measurements at the Atlantic site were carried out from approximately midday on Sunday, August 14 to midday on August 16. Three pushes were made on Sunday to test the **ROST™** performance after it was integrated into the cone penetrometer truck, which was provided and operated by personnel from Fugro. A new device to log depth information independent of the push rod depth gauge was also tested for the first time. It used a rotary encoder which was attached to a roller wheel pressed up against the push rods.

The final demonstration plan (PRC 1994) called for two pushes at each node. Three pushes were made at Node 2, but the data from the first push was discarded because of a depth encoding error. All FVD readings were measured at a fluorescence monitoring wavelength of 400 nm, except for pushes at Node 1, which were performed at 340 nm. The choice of 400 nm for the monitoring wavelength was a compromise since a mixture of coal tar and gasoline contamination was expected at the site; the optimal (most sensitive) wavelength for gasoline detection is around 350 nm, whereas coal tar gives the strongest signal at about 500 nm.

The FVDs are discussed and grouped by node. All of the FVDs were normalized by dividing the actual measured fluorescence intensity at each depth by the intensity of the 20,000 ppm gasoline standard. After the FVD was interpolated to 0.1-foot depth intervals, it was then background corrected. Once the data is background corrected, negative values can be produced as artifacts of background noise (variance), and should be considered zero fluorescence reading. This background corrected data was used to produce the chemical cross section presented on Figure 4-2.

Nodes 1 and 2

The official site demonstration activities began on August 15 with a push at Node 1 on the west end of the site. Based on the data from this push, Node 1 was in a background region, meaning an area of low to no contamination. This interpretation is based on the fact that the FVD was flat over the entire 33 feet of the push.

TABLE 4-1. QUANTITATIVE ROST™ DATA - ATLANTIC SITE

Node	Depth (feet)	No. of Samples	Fluorescence Reading Maximum ^a	Fluorescence Reading Minimum ^a	Mean	Standard Deviation
2	21-22	11	128.40	2.22	71.99	42.82
2	24-25	11	7.04	-2.11	2.94	2.83
3	16- 17	11	69.55	17.16	38.80	20.34
4	6.5 - 7.5	11	108.40	2.78	21.56	31.56
4	10- 11	11	223.30	126.60	174.60	26.87
4	27.5 - 28.5	11	559.20	384.40	498.00	50.31
5	16-17	11	20.89	3.25	12.61	5.63
5	23.5 - 24.5	11	174.20	3.52	67.30	69.26

Note:

^a Fluorescence readings are reported as a percentage of the calibration standard.

TABLE 4-2. QUANTITATIVE ROST™ DATA - YORK SITE

Node	Depth (feet)	No. of Samples	Fluorescence Reading Maximum ^a	Fluorescence Reading Minimum ^a	Mean	Standard Deviation
1	15-16	11	5.51	0.08	2.16	1.62
2	13.5 - 14.5	11	172.00	102.30	132.40	25.05
2	17-18	11	40.93	4.95	20.72	12.75
3	17-18	11	152.90	29.09	101.50	43.84
4	14-15	11	107.76	90.38	97.14	5.74
4	18-19	11	1.16	-3.92	-1.37	1.66
5	1.5 - 2.5	11	74.95	3.45	23.59	21.49

Note:

^a Fluorescence readings are reported as a percentage of the calibration standard.

The cone penetrometer truck was then moved to Node 2. During the first push at Node 2, a mismatch of approximately half a meter between the cone penetrometer truck and ROST™ system depth gauges was noticed. After some experimentation, it was determined that the ROST™ encoder was adversely affected by rod vibration as the hydraulic ram's push-clamp was moved during rod changes. A slight modification in Fugro's rod handling procedures eliminated the problem. The FVD of the second push at this location revealed narrow band of contamination located at 0 to 2 feet bgs and at 21.4 feet bgs. If the depth encoding error for the first push is used to correct the first push data; then there

is a good match between the two FVDs. This indicates that there is adequate back-up for the push-depth monitoring system.

It was noted that the background levels for the first several pushes on August 15 were higher than normal. Based on this observation, the ROST™ operator decided to examine the optical module. After the cone was disassembled, droplets with the odor of fuel were observed on surfaces in the optical module. The ROST™ operator believed that during a test push the previous day near a monitoring well containing free phase gasoline,

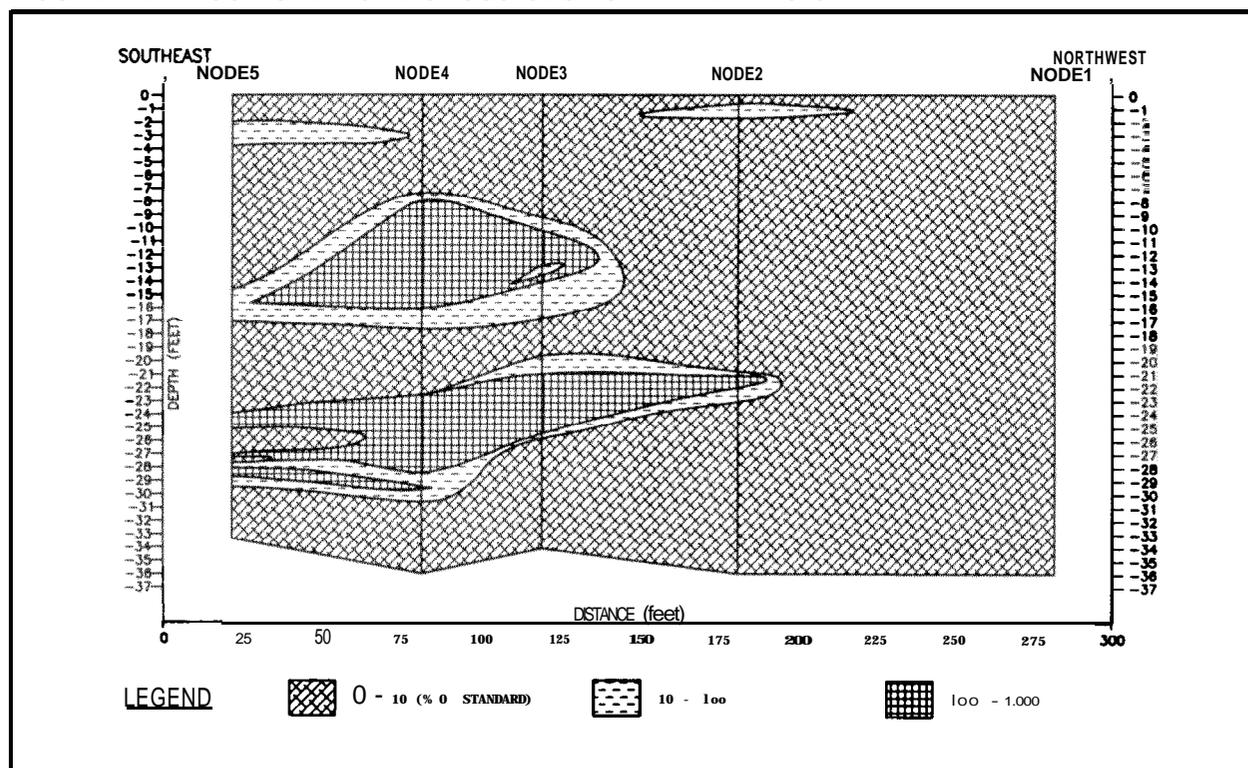
TABLE 4-3. QUANTITATIVE ROST^{MT} DATA - FORT RILEY SITE

Node	Depth (feet)	No. of Samples	Fluorescence Reading Maximum ^a	Fluorescence Reading Minimum ^a	Mean	Standard Deviation
1	2-3	11	44.13	-0.32	16.94	15.62
1	13-14	11	0.35	-0.53	-0.20	0.26
2	6-7	11	57.26	6.50	34.88	18.66
2	17-18	11	143.90	87.15	120.20	17.04
5	10.5- 11.5	11	216.90	164.00	188.40	20.05
5	16- 17	11	208.20	96.13	171.07	41.15

Note:

Fluorescence readings are reported as a percentage of the calibration standard.

FIGURE 4-2. ROST CHEMICAL CROSS SECTION - ATLANTIC S



the cone passed through a thick zone of gross gasoline contamination. Some of this fuel contamination probably leaked into the cone and then worked its way into the optical module overnight. The high, constant background levels were believed to be caused by gasoline contamination on the optical components inside the sensor. The wavelength-time matrices discussed below support this interpretation. Even after the original background correction was applied, the effect of the

elevated background was still detected in the form of a noisier than usual baseline.

After the optical module was cleaned and reassembled, a third push was made at Node 2. The background had been reduced by more than a factor of 10 after the maintenance. In all aspects, the FVDs at Node 2 were exceptionally consistent, probably as much so as at any of the nodes at all three sites.

The cone penetrometer truck was then returned to Node 1 for a second push as a background check.

Nodes 3 and 4

Based on site-specific historical data, the heart of the coal tar source was thought to lie slightly south of Node 3. The FVDs for Node 3 reveal intense fluorescence; maximum amplitudes reach nearly 1,000 percent of the standard. However, even greater fluorescence intensity was found at Node 4. Not only were the signal amplitudes much higher at Nodes 3 and 4 than at Node 2, but the contamination also extended over much thicker depth intervals. Taken as a whole, the four FVDs at Nodes 3 and 4 give a clear indication of two separate, upper and lower, zones of contamination. The fluorescence signal in the upper zone extended from 10 to 17 feet bgs at Node 3 and it was slightly broader (7 to 19 feet bgs) and stronger at Node 4. The lower zone extended from 21 to 31 feet bgs. The FVDs in the lower zone appeared to be more variable than in the upper zone.

Node 5

Node 5 is located across Poplar Street east of the coal gasification site. The distance from Node 4 to Node 5 is considerably greater than the separation between Nodes 3 and 4. Based on historical data, the subsurface groundwater flows to the north. This means that the coal tar plume would have to move a considerable distance cross gradient to reach Node 5. On the other hand, Node 5 is closer to one of the sources of gasoline contamination found at this site.

In general, the contamination at Node 5 was not nearly as great as at Node 4 to the west. Between 24 and 29 feet bgs, there were several very narrow (less than 0.5 feet thick) layers of high concentration contamination. In the second push at Node 5, the contamination reached over 1,500 percent of the standard. It seems likely that it was associated with free phase contaminants moving in a seam; however, the corresponding cone penetrometer truck-generated subsurface geological data offered no evidence of such a seam. Both of the Node 5 pushes exhibited nearly constant high or low fluorescence intensity from ground surface to about 15 feet bgs. This phenomenon was not related to the background elevation problems observed at Nodes 1 and 2. As supported by the fact that the signal returned to background levels from 18 to 24 feet bgs.

Twenty-two WTM analyses were acquired during the course of this demonstration. This data was used to identify types or classes of contaminants. Most of the

WTMs were dominated by the fluorescence of coal tar (Figure 4-3). The exceptions included the ones taken at Node 5 near the source of the gasoline contamination, the ones produced when samples of free-phase gasoline from on-site monitoring wells were analyzed, and two taken relatively near the surface at Nodes 4 and 5, 10.43 feet bgs and 10.79 feet bgs, respectively. The WTM taken at Node 5 resembled free-phase gasoline collected just east of Node 5 (Figure 4-3). The WTM taken at the surface at Nodes 4 and 5 bore some resemblance to gasoline and were distinctly different from coal tar; they most likely represented a mixture of coal tar and gasoline (Figure 4-3).

York Site

The LIF and CP measurements were carried out sequentially from Node 1 to Node 5 with a couple of exceptions. This data was used to produce the chemical cross section presented on Figure 44. After the first push at Node 1 showed that there was very little contamination at this location, the cone penetrometer truck was moved to Node 2. The two pushes at Nodes 2 and 3 were completed before returning for the second push at Node 1. The two pushes at Node 4 went smoothly. After the first push at Node 5, the fiber optic probe suffered a cable break and stopped further data gathering activities for the day.

WTM were obtained in an attempt to identify the types or classes of contaminants present at this site. Based on WTM coal tar was the dominant contaminant at the site (Figure 4-5). However, there is a thin seam of contamination, apparently irregularly spaced around the site, restricted to the upper foot or two of the ground surface. This zone's WTM resembled some type of waste oil.

Node 1

Minimal contamination was observed in the two pushes at Node 1. Each push revealed a slight increase in relative fluorescence intensity between 0.0 and 1 foot bgs. This zone exhibited a stronger relative intensity for the first push. The first push at Node 1 exhibited a nearly constant background of approximately 6 percent of the standard, dropping to baseline at about 12.5 feet. Two narrow low intensity fluorescent areas, equivalent to 5 to 7 percent of the standard, were observed at 15.0 and 16.8 feet bgs in both pushes.

Nodes 2 and 3

The two pushes at Node 2 revealed contamination extending from 10 to 19 feet bgs. There was about a

FIGURE 4-3. TYPICAL WTM - ATLANTIC SITE

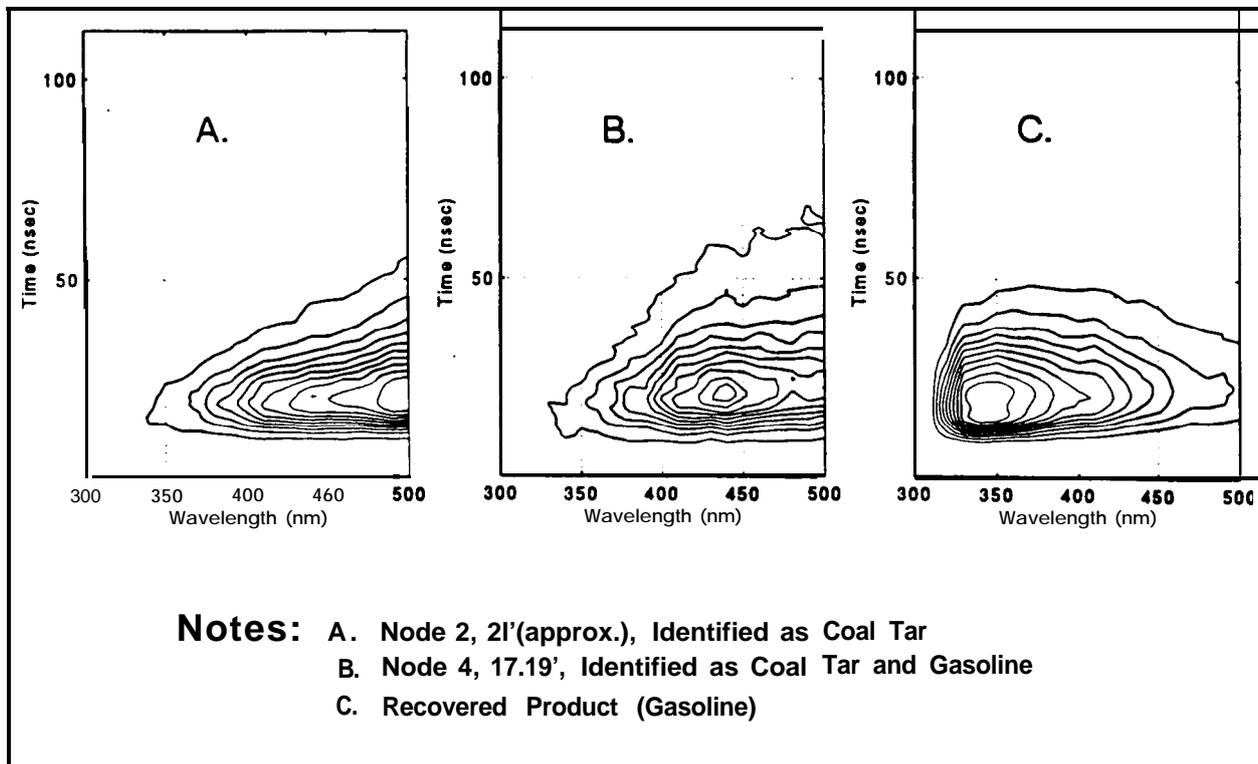


FIGURE 4-4. ROST™ CHEMICAL CROSS SECTION - YORK SITE

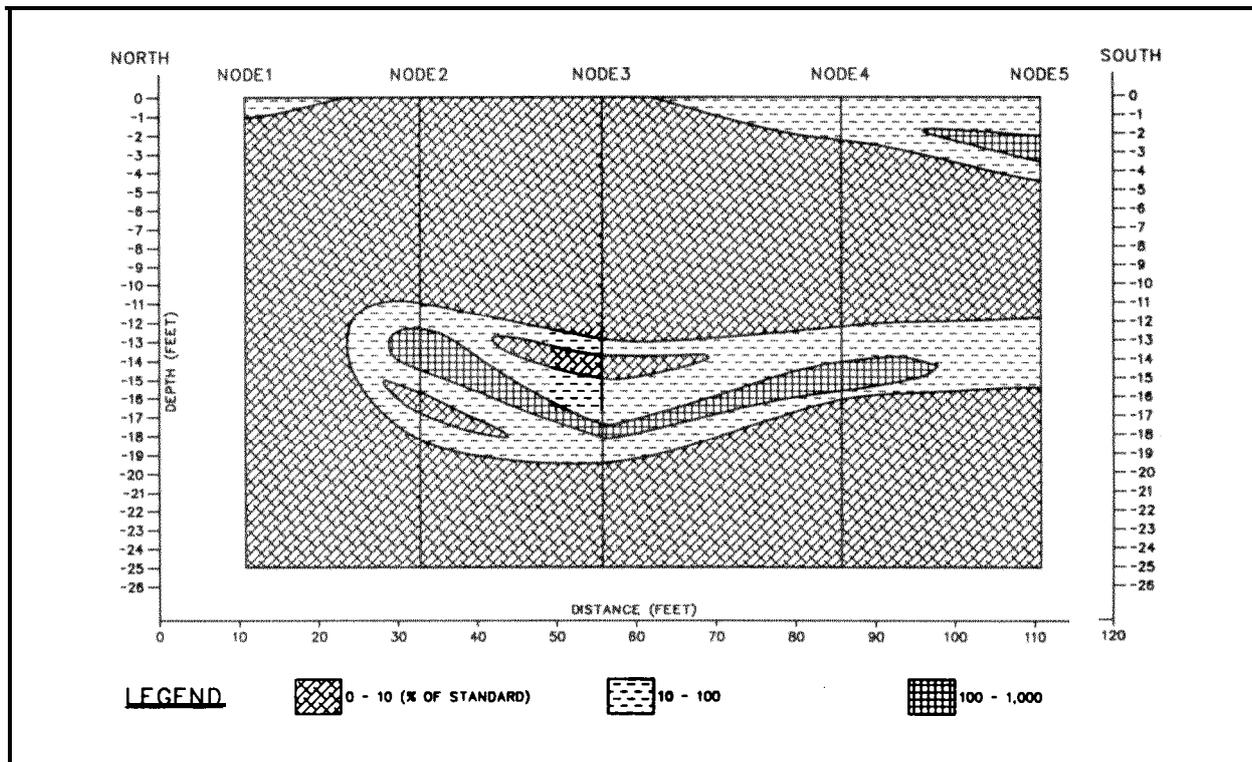
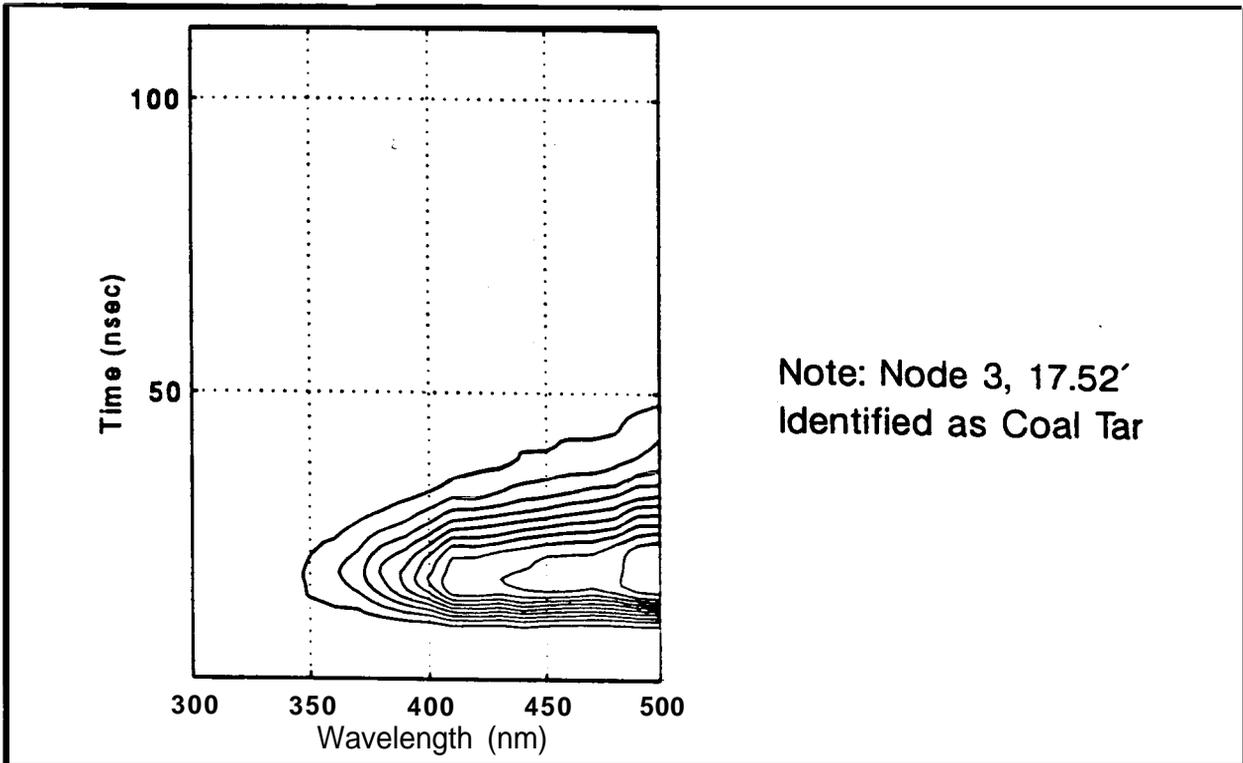


FIGURE 4-5 TYPICAL WTM - YORK SITE



two-fold variation in the fluorescent intensity between the two pushes. The highest fluorescent intensity for this interval was 84 percent of the standard during the second push.

The contamination at Node 3 resembled that at Node 2. The contamination occurred in a slightly deeper range, 12 to 20 feet bgs. The second push showed signals only about half as great as those for the first push.

Nodes 4 and 5

The relative intensities for the two pushes at Node 4 were in good agreement, within 25 percent, but there was more spatial variability as exhibited by FVDs. The level of contamination was lower than at Nodes 2 and 3, being about 20 percent of the standard integrated over the 10 to 20 foot bgs interval. The second push detected a deeper zone of contamination extending from 19 to 22 feet bgs.

The first push at Node 5 was consistent with the previous results. An increase in fluorescence was detected between 11 and 16 feet bgs. However, nearly as high contamination occurred in the 0.0 to 5 foot bgs zone, and the signal remained elevated above background between 5 and 11 feet bgs. Peak intensities

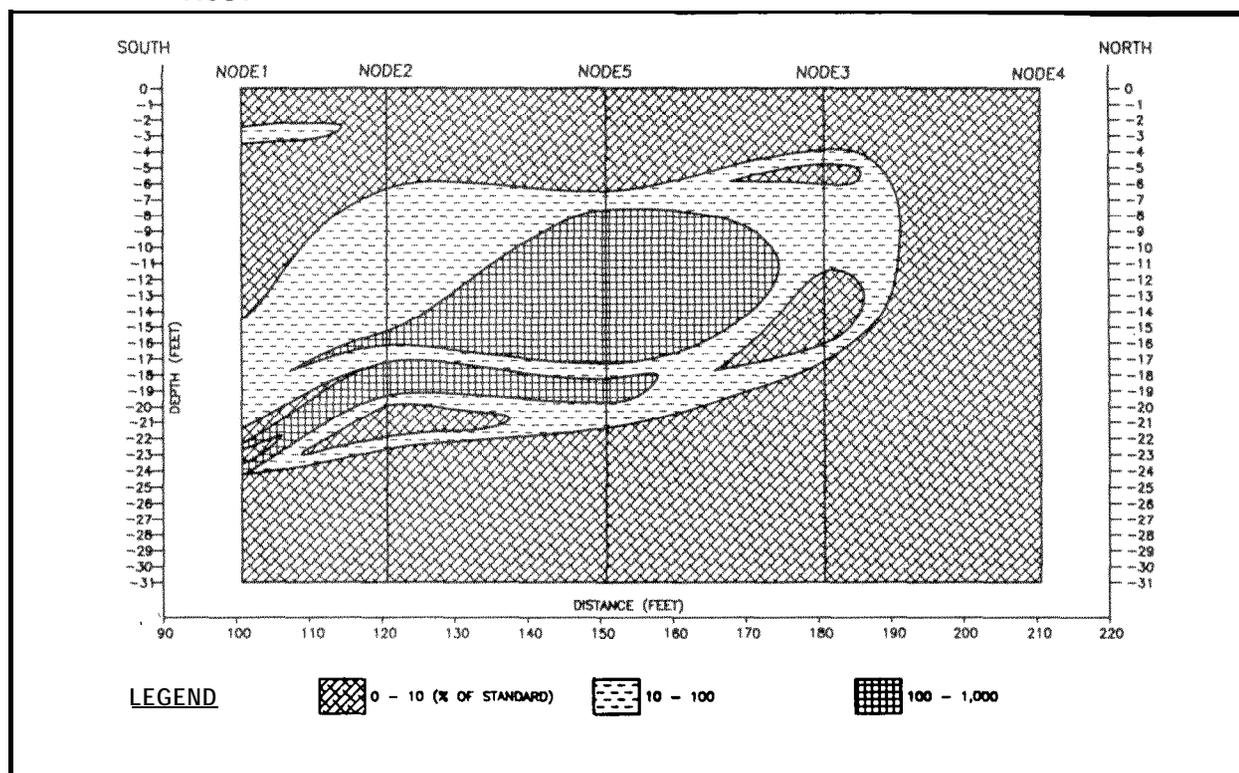
in both the 0- to 5-foot bgs and the 11- to 16-foot bgs intervals exceeded 60 percent of the standard. The fiber optical cable broke after the completion of the first push. After an overnight repair, the investigation resumed in the morning. Two more pushes were made at Node 5. These showed a very flat, broad zone of contamination, after an initial contamination spike in the first few feet. This was very different than the first push at this location the previous day.

Fort Riley Site

Node 1

The two pushes at Node 1 showed some spatial variability. The principal zones of contamination were in the intervals from 2 to 4 feet bgs, 15 to 22 feet bgs, and below 22 feet bgs. This is shown in the FVD presented on Figure 4-7. This type of intra (FVD) output is typical for the **ROST™**. The LIF CP measurements were carried out sequentially from Node 1 to Node 5. This data was used to produce the chemical cross sections presented on Figure 4-6. The monitoring wavelength chosen for this site was changed to 360 nm based on historical data regarding potential contaminants present on site. This information indicated that diesel fuel would be the primary contaminant found at this site.

FIGURE 4-6. ROST™ CHEMICAL CROSS SECTION - FORT RILEY SITE



A fluorescence peak was detected at 2 to 4 feet bgs. The overall fluorescence intensity, at this depth, for the second push was more than five times greater than for the first push, indicating spatial variability in contamination distribution.

A second fluorescence peak was detected at 15 to 22 feet bgs. The distribution of contamination in this zone agreed very well for the two pushes. There appears to be a segmentation of this zone into an upper part and a lower part. The upper part agreed very well for the two pushes. However, the magnitude of the contamination was approximately 10 times higher for the second push in the lower half of the zone. The signal returned to baseline at 22 feet. This depth corresponds to a transition zone from clay to sand occurring between 22 and 25 feet bgs, as recorded by the cone penetrometer.

A third fluorescence peak was detected at depths below 22 feet bgs. The lowest portion of this zone was highly variable between the two pushes. The intensity was much higher for the first push than for the second. The contamination detected in the 22- to 23-foot interval was 2 to 3 times more intense for push 1. Elevated fluorescence intensity was only detected in the 23- to 24-foot interval in the first push.

Significant contamination was found at Node 1. If the contaminant is diesel, then concentrations in excess of 10,000 **mg/kg** are present. However, this appeared to be a highly variable region. It is possible that the close proximity of the two pushes modified the contaminant distribution relative to the sampling volume of the LIF sensor.

Two WTM were recorded at Node 1 from 15 to 22 feet bgs. The wavelength time matrices recorded in Node 1 in the 2- to 4-foot bgs interval showed good consistency and strongly resemble diesel fuel (Figure 4-8). Spectrally, their distribution shifted to somewhat shorter wavelengths than the WTM recorded in the 2- to 4-foot bgs interval. They still retained most of the characteristics of diesel fuel; however, the slight differences may indicate that the diesel fuel has been slightly modified by transport. The shift to shorter wavelength would be consistent with relative loss of the larger, less mobile PAHs, whose emissions tended to occur at longer wavelengths. One WTM was obtained at 22.47 feet bgs in the first push.

This WTM was completely different from all the rest in this node. The 340 nm and the entire intensity distribution shifted to shorter wavelength. The WTM strongly resembled that of JP-4 fuel. A third push was made at Node 1 with emission monitoring shifted to

FIGURE 4-7. FVD - FORT RILEY SITE

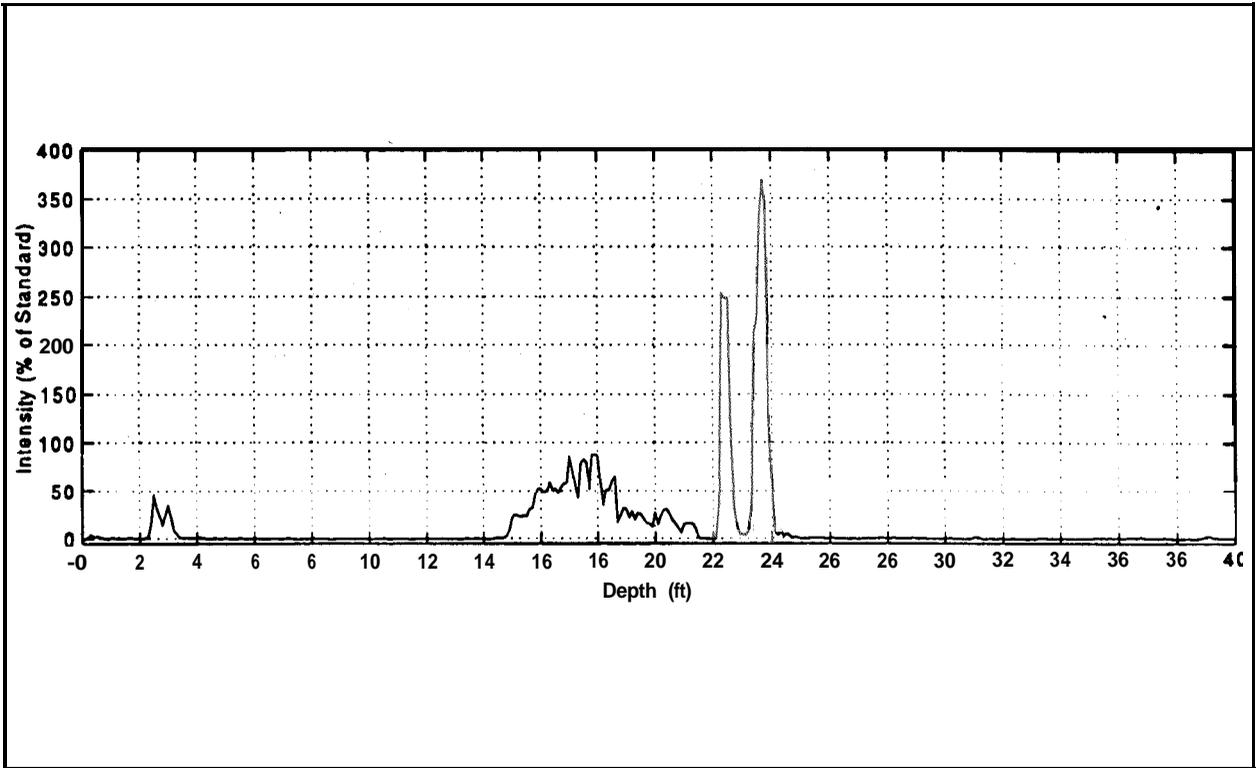
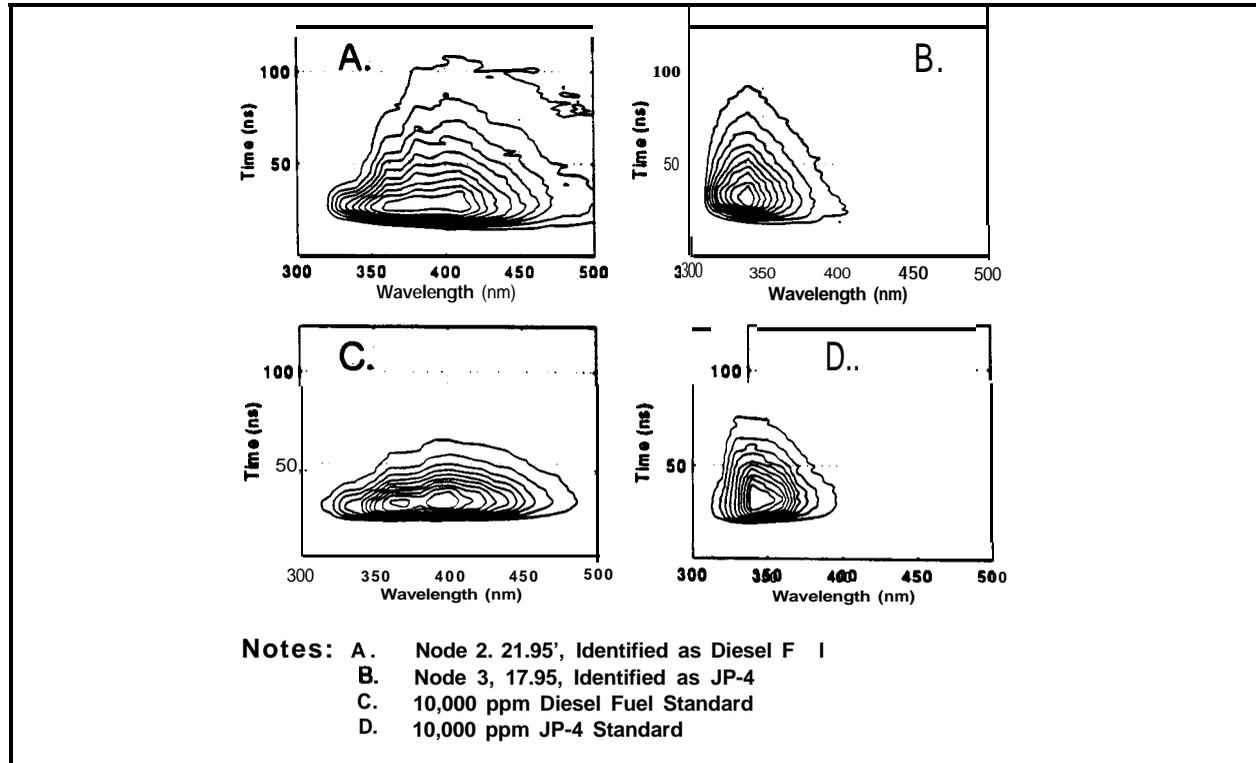


FIGURE 4-8 TYPICAL WTM - FORT RILEY SITE



340 nm. This change in monitoring wavelength was made to optimize the system for the apparent JP-4 contamination. However, no changes in measured fluorescence were observed at this altered monitoring wavelength.

Node 2

The two pushes at Node 2 produced similar LIF data, indicating relatively uniform contaminant distribution. The maximum depth contamination is comparable to that at Node 1. Six WTM were measured at Node 2. There was little variation between them; each one resembled diesel fuel.

Node 3

The pushes in this node were highly variable, similar to Nodes 1 and 2. The pattern of fluorescence for both pushes between 13 and 19 feet bgs showed good similarity, but the amplitudes varied. The overall signal was more than three times higher for the second push at this node. However, in the second push there was a shallow zone of contamination that reached above 40 percent of standard. This zone was between 6 and 12 feet bgs, and it was not present in the FVD from the first push.

Node 4

This node appeared to be located in a background area. No fluorescence signal in excess of 2 percent of standard was observed in either of the two pushes.

No WTM were acquired at Node 4 since it appeared to be a background location. The Fort Riley site was a difficult site to interpret. There was a great deal of variability in pushes, even within the same node. It may be possible that this was caused by the close proximity of the paired pushes, however, this was not observed at any of the other demonstration sites. Some of the paired pushes had spatial separations of approximately 18 inches. This is well under the ASTM recommendation that pushes be separated by 20 cone diameters (32 inches). It is also possible that the variability was representative of true spatial variability of the contaminant distribution.

Node 5

Two pushes were made at Node 5. Node 5 lies between Node 2 and Node 3. The reproducibility between these two pushes was extremely good, the best at any of the nodes at the Fort Riley site. The contamination extended in a broad zone from

approximately 6.5 to 21 feet bgs. Some minor contamination was also detected at 27 feet bgs.

Six WTM were obtained at Node 5. All of them agreed extremely well. Their patterns were indicative of diesel fuel with little or no alteration due to transport or weathering.

Cone Penetrometer Data

The CP stratigraphic logs were used to construct stratigraphic cross sections for each of the demonstration sites. The CP produced individual stratigraphic logs for each push. Fugro, PRC's subcontractor for cone penetrometry services, does not produce cross sections as a standard service. PRC transferred the individual push stratigraphic data and plotted it as a cross section on a scale that matched the one used for the reference methods. The Fugro data package did not include a narrative of the site-specific geology, therefore, a PRC geologist provided the descriptions presented below by site.

Atlantic Site

The transformed stratigraphic cross section for the Atlantic site is presented on Figure 4-9. The CP technology logged the upper portion of the cross section as primarily clay with several silty clay lenses. The bottom of the clay varied from 18 feet bgs in the northwest (Node 1) to 28 feet bgs in the southeast (Node 5). In the south half of the cross section, the CP technology identified a 3-foot thick silty clay layer at about 13 to 16 feet bgs. The northern half contained a 3-foot thick silty sand layer with silty clay lenses identified in Node 1. Below 28 feet bgs in the southeast (Node 5) and 18 feet bgs in the northwest (Node 1), the cross section is predominantly sand and silty sand lenses.

York Site

The transformed stratigraphic cross section for the York site is presented on Figure 4-10. The CP technology logged the upper portion of the cross section as clay with several silty sand and silty clay lenses in the upper 12 to 14 feet bgs. Below 12 to 20 feet bgs on the south side (Node 5) and 14 and 20 feet bgs on the north side the section became predominantly silty sand with some silty clay lenses included. From 20 to 26 feet bgs the cross section was identified as sand.

Fort Riley Site

The transformed stratigraphic cross section for the Ft. Riley site is presented on Figure 4-11. The CP

FIGURE 4-9. CONE PENETROMETER STRATIGRAPHIC CROSS SECTION - ATLANTIC SITE

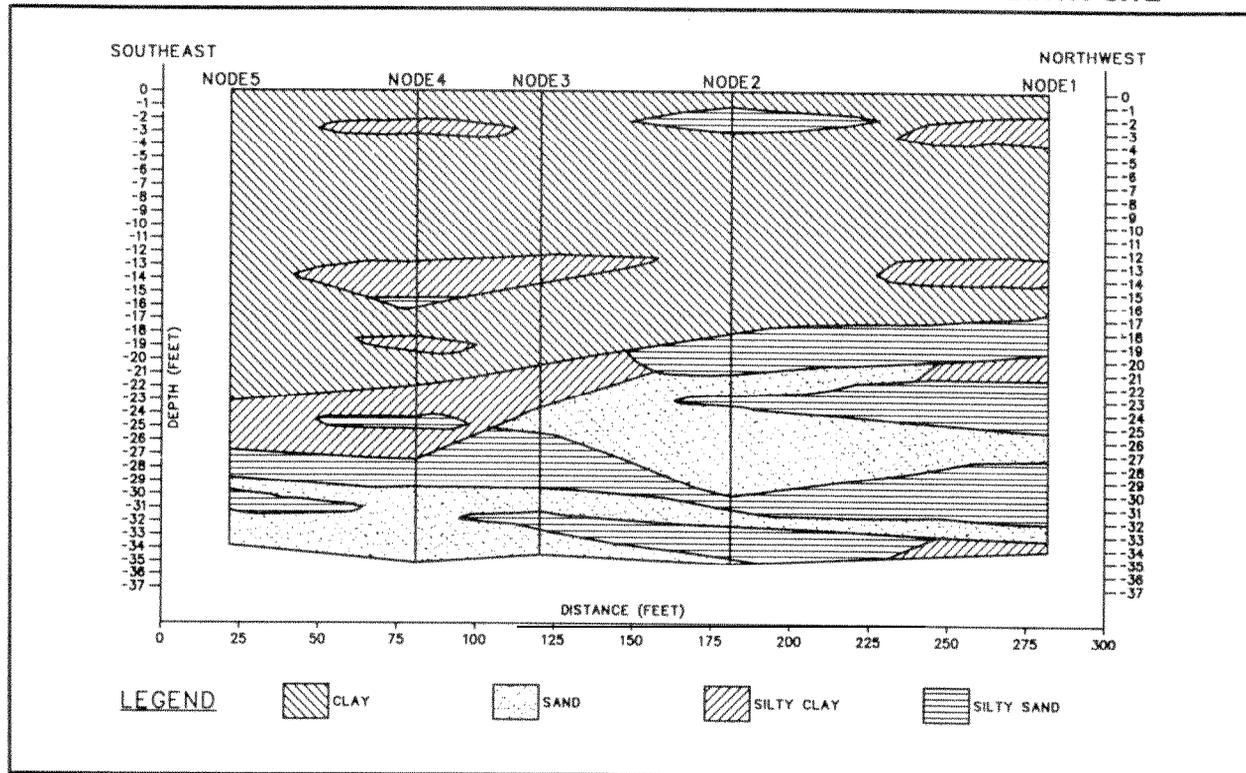


FIGURE 4-10. CONE PENETROMETER STRATIGRAPHIC CROSS SECTION - YORK SITE

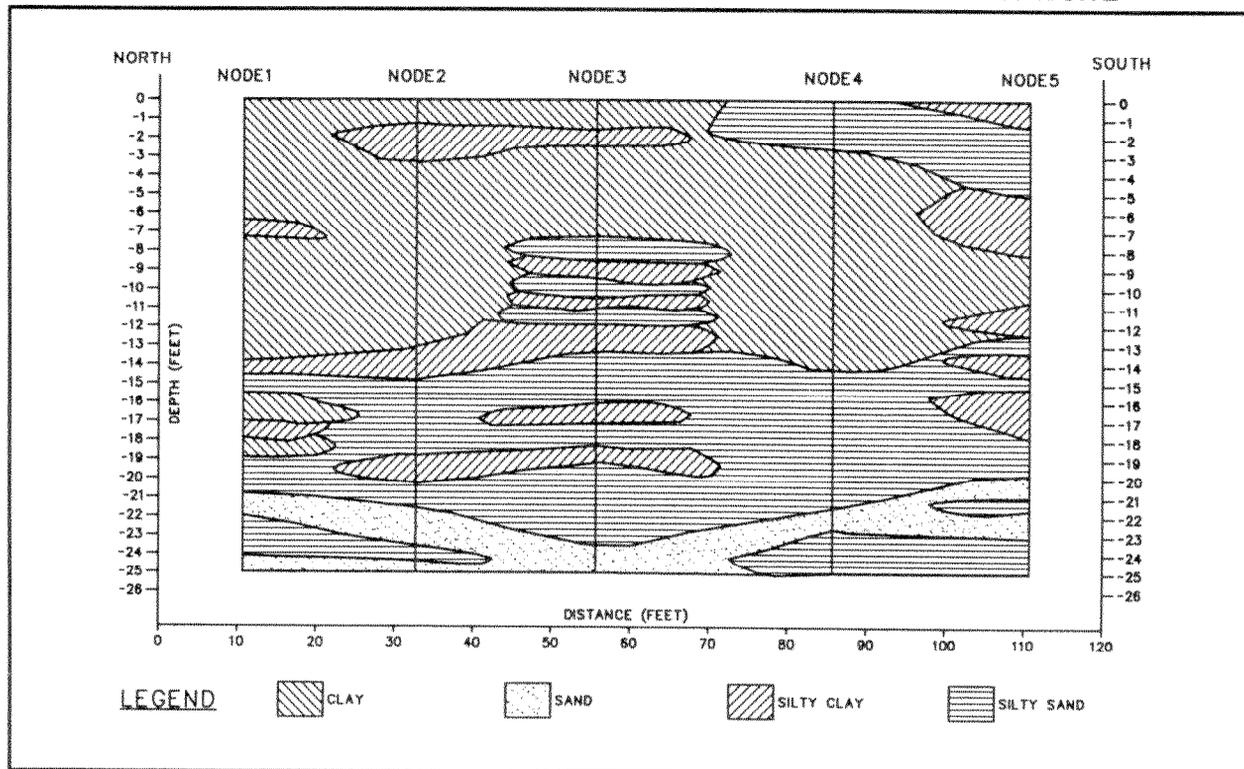
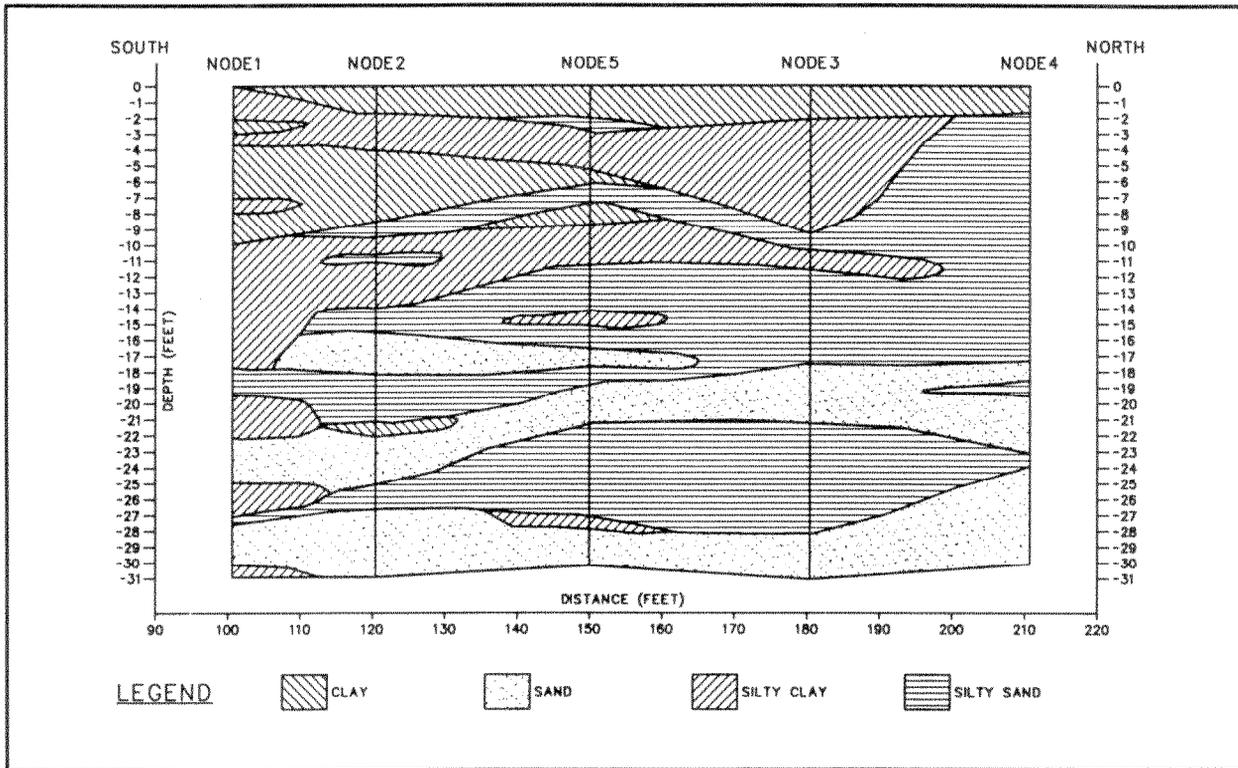


FIGURE 4-11. CONE PENETROMETER STRATIGRAPHIC CROSS SECTION - FORT RILEY SITE



technology logged most of the site as silty sand or sand with some silty clay and clay lenses. The upper 12 feet of the southern three quarters of the cross section was logged as clay and silty clay with a 2-foot-thick bed of

silty sand running across it at 7 to 10 feet bgs. From 2 feet bgs in the north (Node 4) to 17 feet bgs in the south (Node 1), the Fugro primarily logged silty sand or sand. The sand became cleaner at depth.

Section 5 Data Comparison

The data produced by the **ROST™** technology and the CP was evaluated using the criteria described in Section 1. The qualitative and quantitative data evaluations are discussed separately. The qualitative evaluation examined the chemical cross section produced from the **ROST™** data, and stratigraphic cross sections produced from the CP data. The quantitative evaluation statistically compares the **ROST™** technology's data with analytical data produced by the reference methods.

Qualitative Assessment

The qualitative assessment presents the evaluation of both the stratigraphic and chemical mapping potential of the **ROST™** and CP relative to the reference methods. In addition, the potential affects of TOC on the **ROST™** technology's measurements are examined. Both the reference and technology cross sections were produced from collocated sampling areas as discussed in Section 1. Since these methods were sampling spatially different locations, matrix heterogeneity will impact the comparisons of both the physical and chemical cross sections. Based on a review of the demonstration data, this impact appears to have had minimal impact on the qualitative data evaluation. The qualitative nature of the comparisons, and the level of data quality may have masked much of the effect of matrix heterogeneity for this evaluation.

Stratigraphic Cross Sections

The following sections present descriptions of the similarities and differences observed between the stratigraphic cross sections produced from the CP data and the reference method. For this comparison, PRC used the CP sensor cross sections shown in Section 3. These cross sections were produced directly from the individual stratigraphic logs produced at each node. These cross sections have been produced at the same scale as the reference stratigraphic cross sections shown in Section 2. These comparisons are qualitative and, as such, are subjective in nature. However, these

comparisons were made by a certified professional geologist (American Institute of Professional Geologists) with over 17 years of experience in this field.

Atlantic Site

The cone penetrometer truck subsurface geological cross section compared favorably to the reference methods' cross section as far as general mapping of stratigraphy. The CP logged the upper portion of the cross section primarily as clay with several silty clay lenses. The corresponding portion of the reference stratigraphic cross section identified this portion as silty clay and clayey silt with several silt lenses. The depth of the clay and silty clay in the CP cross section varied from 19 feet bgs in the northwest (Node 1) to 28 feet bgs in the southeast (Node 5), and the reference cross section identified these same soil textures at 21 in the northwest (Node 1) and 28 feet bgs in the southeast (Node 5). Below 28 feet bgs in the southeast (Node 5) and 19 feet bgs in the northwest (Node 1), the CP cross section is predominantly sand with silty sand lenses which closely matches the reference cross section.

At the Atlantic site, the technology showed good correlation with the respective reference geological cross sections. However, one difference was noted. The reference methods had trouble collecting samples for logging purposes in the running sands that generally occurred from 20 feet bgs to the termination of the borehole. This lack of complete sample recovery is common for this method of borehole logging. The on-site geologist used indirect logging methods, such as logging drill cuttings or monitoring drilling rates and down pressure of the drill rig during drilling, to fill in the resultant gaps in the borehole logs at depth. The CP technology does not need to physically collect soil samples to produce borehole logs, and thus, is not as affected by running sands. This explains the greater detail shown in the CP cross section below approximately 20 feet bgs.

Seven samples were collected at the Atlantic site for geotechnical analysis. Only six of these samples corresponded to measured intervals by the CP. The results of these analyses were compared to the corresponding CP stratigraphic data. Three out of the six samples showed intermethod agreement. The three remaining samples were not matched due to the CP, once overestimating the fraction of fines (DR19), and twice underestimating the percentage of sand (DR17 and DR18). This resulted in the CP technology identifying intervals as silty sand when it was identified by the reference methods as a sand once, and identifying a sandy lean clay as a clay or silty clay twice. This indicates that the CP technology cannot resolve small shifts in particle size distribution.

York Site

The CP stratigraphic cross sections showed good correlation with the reference cross sections at the York site. The CP did not identify the surface fill which was identified by the reference methods as extending from the ground surface to 2 feet bgs. Below this zone, the CP logged primarily clay with several silty sand and silty clay lenses extending from 12 to 14 feet bgs. The reference methods logged this section similarly except that the clayey silt extended from 15 to 19 feet bgs. The CP logged the remainder of the section below 12 feet bgs, on the south side (Node 5), and 14 feet bgs, on the north side (Node 1), as predominantly silty sand and sand with some silty clay lenses included. The reference methods identified this same portion of the section as well graded sand with silt and silty clay and sandy silt lenses. The lack of correlation relative to the thin sand, silt, and clay lenses may be more representative of the reference methods' inability to resolve thin strata, in a standard field logging mode. The detail of the reference method can be increased by spending more time examining sample cores, however, time and cost factors often prohibit fine detailed examination of sample cores. The CP produces the same level of detail whenever it is used. Running sands were not a problem at this site.

Six samples were collected at the York site for geotechnical analysis. The results of these analyses were compared to the corresponding CP stratigraphic data. Four out of the six samples showed intermethod agreement. The remaining two samples were not matched due to the CP's lack of resolution relative to detecting small increases in the distribution of coarse particles (Node 1-18.5 to 19 feet bgs and Node 3-16.5 to 17 feet bgs). This indicates that the CP has trouble resolving shifts in coarse particle size distribution in a matrix dominated by silts and clays, relative to the reference methods.

Fort Riley Site

The CP's cross sections showed good correlation with the reference methods' cross sections at the Fort Riley site. The CP technology logged most of the section as silty sand or sand with some silty clay and clay lenses as did the reference methods. The upper 12 feet of the southern portion of the CP cross section is logged as clay and silty clay with a 2-foot-thick bed of silty sand extending from 7 to 10 feet bgs. The reference methods did not identify the sand layer, rather it logged it as silty clay, silt and fill. From 2 feet bgs in the north (Node 4) to 17 feet bgs in the south (Node 1), the CP primarily logged silty sand or sand. The reference methods logged this as poorly graded sand starting at 5 feet bgs in the north (Node 4) and extending to 19 feet bgs in the south (Node 1). The sand logged by the CP became well graded at depth; this agrees with the reference methods which identified all the sand below 17 feet bgs as well graded sand. The CP exhibited a finer resolution of stratigraphy in the saturated sands identified at depth. This is similar to the findings at the Atlantic site.

Eight samples were collected at the Fort Riley site for geotechnical analysis. The results of these analyses were compared to the corresponding CP stratigraphic data. Six of the samples showed acceptable intermethod matches. The two samples that did not match may have been caused by the CP's inability to resolve small change in particle size distributions. The CP identified one sample as a silty clay when the reference method laboratory identified the sample as a silty sand or sandy clay and the second sample was identified as a sand by the CP and as a silty or clay sand with gravel by the reference method (DR02 and DR05, respectively).

Summary

The CP and the reference methods produced similar stratigraphic cross sections relative to the reference method. Generally, the CP and the reference methods showed good agreement in identifying the dominant particle size in soil. However, the CP did show deviation from the reference methods when small shifts in particle size distribution occurred. However, the CP provided a finer resolution of strata, identifying more thin stratigraphic units than the reference method. This difference was magnified when running sands were encountered at the Atlantic and Fort Riley sites. This may be due to its ability to continuously acquire soil textural data during a push, and the common limitations of a geologist's logs where strata are less than several inches thick. An additional difficulty with the reference methods was their inability to retrieve samples from running sands. This caused significant data gaps at

depth. The CP does not require active soil sampling to log a hole, and therefore, it is not as affected by running sands, and may produce more representative subsurface stratigraphic logs than the reference methods in running Sands.

Chemical Cross Sections

The following sections present descriptions of the similarities and differences observed between the chemical cross sections produced from the **ROST™** data and the analytical results from the reference methods. Unless otherwise specified, the comparisons are made in consideration of both reference cross sections, TPH and total PAH. PRC used the **ROST™** cross sections shown in Section 3 and the reference cross sections shown in Section 2 to conduct this evaluation. The **ROST™** LIF cross sections were made directly from the **ROST™** LIF data, and plotted to the same scale as the reference method cross sections. These comparisons are qualitative and, as such, are subjective in nature. The effects of heterogeneity may influence this data comparison, however, the qualitative nature of this comparison should greatly reduce the potential impact of heterogeneity in contaminant distribution. These comparisons were made by a soil scientist with over 9 years of experience in site characterization activities.

Atlantic Site

Both the **ROST™** and the reference methods showed good correlation for background characterization. This is exhibited by both the **ROST™** and the reference method's data showing Node 1 to be outside the area of contamination. Both the **ROST™** and the reference methods identified shallow contamination intermittently spaced across the cross section within 5 feet of the ground surface. Both the **ROST™** and the reference methods detected the zone of contamination at Node 2, which extends from approximately 20 to 28 feet bgs for TPH and from 16 to 31 feet bgs for total PAH. The **ROST™** identified this zone being from 2 to 9 feet thinner than the reference method for TPH and total PAH, respectively. This difference can be explained as an artifact of data interpolation which was used for the reference method to create the reference cross sections. This is common when relatively few samples are used to define zones of contamination. Both the **ROST™** and the reference methods identified a zone of elevated contamination 1.5 feet bgs at Node 2.

Overall, the remaining zones of elevated **ROST™** data corresponded with general zones of contamination shown in both reference cross sections. The differences, such as upper boundaries of contamination and

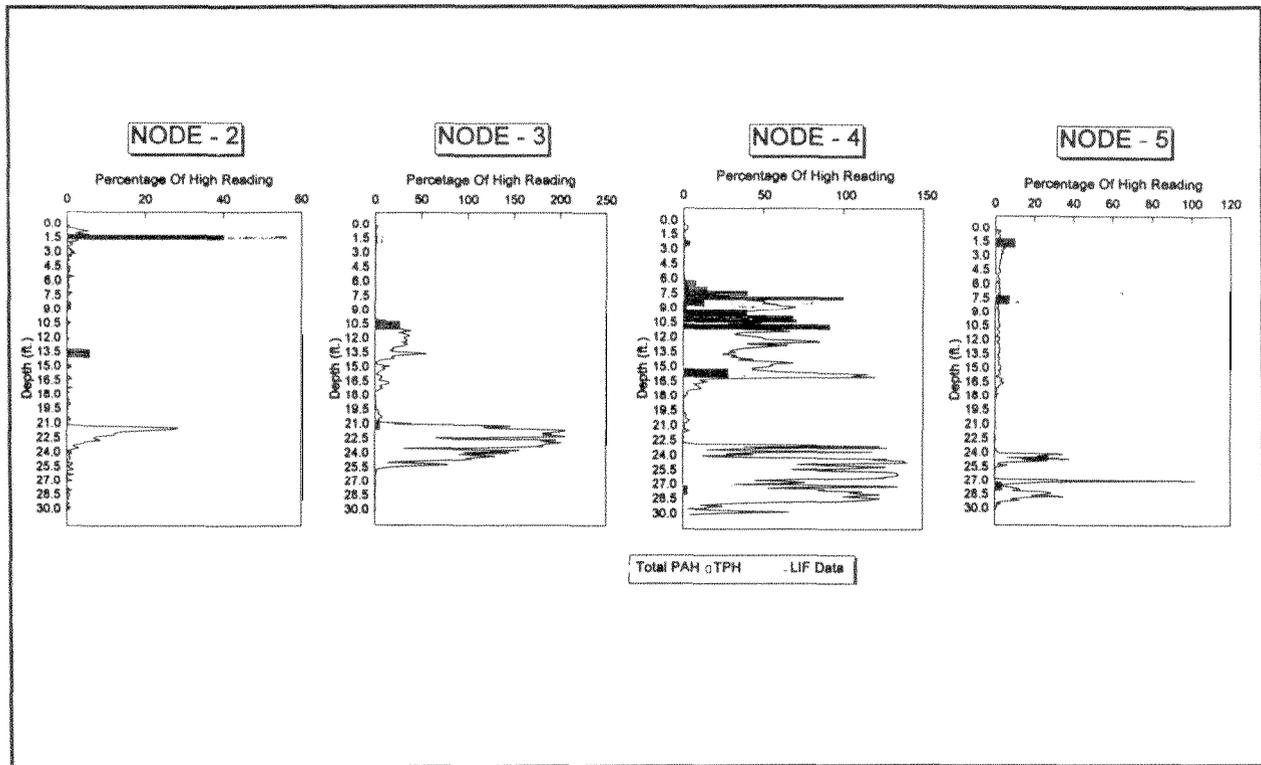
delineation of distinct zones of contamination in the cross sections, can be attributed to a data interpolation artifact of the reference methods.

The major differences between the **ROST™** and the reference two methods were exhibited at Node 5. At Node 5, the **ROST™** technology identified three distinct plumes occurring from approximately 2 to 4 feet bgs, 14 to 17 feet bgs, and 24 to 30 feet bgs. The reference method produced a single TPH plume at Node 5 extending from the ground surface to approximately 27 feet bgs. Historical data for this site indicated that the zone of extended contamination shown in the reference TPH cross section reflected gasoline contamination exclusively. The total PAH cross section produced by the reference method identified two zones of contamination: one extending from approximately 0.0 to 1 foot bgs, and a second zone extending from 6 to 17 feet bgs. These two zones overlap the upper two zones identified on the **ROST™** cross section, however, their thicknesses and depth intervals vary. This variance may be due to the difference in data collection techniques discussed above. The lack of correlation between the deepest contamination detected by **ROST™** at Node 5 and the reference method can be attributed to the lack of sampling in this interval by the reference method. The lack of sampling was due to the failure to collect samples in the running sands below approximately 19 feet bgs.

Another way to examine the relationship between the **ROST™** LIF data and the qualitative reference data is to superimpose the two data types on a single plot of fluorescence intensity and reference method concentration against depth. To make the plot scales meaningful, the **ROST™** LIF and reference data had to be normalized. The reference data was normalized to the highest TPH and total PAH concentrations measured during the qualitative sampling. The LIF data was normalized to the average high reading measured over a qualitative method reference sampling point at this site. This normalization allows a general comparative evaluation of the data.

Figure 5-1 shows the normalized data plots for nodes where qualitative reference data was generated. In all cases where the LIF data recorded increased fluorescence relative to background, the reference data showed TPH and PAH contamination. A detailed review of this data shows that the qualitative reference data and the **ROST™** LIF data generally agree in their identification of zones of high, medium, and low contamination. Some exceptions to this can be seen in Node 3 (21 feet) and Node 4 (15.5 feet). In these cases, the LIF data identification of high contamination did not match the reference data. It is possible that these

FIGURE 5-1. NORMALIZED LIF AND QUALITATIVE REFERENCE DATA - ATLANTIC SITE



differences are due to matrix heterogeneity and/or slight errors in relative sampling depth recording.

York Site

The **ROST™** cross section showed little correlation to the reference method's cross sections at Node 1. The **ROST™** technology only detected contamination from 0 to 1 foot bgs at this node, however, the reference method detected both TPH and total PAH contamination from 12 to 18 feet bgs at this node.

Nodes 2, 3, 4, and 5 showed better correlation between the reference methods' cross sections and the **ROST™** cross section.

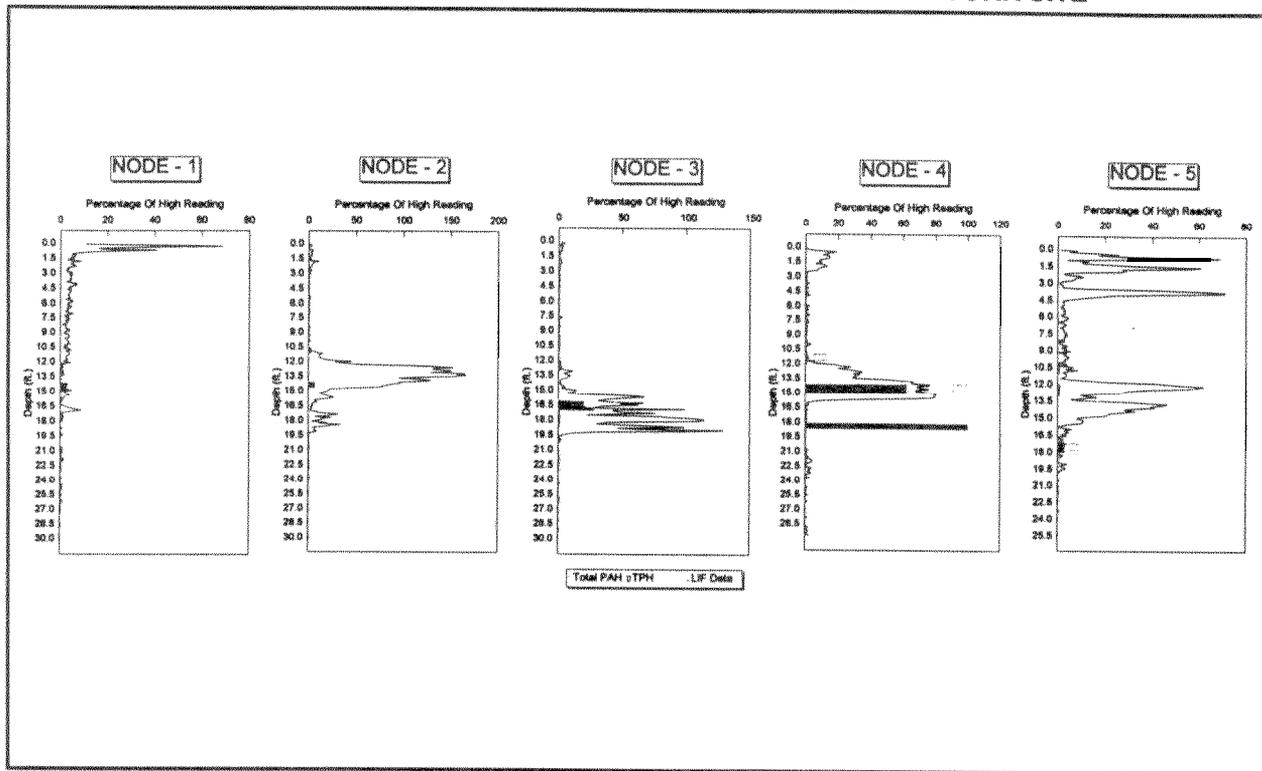
The differences between the reference cross section and the **ROST™** cross section could be the combination of an artifact of data interpolation for the reference cross section, and the finer definition provided by **ROST™** which produces continuous profiles with a 2 cm resolution. The variation between the **ROST™** and reference methods cross sections could also be attributed to the small sample volume used by the **ROST™** technology relative to the reference method.

Figure 5-2 shows the normalized line graphs of the five **ROST™** LIF pushes at the York site.

In all but one case, the LIF data exhibited elevated fluorescence relative to background, at the point where qualitative reference data reported TPH or total PAH contamination above background. At Node 4 (18.5 feet bgs), the reference data reported TPH and total PAH contamination at 100 percent and 80 percent of the highest reading, while the LIF data detected no fluorescence above background. The reference TPH concentration was 13,000 ppm, and the total PAH concentration was 1,130 ppm. The reference sampling point and the LIF sampling point was separated horizontally by approximately 2 feet. An examination of the corresponding CP log shows that at this LIF sampling interval the LIF window was measuring fluorescence inside a clay seam. It is possible that this clay lens has resisted contaminant infiltration, supporting the LIF data showing no contamination. This illustrates the value of the combined LIF and CP data. The high contamination detected by the reference sampling may reflect its larger sample volume and sample homogenization, or heterogeneity in the geometry of the clay lens.

A detailed review of the remaining data shows that the relative magnitudes between the two types of data were in agreement. Zones of high reference readings corresponded to zones of high LIF readings. This relationship appears to hold for medium and low zones of contamination.

FIGURE 5-2. NORMALIZED LIF AND QUALITATIVE REFERENCE DATA - YORK SITE



Fort Riley Site

The **ROST™** cross section showed good correlation to the reference methods' cross sections at all nodes with the exception of the upper limit of contamination at Node 1 and the middle of Node 4.

At Node 1, the **ROST™** technology found contamination primarily from 15 to 25 feet bgs, while the reference method's total PAH contamination was detected from 1 to 24 feet bgs. The reference method detected an isolated area of low TPH contamination at a depth of approximately 15 bgs in Node 4. The **ROST™** technology detected no zones of elevated contaminant concentrations at Node 4. For Nodes 2, 3, and 5, the relative depths, thicknesses, and intensities of the contamination were similar between the reference method and the **ROST™** cross sections. The differences noted at Node 1 and 4 involved low concentrations of contaminants, and it is possible that the differences were caused by matrix heterogeneity rather than due to inaccuracies of the technology.

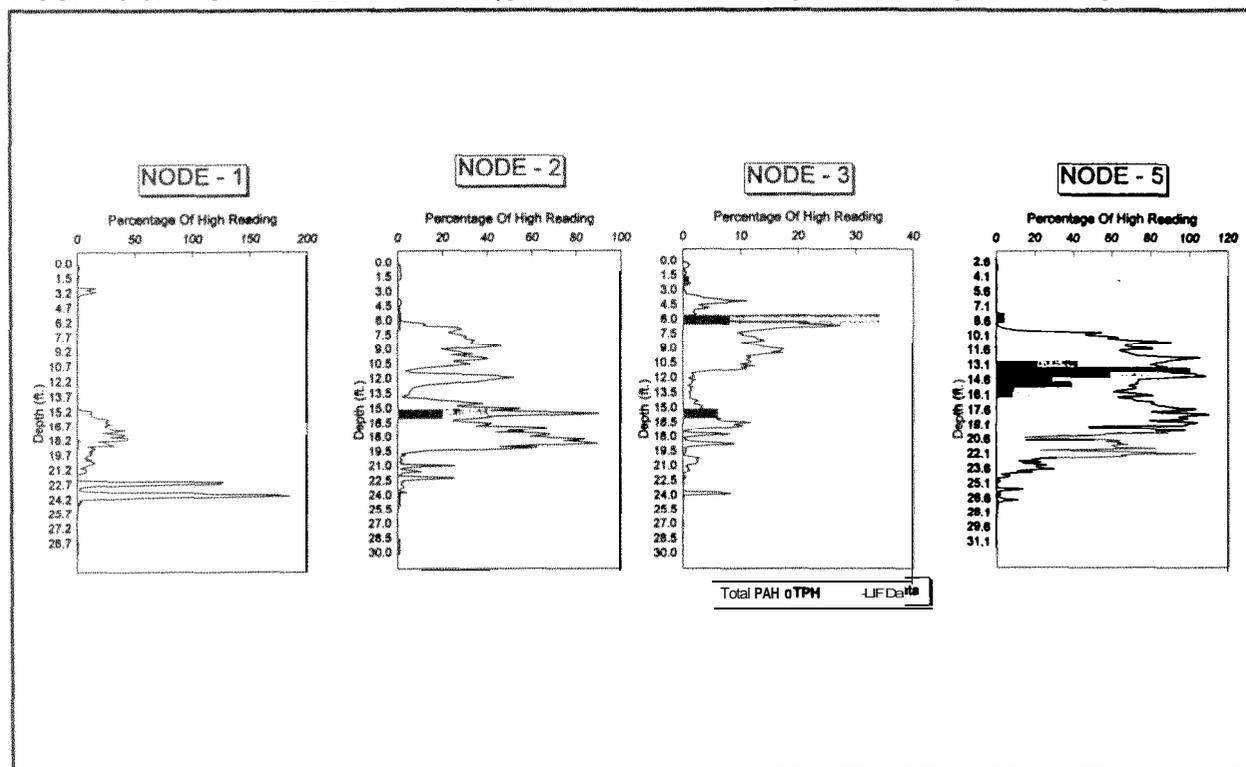
The greater definition of potential contaminant lenses in the **ROST™** cross sections was most probably due to the 2 cm sampling resolution provided by the technology. The need to interpolate data for the reference method reduced the potential for identifying distinct smaller lenses of contamination.

Figure 5-3 shows these normalized line graphs of the **ROST™** LIF pushes at the Fort Riley site. Only pushes where qualitative reference sampling was conducted are shown on this figure.

In all cases where the qualitative reference sampling detected contamination above background, the LIP data also showed elevated fluorescence. A detailed review of this data shows that for all pushes the general contamination trends identified by the technology match the trends detected by the qualitative reference data. Similar zones of low, medium, and high contamination were identified by the technology and the reference methods.

Generally, the **ROST™** technology showed a good relative correlation with the reference methods' cross sections. The **ROST™** technology provided greater resolution in identifying contaminated zones, relative to the reference method due to the absence sample collection the **ROST™** data relative to the reference methods. Sampling difficulties and cost restrictions limited the number of samples collected and analyzed by the reference methods. This forced the reference method to use data interpolation to create the cross section. In addition, the **ROST™** data and quantitative reference data were well correlated in their identification of zones of low, medium, and high contamination.

FIGURE 5-3. NORMALIZED LIF AND QUALITATIVE REFERENCE DATA - FORT RILEY SITE



The observed differences between the **ROST™** and reference methods' cross sections could be caused by several factors. The **ROST™** sampling volume covers a circle less than 0.5 cm in diameter, and approximately only a few molecules thick (approximately 0.2 cubic centimeter). This makes the technology hypersensitive to the natural spatial variability of contaminant distribution. The reference methods analyze 30 gram aliquots from a homogenized sample of approximately 1,000 grams, which is several thousand times larger than for the technology. This larger sample volume may average out some of the smaller heterogeneities detected by the **ROST™**. Some of this effect is canceled out by the fact that the **ROST™** collects much more data. In the case of this demonstration, the reference method used a total of 76 samples, compared to over 1,300 sample points provided by the **ROST™**.

Total Organic Carbon

PRC compared the **ROST™** intensity measurements for areas free from contamination to the corresponding TOC concentrations. This evaluation examined the potential for gross humics to affect **ROST™** intensity measurements. **ROST™** data from the York, Atlantic, and Fort Riley sites were reviewed. The samples collected for this evaluation contained TOC concentrations from not detected to over 3,000 ppm. Based on the limited data base (11 samples), there

appears to be no effect of TOC on **ROST™** intensity at any of the three sites. This is based on the fact that although the TOC concentrations varied over three orders of magnitude, the **ROST™** measurements remained relatively constant. However, some literature suggests that TOC becomes a potential interferant in the presence of organic solvents or petroleum products. This interference may be created by the contaminant's activation of fluorescent properties in the TOC, specifically humics. Isolation and examination of the potential for this activation of fluorescence in humics was beyond the scope of this demonstration.

Quantitative Assessment

This section presents the comparative evaluation of the **ROST™** data and the reference methods' analytical data, and an evaluation of the precision of the technology. The precision discussion is presented after the regression analysis discussion.

The reference method sampling and analysis identified considerable heterogeneity in the distribution of contaminants in the soil matrix. The experimental design of this demonstration expected heterogeneity and intended to define it through co-located replicate sampling. This sampling did define the heterogeneity. However, in many cases the heterogeneity was greater than expected. In almost 50 percent of the 21

itative sample intervals the heterogeneity produced ranges between maximum and minimum concentrations in excess of one order of magnitude. This heterogeneity coupled with the developer's inability to specifically identify the compounds it is measuring, the lack of a reference analytical method that monitors the exact suite of the compounds measured by the technology, the mixed distribution of constituents in the contamination, and the varied age of the contaminants cause uncertainty to be introduced into the point by point comparison of data in the quantitative evaluation. Therefore, any conclusions stated in this section should be considered as trend indicators and not definitive statements on technology performance. However, the conclusions are likely to be duplicated if similar field in situ verification is attempted.

The quantitative assessment evaluated **ROST™** data at distinct intervals relative to corresponding data from the reference method. This evaluation was intended to quantify relationships between the **ROST™** data and individual compounds or class-specific analytical data produced by the reference methods. According to the developer, due to spectral overlap of fluorescing compounds, it is virtually impossible to select excitation and emission monitoring wavelenths to quantitate individual compounds, however, quantitation for classes of compounds is possible. Therefore, any correlations noted for individual compounds are going to be site specific and dependent on a consistent distribution of the compound in the overall class of contaminant. The lack of observed correlations for individual compounds does not indicate a performance problem, rather, it is probably due to spectral overlap interferences or the random distribution of individual compounds over a given site. This type of random distribution can be caused by contaminant aging or changes in waste generation processes.

The target analytes for the quantitative evaluation were TPH, VPH, BTEX, total BTEX, naphthalene, I-methylnaphthalene, 2-methylnaphthalene, acenaphthene, fluoranthene, phenanthrene, pyrene, benzo-a-pyrene, total PAH, and total naphthalene. The TPH, VPH, total naphthalene, total PAH, and total BTEX groupings were made in an effort to most closely match the **ROST™** data. The developer felt that at the current stage of this technology's development, classes of compounds would show the closest match to the **ROST™** data.

This data evaluation involved regression analysis of the **ROST™** data against the corresponding reference data. As defined in the final demonstration plan, a coefficient of determination of 0.80 or better defines a useable predictive model.

The **ROST™** made two collocated pushes at each node. The first push was intended to produce the primary data for the qualitative and quantitative evaluation. The second push was intended to examine the **ROST™**'s precision. The second push also produced continuous **ROST™** data to depth. The primary data evaluation focused on the data from the first push at each node, however, PRC did examine the possible impact of averaging the two pushes for the regression evaluation. This averaging had very limited impact on the outcome of the regression analysis and will only be discussed where its findings differ from the single push data.

The data sets were initially examined as a whole and then post-hoc techniques were used to eliminate data outliers. The total data set for this evaluation consisted of 21 sampling intervals, 8 at the Atlantic site, 7 at the York site, and 6 at the Fort Riley site. Each one of these intervals produced one data point for the regression analysis, however, each of these data points represents the mean concentration from five collocated samples. Therefore, this evaluation was based on the analytical results of 105 individual samples and analyses. The data presented is based on nontransformed data. PRC mirrored the analyses discussed below with log-transformed data, however, in no case did the correlations improve. This suggests that the high and low concentration points did not disproportionately bias the regression. PRC also examined the data in its raw form prior to averaging the reference data. This approach did not improve the correlation of the data.

The initial regression analysis examined the data set of mean concentrations as a whole. In this analysis the technology's data was considered to be a dependent variable. From this evaluation, no coefficient of determination of greater than 0.15 was observed (Table 5-1). An examination of the maximum and minimum concentrations for each set of collocated samples indicated that several locations at each site exhibited considerable heterogeneity. This was expected and is normal for environmental sampling. Using data points from confirmatory sampling depths that exhibit wide ranges in contaminant concentration introduces additional uncertainty into the data evaluation. In these cases, it is hard to define a representative mean concentration. Concentrations are highly location dependant. In an effort to reduce the impact of this heterogeneity on the data evaluation, all data points exhibiting greater than 1 order of magnitude range between the maximum and minimum were eliminated. This range was selected after consultation with **ROST™** operators. In most cases, this resulted in almost a 50 percent reduction in useable data. For this reason the subsequent data analyses should be considered indicators of trends in correlation, and not well defined predictive models.

TABLE 5-1. REGRESSION ANALYSIS RESULTS FOR INITIAL ROST™ PUSH AND THE REFERENCE METHODS-ALL SITES

Compound	Initial Regression				Final Post-Hoc Data Reduction			
	n	r ²	slope	y-intercept (ppm)	n	r ²	slope	y-intercept (ppm)
TPH	21	0.04	9.6	2,817	8	0.06	20.0	2,311
VPH	20	0.09	1.1	212	9	0.45	1.6	-15.8
Benzene	16	0.06	12.5	4,374	6	0.68	52.7	8.8
Toluene	19	0.10	63.5	9,367	10	0.55	411	-3,930
Ethylbenzene	20	0.06	28.1	9,376	10	0.63	151	-3,212
Xylene	20	0.13	131.8	20,551	11	0.38	237	-246
Naphthalene	21	0.01	-0.05	42.8	8	0.66	0.00	1.8
1-Methylnaphthalene	18	0.00	0.01	57.0	12	0.09	0.16	37.6
2-Methylnaphthalene	20	0.00	-0.02	34.4	10	0.21	0.20	12.0
Acenaphthene	12	0.05	-0.08	51.5	4	0.12	0.34	33.6
Fluoranthene	19	0.00	0.00	3.06	12	0.02	0.00	1.00
Phenanthrene	21	0.01	-0.02	18.0	10	0.15	0.06	4.33
Pyrene	17	0.00	-0.01	8.02	8	0.69	0.09	-0.37
Benzo-a-Pyrene	19	0.02	-0.00	1.76	11	0.00	0.00	0.80
Total Naphthalene	21	0.00	-0.12	200	12	0.32	0.75	28.0
Total PAH	21	0.00	-0.04	115	10	0.37	1.01	24.2
Total BTEX	20	0.12	245	40,375	11	0.33	826	14,108

After these data points were removed the regression analysis was run again. No significant changes in the regression parameters were observed (Table 5-1). However, a post-hoc examination of the residuals identified several outliers for each regression.

A final regression analysis was conducted on the data sets after the outliers were removed. This regression showed considerable improvements in the data correlation (Table 5-1), however, none of the target analytes exhibited an acceptable correlation. Regressions based on the benzene, ethylbenzene, naphthalene, and pyrene exhibited coefficients of determination of between 0.6 and 0.7. With regard to these compounds, and based on the slopes and y-intercepts of the regression equations, the **ROST™** appears to be most sensitive to PAH compounds relative to the single ring aromatics. The slopes for the PAH compounds were all less than 1.0, indicating that changes in PAH concentration would cause relatively larger changes in **ROST™** readings. Conversely, the

slopes of the single ring aromatic compounds were greater than one, indicating that a given change in contaminant concentration would cause a relatively smaller change in **ROST™** measurements.

The lack of correlation for the quantitative evaluation cannot be solely attributed to the technology. Rather, it is likely due to the combined effect of matrix heterogeneity, lack of technology calibration, uncertainties regarding the exact contaminants being measured, and the age and constituents in the waste. Based on the data from this demonstration, it is not possible to conclude that the technology can or cannot be quantitative in its current configuration.

Similar conclusions are drawn if the data from the two **ROST™** pushes are averaged and used in the regression analysis (Table 5-2). However, the correlations are generally improved. Under this scenario of data evaluation, the naphthalene regression produced an acceptable coefficient of determination value,

TABLE 5-2. REGRESSION ANALYSIS RESULTS FOR AVERAGED ROST™ PUSH AND THE REFERENCE METHODS-ALL SITES

Compound	Initial Regression				Final Post-Hoc Data Reduction			
	n	r ²	slope	y-intercept (ppm)	n	r ²	slope	y-intercept (ppm)
TPH	21	0.01	3.2	3,315	8	0.07	19.8	2,241
VPH	20	0.05	0.68	236	8	0.67	2.1	-28.0
Benzene	16	0.03	7.5	4,658	5	0.79	50.0	-164
Toluene	19	0.08	45.9	10,224	10	0.38	249	3,056
Ethylbenzene	20	0.02	13.3	10,475	10	0.76	181	-2,119
Xylene	20	0.08	83.1	23,518	10	0.62	308	2,821
Naphthalene	21	0.01	-0.001	41.5	8	0.83	0.06	5.14
1-Methylnaphthalene	18	0.00	0.00	57.5	12	0.05	0.11	42.5
2-Methylnaphthalene	20	0.03	-0.04	36.9	9	0.17	0.16	17.2
Acenaphthene	12	0.08	-0.09	52.5	4	0.23	0.71	18.0
Fluoranthene	19	0.01	-0.00	3.53	11	0.02	-0.004	1.71
Phenanthrene	21	0.06	-0.03	19.8	9	0.10	0.07	9.43
Pyrene	17	0.04	-0.01	8.92	8	0.62	0.13	-1.55
Benzo-a-Pyrene	19	0.06	-0.00	1.92	11	0.04	-0.003	1.04
Total Naphthalene	21	0.04	-0.31	221	11	0.28	0.69	44.9
Total PAH	21	0.03	-0.15	127	9	0.23	0.75	63.3
Total BTEX	20	0.08	160	45,381	9	0.66	949	-9,542

0.83. The slope of this regression equation was **0.06** supporting the conclusion that the **ROST™** is most sensitive to the PAH compounds. The y-intercept for this regression was 5.14 percent of the standard. This suggests that **ROST™** readings of greater than 5.14 percent of the standard are required before the predictive model for naphthalene should be applied. The coefficient of determination values for benzene and ethylbenzene were between 0.75 and 0.80. These regressions produced slopes much greater than 1.0, supporting the conclusion that the **ROST™**, in its configuration during the demonstration was less responsive to single ring aromatics than to PAHs. Pyrene, xylene, total BTEX, and VPH produced coefficients of determination between 0.6 and 0.7. The slopes for the pyrene, xylene, and total BTEX were consistent with the trends already discussed for PAHs and single ring aromatics. The VPH regression produced a slope of 2.1. The slope data cannot be used to assess data quality since the LIF data was not in the

same units as the reference data. However, the slope data can be used to indicate general trends in the relative fluorescence, as discussed above.

The qualitative determination of a detection limit or threshold for the **ROST™** technology was not possible given the data produced from this demonstration. Review, of the data presented in Table 5-2 shows that the relationship between the **ROST™** data and the compounds exhibiting the best correlation based on the averaged push data was not consistent, even when only the data used in the final regression is considered.

Qualitative observations regarding the detection limits of this technology can be made with the data produced from this demonstration. Measurable relative fluorescence was reported for benzene concentrations as low as 264 mg/kg, ethylbenzene as low as 807 mg/kg, naphthalene as low as 1.1 mg/kg, and pyrene as low as 0.03

ROST™ reported negative relative fluorescence for two quantitative samples. For these samples, **ROST™** reported a relative fluorescence of -1.37 and -0.20 (Table 5-3). These readings are equivalent to zero fluorescence. The reference methods indicated that these intervals contained measurable concentrations of these four compounds (Appendix A). The **ROST™** reading of -1.37 occurred at a sample interval that contained, at its minimum, total PAH, TPH, and VPH concentrations of 799 ppm, 1,878 ppm, and 175 ppm, respectively. The **ROST™** reading of -0.20 occurred at a sample interval that contained, at its minimum, concentrations of total PAH, TPH, and VPH of 31 ppm, 1,416 ppm, and 1,102 ppm, respectively. This could be interpreted as false correlation based on the averaged push data was not consistent, even when only the data used in the final regression is considered. Increases in relative negative readings. Two false negatives out of 21 sample points equates to a false negative rate of 10 percent.

Another qualitative method for assigning a detection threshold is to determine the relative fluorescence at the x-intercept for the benzene, ethylbenzene, naphthalene, (based on averaged pushes) and pyrene regression models discussed above. The x-intercept represents the 0 mg/kg point on the fluorescence versus concentration graph. For the benzene and ethylbenzene the relative fluorescence intensity at the x-intercept was -0.17 and 21, respectively. For the naphthalene and pyrene the relative fluorescence at the x-intercept was 85 and 4, respectively.

To examine the potential for site-induced affects on the data evaluation, the data was divided by site and regression analyses were nm on the resultant three data sets. This regression analysis began with data sets whose gross outliers had been removed. These outliers were defined as data points where the maximum and minimum values varied by over one order of magnitude.

This site-specific regression showed the following: xylene, naphthalene, pyrene, and total PAH regressions exhibited acceptable correlations (r^2 greater than 0.80) at the Atlantic site; no compounds showed acceptable correlations at the York site; and acceptable correlations were exhibited for VPH, naphthalene, and total BTEX at the Fort Riley site. The number of samples resulting in these acceptable correlations ranged from 3 to 5, out of a maximum of 6 to 8. This small sample set greatly limits the use of this data to form predictive models. However, these regressions exhibited the same trends in their slopes, as exhibited in the data set as a whole. The slopes for the PAHs were all less

than 1.0, and the single ring aromatic compounds produced regression equations with slopes greater than 1.0.

The potential causes other than sample matrix effects such as heterogeneity, of the relatively poor correlations of **ROST™** data to reference data seen during this demonstration were examined. The FVD wavelengths used for emission wavelength monitoring may have affected the comparability of the **ROST™** data to the reference method data. **ROST™** utilized an FVD wavelength of 400 nm for the Atlantic and York sites, and 360 nm for the Fort Riley site. **ROST™** explained that 400 nm would provide the best FVD-monitoring wavelength for coal tar-contaminated sites, and that 360 nm would provide the best FVD-monitoring wavelength for petroleum-contaminated sites. To assess the use of these wavelengths, WTM's were compared to the emission monitoring wavelengths used at each site. It was observed that the WTM's from the Atlantic and York sites produced maximum fluorescence intensities at greater wavelengths than the ones used for the emission wavelength monitoring. This means that the **ROST™** was not monitoring the wavelength which exhibited the greatest fluorescence intensity. For fluorescence methods the wavelengths of the greatest fluorescence intensity provides the most accurate and linear results. By not monitoring at the wavelength of maximum fluorescence intensity the **ROST™** was monitoring on the rising or falling limbs of the fluorescence wave forms of the primary fluorescing contaminant. In this area, similar to a side slope of a hill or mountain, large shifts in the fluorescence intensity of the contaminant matrix could result in relatively smaller changes in measured fluorescence.

According to the developers, saturation effects for the detection system used in the **ROST™** do not appear until soil contamination exceeds approximately 1,000 ppm. These effects could result in inaccurate LIF data. This type of error would only impact the most contaminated areas seen during this demonstration, and it would result in underestimates of contamination. It is likely that the areas of contamination potentially causing this effect would be identified as grossly contaminated even with underestimated LIF results. **ROST™** was monitoring the rising and falling arm of the fluorescence wave form, and therefore, was not monitoring the wavelength of maximum fluorescence intensity that should produce the most accurate and linear results.

A related problem was noted concerning the calibration procedures employed by **ROST™**. **ROST™** performed calibration before each CP push by placing a solution of 10,000 pg/mL gasoline over the sapphire

TABLE 5-3. DATA FOR MEAN ROST™ -ALL SITES

Site	Node	Depth (feet)	ROST™ Relative				
			Fluorescence Intensity	Benzene (mg/kg)	Ethylbenzene (mg/kg)	Naphthalene (mg/kg)	Pyrene (mg/kg)
Atlantic	2	21-22	71.99	2,200	34,000	151	26
	2	24-25	2.94	8,128	14,960	65	13
	3	16-17	38.78	1,100	3,900	2.0^{a,b}	0.2
	4	6.5 - 7.5	21.56	573	1,410	1.6^{a,b}	0.7
	4	10- 11	174.6	1,334	31,600	19	2.4
	4	27.5 - 28.5	498.0	6,300	10,520	33^a	8.3
	5	16-17	12.1	3,420	1,198	1.1	No data
	5	23.5 - 24.5	67.30	3,190	1,174	1.4^{a,b}	0.03
York	1	15-16	2.16	ND	807	23	12
	2	13.5 - 14.5	132.43	ND	4,760	56^a	9.0
	2	17-18	20.72	ND	4,860	35^a	5.7
	3	17-18	101.5	ND	1,558	17^{a,b}	8.1
	4	14- 15	97.14	1,148	9,900	99^a	12
	4	18-19	-1.37	1,156	21,811	249	31
	5	1.5-2.5	23.59	ND	ND	No data	0.2
Fort Riley	1	2 - 3	16.94	264	1,076	8.1^{a,b}	0 . 3
	1	13- 14	-0.20	1,437	8,595	5.0^{a,b}	ND
	2	6 - 7	34.88	811	763	No data	ND
	2	17-18	120.2	16,800	39,600	11^{a,b}	ND
	5	10.5- 11.5	188.4	5,114	13,680	21^{a,b}	ND
	5	16- 17	171.1	5,100	31,400	5.0	No data

Notes:

mg/kg Milligrams per kilogram.

ND Not detected.

^a Data points remaining after the initial removal of outliers based on maximum and minimum comparisons.

^b Data point used in the final regression analysis.

window and standardizing the ROST™ system. The response of the standard is then measured at the FVD-monitoring wavelength. The ROST™ system then normalizes the response of the gasoline to equal 100 percent fluorescence. At the Atlantic and York sites, 400 nm was used as the FVD-monitoring wavelength. WTM's performed for the gasoline standard showed that the wavelength of maximum fluorescence intensity was 340 nm. Again, this means that ROST™ was not monitoring the wavelength of maximum

fluorescence intensity, where accuracy and linearity is greatest.

Calibration procedures were evaluated to determine a cause of the relatively poor correlation between ROST™ and the reference methods. ROST™ performs a calibration by analyzing a single level of gasoline. This procedure does not provide any information concerning the linearity of the ROST™ system. Typically, fluorescence methods are extremely sensitive

and linear over a wide range, a 1,000-fold or greater linear range is not uncommon. However, fluorometry is limited to low concentrations.

Inherent instrument precision for the **ROST™** measurements at the York, Atlantic, and Fort Riley sites was evaluated by calculating the percent relative standard deviation (%RSD) of each set of 11 measurements for each depth sampled. Replicate measurements were taken at three separate nodes at the Atlantic and Fort Riley sites and at only one node at the

York site. The precision measurements taken at the Atlantic and Fort Riley sites were at a total of five and four different depths, respectively. The York site only had one depth sampled. The %RSD was calculated by dividing the standard deviation from the 11 replicate measurements by the mean. This number is multiplied by 100. The maximum inherent instrument precision at the York, Atlantic, and Fort Riley sites was 4.1, 3.5, and 1.7, respectively. Based on this data, the standard deviations are most likely due to heterogeneity in contaminant distribution.

Section 6 Applications Assessment

The **ROST™** technology is only available as a service from the developers and it is designed to be operated by trained technicians. The **ROST™** does require some type of platform to advance the sensor into the ground. Currently, this is done with a cone penetrometer truck either provided by the developers or by the customer. The **ROST™** is designed to be compatible with most standard cone penetrometer trucks. This technology has been tested at a variety of military and industrial installations, and as of the date of this report, it has been used for several commercial site characterizations. As demonstrated, this technology can rapidly acquire data defining zones of general contamination, as long as the contamination has a fluorescent signature. This data can greatly facilitate site characterization activities.

During this demonstration, the cost of this technology, including a CP sensor, was less than the reference methods used to produce the qualitative data. The LIF sensor and CP sensor produced far more data in real-time, resulting in improved physical and chemical resolution relative to the reference method. However, this improved resolution and real-time data was at a lower level of data quality (screening versus definitive).

The qualitative assessment portion of this demonstration showed that this technology is comparable to reference methods in its ability to map subsurface contaminant plumes at petroleum fuel and coal tar contamination sites. This demonstration showed that both **ROST™** and the reference methods identified similar zones of subsurface petroleum and coal tar contamination at each of the three demonstration sites. Many of the differences between the **ROST™** and the reference methods can be explained by their respective methods of data collection. The **ROST™** produces a continuous profile, while the reference methods take a few selective samples targeting boundaries and zones of contamination. In addition, the reference methods had difficulty retrieving samples in running sands, adding potential data gaps. The **ROST™** technology produced relatively continuous data on petroleum and coal tar

contaminant distribution over a 30-foot depth in approximately 1.5 hours during the demonstration. The reference methods would be able to collect samples over this interval, however, definitive analytical services would require, at best, several days. Even if the reference methods used on-site analysis, and produced only screening level data, it would take several hours to provide data on the samples. Therefore, on-time critical projects that can use screening level data, or on projects where it is more critical to cover large areas in greater detail, the **ROST™** technology seems appropriate.

Another powerful aspect of this technology is that it can be advanced with a standard CP to provide continuous descriptions of the subsurface soil concurrently with the chemical data. This demonstration found that the subsurface logging capabilities of the CP were comparable to the reference methods. Similarities between the two data sets were observed even without site-specific borings to calibrate the CP logging tool prior to deployment. The major limitation of the CP logging was its apparent inability to detect slight shifts in particle size distribution. It is questionable if this limitation would greatly impact the use of the data. For example, a silt and clayey silt would probably be dealt with similarly in a hydrogeological perspective.

The quantitative data assessment for this technology indicated that the **ROST™** data was most correlated to naphthalene concentrations. The small data set sizes limit the use of the predictive model (created from the regression analysis). Any predictive model should be based on site-specific calibration and confirmation. The regression analysis showed some correlation between the technology's results and individual compounds. The technology's data was not well correlated to TPH and VPH measurements (.07 and .67, respectively). The generally poor correlation with the quantitative data from classes of compounds may be partially due to matrix heterogeneity, analytical limitations of the reference methods, **ROST™** calibration procedures, and the emission monitoring wavelengths used by the **ROST™** during the demonstration. Basically, the calibration and

emission wavelength selection were not optimum for the site-specific classes of contaminants. This apparently did not greatly affect the qualitative evaluation, only the quantitative evaluation. This is consistent with the current evolutionary stage of this technology at the time of the demonstration in August 1994. The identification of individual compounds is not a current application of this technology. However, the collection of WTM data allows the **ROST™** to identify changes in constituent composition, and in many cases, allows **ROST™** to identify types of contaminants such as diesel fuel, gasoline, jet fuel, and coal tar. This capability can assist in the identification and attribution of contaminant sources.

Based on the results of this demonstration, the use of site-specific calibration samples for the application of **ROST™** may be of most value in determining emission monitoring wavelengths and possibly in calibration activities. Future development of this technology may allow this type of calibration for quantitation (see Section 7). The effects of site-specific calibration samples for the **ROST™** was not evaluated during this demonstration. Site-specific calibration may allow a more representative estimation of contaminant concentration distribution. In other words, with this type of calibration, perhaps the **ROST™** data would exhibit more similar trends to the reference method data, for example, as the contaminant concentrations increase or decrease, the **ROST™** data would show a more consistent relationship relative to increases or decreases in contaminant concentration.

Based on this demonstration, this technology appears to produce screening level data. The lack of better correlations may not be wholly attributable to the technology performance, rather it may have been due to the relatively small reference method data set size, the lack of a reference method that measures the same suite of compounds as the **ROST™** sensor monitors, the complex interactions between the fluorescing compounds, and the soil matrix which resulted in the observed heterogeneity. The first two factors can be addressed with changes in experimental design and innovations in analytical methods, however, the final factors will require more research to isolate specific matrix interactions and to resolve the heterogeneity issue.

If this technology, in the configuration demonstrated, is to be evaluated in the field, this demonstration has shown that on a point-by-point quantitative basis, it is unlikely that significant correlation to reference data will be observed. This is due to a combination of heterogeneity effects, limitations in conventional sampling and analysis, and the complex interaction of waste aging and constituent distribution of relative fluorescence. It is possible that site-specific calibrations,

different reference analytical methods, alternative sampling methods, or a less heterogeneous matrix would improve the potential for significant correlation between **ROST™** and the reference method data. Therefore, based on the results of this demonstration, field evaluations of this technology should be restricted to qualitative evaluations consisting of cross section comparisons of simply verifying that LIF highs correspond to higher levels of contamination. This latter comparison will also be affected by effects listed above.

Although there are many advantages to this technology, a potential user should be aware of potential disadvantages. This technology has a sampling volume several thousand times smaller than conventional sampling analysis. This makes the technology very sensitive to matrix heterogeneity. Some of this sensitivity is reduced (vertically) by the averaging of fifty data points every 2 cm. This effect can also be minimized by the sampling of more push locations to reduce the sensitivity in a horizontal orientation. At a data collection rate of approximately 300 linear feet per day (4,572 data points), additional pushes can be conducted without greatly increasing project duration. The LIF results can be influenced by the age and constituent distribution of wastes. This fact coupled with heterogeneity effects, and a lack of site-specific instrument calibration, makes field verification of LIF results difficult. The use of the LIF and CP sensors is restricted to the maximum push depth of the cone penetrometer truck. This depth can be as much as 300 feet, or in the case of the demonstration, 30 to 70 feet. These shallow depths were realized when deeper strata exhibited increased cone tip resistance and sleeve friction, and at location where strata at shallower depths would not provide adequate lateral support for the push rod. These conditions greatly increase the chance for push rod breakage and sensor loss.

This technology can currently provide rapid assessment of the distribution of fluorescent material in the subsurface. When these materials are PAHs or petroleum fuels, the technology can be used to map the extent of subsurface contamination. The WTM data can also be used to provide qualitative identification of waste type or at a minimum, it can identify changes in constituent distributions. All of this data can be used to guide critical conventional soil sampling, and the placement of groundwater monitoring wells. All of this data can be produced and interpreted in the field. This real-time sampling and analysis allows the use of contingency based sampling, which assists in characterizing a site with a single mobilization. These aspects coupled with its low waste production during decontamination make this technology a powerful and effective site characterization tool.

Section 7

Developer Comments and Technology Update

The developers of the ROST™ technology submitted both editorial and technical comments on the draft ITER. Only comments not resulting in changes to the report are presented below. The technical comments are presented verbatim in italics. The response to the comments is presented below each developer comment in plain type.

Loral Comments (April 1995)

1. *Complications caused by spatial inhomogeneity. The statistics of the quantitative sampling, shown in Table 7-1, emphasize how large are the variances in the chemical concentrations obtained by the reference methods. The RSD is greater than 50% for 17 of the 21 (81 %) quantitative evaluation sampling intervals, and greater than 100% for 12 of the 21 (57%) intervals. At the 99-percent confidence level only three of the 21 locations for quantitative evaluation give TPH concentrations different from zero.*

We feel that the draft report minimizes the difficulties posed by the heterogeneity problem and, more significantly, fails properly to take it into account in the quantitative evaluation of ROST™'s performance. From page 4-10 of the draft ITER; "An examination of the maximum and minimum concentration for each set of collocated samples indicated that several locations at each site exhibited considerable heterogeneity. This was expected and is normal for environmental sampling. Using data points from confirmatory sampling depths that exhibit wide ranges in contaminant concentration introduces additional uncertainty into the data evaluation. In these cases, it is hard to define a representative mean concentration. Concentrations are highly location dependent (sic). In an effort to reduce the impact of the heterogeneity on the data evaluation, all data points exhibiting greater than 1 order of magnitude range between the maximum and minimum were eliminated. This range was selected after consultation with ROST™ operators. In most cases, this resulted in almost a 50percent reduction in usable data. For this reason the subsequent data analyses should be

considered indicators of trends in correlation, and not well defined predictive models. "

We are troubled by several things. In the first place, the "ROST™ operations" were not consulted about eliminating data points on the basis or range between minimum and maximum. To state that we agreed with this procedure is untrue. We don't believe that this method of rejecting data is statistically valid. It is also unclear whether the procedure was to reject all five values (for the set of five collocated samples) or just those that led to more than an order of magnitude variation. Note that the rejection criterion eliminates Node 4, 6.5-7.5 feet at the Atlantic site with a RSD of 65 percent (one of the lower values) and retains Node 4, 14-15 feet at York with a RSD of 104 percent.

PRC consulted both ROST™ and SCAPS representatives regarding the elimination of data points. PRC conducted the initial data review for the quantitative evaluation based on the entire data set. This initial data review showed no correlation between the technology's results and the reference method data. In addition, PRC noted that several data points exhibited considerable spatial variation. To reduce the impact of the observed spatial variability, PRC conducted a post-hoc review of the raw data in an attempt to identify points that showed the greatest spatial variability. PRC reviewed the 99 percent confidence intervals around the mean concentrations for the quantitative data. In many cases, the confidence intervals ranged into negative concentrations on the low ends, and at both the high and low ends were far more extreme than actually measured. PRC then considered the concentration ranges within a replicate sampling interval. These ranges represented actual measured concentrations of contaminant within a sampling interval. This nonparametric approach is more representative of reality than statistically generated confidence intervals that span negative concentrations for intervals where the low concentration was in the 100's or 1,000's of ppm. When sample intervals were identified as outliers based on this criteria, all the replicate data for the interval was eliminated.

TABLE 7-1. SUMMARY OF TPH RESULTS FOR QUANTITATIVE EVALUATION

Site	Node	Depth	TPH-mean	TPH-SD	RSD (%)	
At/an tic	Node 2	21-22	11,090	2,690	24	
		24-25***	4,004	4,592	114	
	Node 3	16-17***	425	577	136	
	Node 4	6.5-7.5***	255	166	55	
		10-11	2,436	1,130	46	
		27.5-28.5***	1,094	1,157	106	
	Node 5	16-17	201	177	88	
		23.5-24.5***	239	367	154	
	York	Node 1	15-16***	773	905	117
		Node 2	13.5-14.5**8	1,539	1,036	67
17-18***			497	535	108	
Node 3		17-18	778	513	66	
Node 4		14-15	2,281	2,361	104	
		18-19***	1,878	2,155	115	
Node 5		1.5-2.5	60	68	113	
Fort Riley	Node 1	2.3***	5,728	6,699	117	
		13-14***	1,416	1,608	114	
	Node 2	6-7***	2,169	3,187	147	
		17-18	13,150	4.18	32	
	Node 3	10.5-11.5	22,480	4,935	26	
	16-17	3,926	3,471	88		

Notes:

*** Data rejected by PRC on the basis of range criterion.
 TPH varies in mg/kg.

The report then goes on to apply a correlation coefficient criterion even though the independent variables (the reference data) are so imprecise. The standard regression analysis is inappropriate when there is a high degree of imprecision in the independent variable. Replacement of the widely varying values by the mean does not improve matters. Moreover, allowance was not made for any similar variability's in the ROST™ values, even though they will also be affected by the spatial inhomogeneity.

As defined in the final demonstration plan (PRC 1994), the reference dam was considered accurate and precise. PRC concedes that the reference data exhibited some variation within each interval, however, this impact was reduced when PRC eliminated over 50 percent of the data based on the criteria discussed above. In addition, PRC also evaluated the ROST™ technology based on the mean of its replicate pushes

over all quantitative sampling intervals. This showed little improved correlation. The ITER has been revised to include a detailed discussion of the impact of matrix heterogeneity and it will explain that the lack of correlation could be due to matrix, instrument, and analytical factors in any combination. PRC feels that this data must remain in the report to give potential users some frame of reference if they plan to conduct confirmatory sampling. In addition, the trends identified by the slope data from the regression data also seems to present consistent and valuable data.

We all knew going into the demonstration that sampling could turn out to be the Achilles heel of the evaluation. Note the following quote from the Final Demonstration Plan: "Total precision is controlled by two sources: analytical error and spatial soil variability. These sources cannot be readily separated and the most serious concern for this demonstration is the total

precision, not its sources." The QA/QC checks address the analytical error, which is negligible. The spatial soil variability was to have been address through the establishment of 99-percent confidence intervals: "To create (these) confidence intervals, PRC will collect five replicate samples from 6-inch intervals, collocated to the Unisys and Tri-Services technologies quantitative sampling intervals. " (Page 6-8)

The final demonstration plan (PRC 1994) explains that the 99 percent confidence intervals were intended to create pseudo PE samples. If the resultant technology data fell within this confidence interval, the technology would be determined to have acceptable accuracy. However, since the technology did not produce data that represented contaminant concentrations in ppm or any other comparable unit of measure, this comparison could not be made. This is explained in the ITER.

Obviously it was expected that analytical error would be of much less significance than the uncertainties cause by inhomogeneity in the contaminant distribution of the soil. The quality control/quality assurance procedures described in Chapter 2 verified that good laboratory practice was followed in the chemical analyses. Thus, we accept the stipulation on page 2-8 "Based on a review of this data, the reference method accuracy requirements were met: if it is understood that the terms reference method accuracy and precision refers to the analytical measurements, but not the overall measurement. The total precision (dominated by the sampling problem) is poor and the reference methods cannot be considered as a "gold standard " for purposes of assessing ROST™s capabilities. Consider, for example, a precision test to the "reference " data. How many of the individual reference values fall within 20% of the mean value for each co-located sampling interval? In the case of Atlantic, only 6 of the 38 total determinations satisfy a 20% precision criterion. In fact, less than half (16/38) even satisfy a 50% precision criterion. To use the mean values and treat them as errorless is highly misleading.

Matrix heterogeneity is an inherent condition in the environment, and not an artifact of sampling as implied in the comment above. In the case of this demonstration, and possibly any other attempt to quantitatively evaluate the ROST™ technology, the smaller size of the ROST™ sampling volume may magnify the effect of matrix heterogeneity. The sampling volume of the ROST™ technology is 100's to 1000's of times smaller than the sample volume used to drive regulatory decisions.

PRC agrees that the reference methods used may not even measure the same compounds measured by the

technology, however, these methods were chosen and presented in the final demonstration plan (PRC 1994) as being the closest matches in the suite of regulatory analytical methods. The ITER has been revised to clarify that the analytical methods are merely attempts to identify potential correlation between the technology's data and analytical data used to drive regulatory decisions. In addition, the ITER has been revised to clarify that the quantitative evaluation is only intended to provide a baseline look at the quantitative potential of the technology.

The developer's use of the precision criteria as a comparative tool to assess the heterogeneity of the matrix is a misuse of the criteria. The 20 percent criteria was intended to evaluate inherent method precision. The reference analytical methods produced data that met or exceeded this criteria.

PRC will clarify that the reference data is affected by heterogeneity, and discuss the potential impacts of this heterogeneity on the results and data interpretation for this ITER.

Given the above facts, we are particularly dismayed that the confidence intervals were deleted from the dara interpretation yet language such as "The quantitative assessment found that the ROST™ data was [sic] poorly correlated to any of the concentrations of the target analytes. The data produced from this demonstration did not identify a consistent relationship between ROST™ fluorescence data and the reference data. " These statements are unjustified and too easily taken out of context.

The ITER has been revised to clarify that given the configuration of the technology, as used in this demonstration, it cannot produce quantitative data. This is based on a lack of calibration and the inability to evaluate the technology's performance in an in situ mode. However, the regression data will remain in the report to provide potential technology users with information regarding attempted quantitative evaluation.

We also feel that the quantitative evaluation is emphasized out of proportion in the draft report. We discussed with PRC on several occasions that the quantity directly measured by ROST™ (as well as SCAPS) is a fluorescence intensity that depends (predictably) on instrumental parameters (laser power, gain settings on detectors, etc.) And is propom'onal to concentration. However, the proportionality factor can be approximated only be calibrations on spiked samples. The calibrations require using soil and petroleum products as close as possible to what is encountered in the ground and have to be repeated if there are large

variations in the soil lithology or product composition (gasoline vs. Coal tar, for example). Since ROST™ is a screening tool and was being evaluated as such, the parties agreed not to include such calibrations. We were agreeable to a comparison of the ROST™ data and the quantitative evaluation results to see what sort of correlations might emerge, but were never claiming the ROST™ in the tested configuration is a “definitive” method.

PRC agrees that the ITER focused too heavily on the quantitative aspect of the technology. The ITER has been revised to focus on the qualitative application and performance of the technology.

PRC collected two sets of site-specific samples for each site and presented them to the developers, including analytical data. The developers were aware that PRC expected them to produce some type of concentration data, as explained in the developer-approved demonstration plan. The developers opted not to calibrate the technology. Therefore, any calibration claims not supported by data collected during the demonstration will be written by the developers, and included in Section 7 Developer Comments and Technology Update. In addition, the ITER has been revised to clarify that this technology, in the configuration demonstrated, cannot produce quantitative data, and produces screening level data that cannot be confirmed by existing analytical methods.

Using the mean values without accounting for the variability in the reference values renders the whole “ $r^2 > 0.80$ ” exercise meaningless. In fact, if one applies regression criteria to the reference data themselves, they fail miserably! Let’s pretend that five different combinations of drilling companies and testing laboratories of their choice were involved in the quantitative test. Assign the square that come first in alphabetical order at each unique node-depth combination to the results obtained by drilling company “alpha” and the laboratory they use. Assign the results from each node for the next letter in alphabetical order to the “beta” and so forth. Then use the mean value of the results for each node/depth as the “right” answer (ignoring the standard deviations) and compare against the results of the alpha test, the beta test, etc. What do we find? Most of the determinations fail at the $r^2 > 0.80$ criterion.

The replicate sampling was conducted to define the spatial variability of the matrix. This allowed the elimination of quantitative evaluation samples that exhibited excessive spatial variability. If the above comparison is conducted on the reduced data set, the

reference method would not perform as described above. In addition, the correlation coefficient criteria stated above was only used to determine if the technology was producing definitive or screening level data. All regression data is included in the ITER to allow potential users to determine the value of this approach of data evaluation, relative to the technology. The ITER has not been revised based on this developer comment.

DTI Comments (May 1995)

On May 31, 1995, DTI submitted additional comments on the draft ITER. A total of eight comments were submitted, in addition to a ROST™ executive summary. Of these comments five were revisits&ions of comments made in Loral’s April 1995 comment letter. Two of the remaining three comments were new and are presented and responded to below. The last remaining comment was an update of the technology application and it will be included in the technology update that follows the response comments.

We strongly urge that you eliminate all attempts to correlate ROST™ fluorescence data with concentrations of individual compounds (e.g. xylene or pyrene). This is comparable to trying to correlate a TPH-gasoline measurement with the concentration of a single component, say isooctane, from a complex mixture. The nature of the fluorescence measurements is such that any such apparent correlation is an illusion since the spectra of the different compounds overlap with each other. It is virtually impossible to choose a set of excitation and emission conditions such that only a compound is excited. We never claimed this sort of capability.

You make the statement in the draft ITER “For the purpose of this demonstration, the lack of approved EPA methods did not preclude ROST™ from being considered a definitive level technology.” This is setting up a brick wall for us. As you note, “Definitive data are generated using rigorous analytical methods, such as approved EPA reference methods. Data are analyte specific, with confirmation of analyte identity and concentration.” We never stated that ROST™ could be a definitive level technology and were always careful to point out that the fluorescence intensity is compound class sensitive, not individual compound sensitive. On the other hand, it does make sense to examine correlations of ROST™ fluorescence data with concentrations of classes of compounds, such as naphthalenes, PAHs, BTEX or measurements such as 418.1 or OA-1.

The ITER has been revised to reflect the developer-intended use of the technology and the complexities associated with individual compound quantitation.

Did you check on the TRPH values from continuous sampling at Atlantic? The TPH values for 8-8.5 feet and 8.5-9 feet seem very low in comparison to the trends in the naphthalene concentrations.

The concentrations reported in the data tables match the concentrations reported by the laboratory.

Technology Update

This update is based on on direct correspondence from DTI and Loral Corp.

As of June 1, 1995, **ROST™** can be used to generate semiquantitative estimates of TPH concentration. This involves post-data collection processing and waiting for confirmatory analysis on select, site-specific calibration samples.

Some type of calibration is necessary to convert from percentages to actual units, such as ppm. Choosing calibration factors is not simple in this case. One thing learned from this demonstration is that the sampling should be as close as possible to the **ROST™** measurement to minimize heterogeneity. The procedure by the Navy SCAPS for validation reduces this distance to only a few inches. They have not quantitated what sort of variation is observed in this case. Overboring the same sample (true overboring) might be even better and the Army SCAPS is exploring this alternative. Another option is to place recovered material on the window. This removes the sample variability problem, but leaves the sample disruption problem.

By observation, DTI found that a scale factor of 10 to 12 works best for the two coal tar sites (Atlantic and York) and a factor of 100 works best for the Fort Riley site. Multiplying the fluorescence percentages by these scale factors gives an estimate of the TPH values. This type of post field work data processing is now a standard **ROST™** practice.

The following technology update was supplied by the developers on June 5, 1995.

Since the time of the SITE demonstration measurements (August 1994), the ROST™ instrumentation and procedures have been improved in several ways:

1. As before, the fluorescence intensity is reported as a percentage relative to the fluorescence intensity of a reference solution which is acquired prior to each push. We formerly referred to this as a "percent of standard." We now refer to it as "percent of reference. The reference solution provides an end-to-end system check and normalizes the data for any variation in the power of

the laser light used to excite the contaminant, length of cable carrying the excitation and emission light, background noise, and other instrument settings such as monochromator slitwidth. We have now gone to a single reference solution, referred to as "M-1", to provide better comparability from one site to another. The composition of M-1 has been chosen so that its fluorescence emission covers the wavelength range of commonly occurring POLs.

2. The voltage distribution on the photomultiplier tube has been modified. Two benefits have resulted. The linear response range extends to higher signal levels and the noise has been reduced.

3. Software procedures for subtracting the instrumental baseline from the fluorescence vs. depth plots have been elaborated. These procedures, in conjunction with the reduced electrical noise mentioned above, have drastically improved the ROST™ ability to detect small, but real fluorescence signals.

4. The ROST™ module that fits between the cone and the push rods and contains the sapphire window has been redesigned. The opportunity for contamination to get on the mirrors has been eliminated. The collection efficiency of the optics has been increased.

5. A multiple wavelength capability, such that the fluorescence vs. depth measurements can be made at up to four wavelengths simultaneously, is under development.

6. Several calibration procedures for converting the ROST™ fluorescence data from the percent of reference format to concentration units have been developed and are under evaluation. These procedures are outlined in the accompanying document.

Converting Rapid Optical Screening Tool (ROST™) Fluorescence Intensities to Concentration Equivalents

ROST™ senses the aromatic hydrocarbon constituents of petroleum, oil, and lubricants (POL) by their fluorescence response to ultraviolet wavelength laser excitation. All chemical analysis methods (including laboratory-based ones) measure variables related to concentration, not concentration itself. Conversion from the measured variable to concentration requires a calibration curve. Several calibration options for relating the raw ROST™ fluorescence data to contaminant concentrations are under evaluation, but the best option (or options) have not been determined yet. The SITE demonstration and similar ROST™ studies show how difficult it is to validate in situ measurements.

The reference percentage data format is well-suited for field screening applications, in which the goal is to delineate contaminant plume boundaries and to define the relative distribution of contamination over the site. The fluorescence intensity is proportional to POL concentration over a wide range of concentration. The reliability of LIF-CPT for screening sites in this fashion, i.e., without any formal calibration procedure, has been demonstrated on many occasions. This form of data presentation, in which the instrument response is expressed relative to some reference compound (that may or may not be actually present at the site) is similar to other site assessment methods, e.g., organic vapor monitors. However, since ROST™ is much closer to conventional analytical methodology in its amendability to QA/QC criteria, its flexibility, and the level of detail it provides, a client may want to perform an instrument calibration, which allows POL concentrations to be reported in concentration units such as mg/kg.

The following factors must be considered in the selection and preparation of calibration standards:

1. The measured fluorescence is a composite of the contributions from all fluorescence chemical components in the sample. Thus, aging and weathering processes that affect chemical composition must be considered.
2. The fluorescence response of a petroleum-impacted soil sample is affected by the soil composition and physical properties. For example, a contaminant exhibits higher fluorescence intensity on sand than it does on a soil matrix with high clay content. The effect is believed to be related to available surface area considerations.
3. Calibration standards can be difficult to prepare for low concentrations of volatile fuels, such as gasoline and jet fuel.

Two basic strategies are available: (1) Obtaining the calibration "standards" by actual sampling at the site; (2) Making calibration standards based on assumptions on the soil type and POL that exists in the ground. Each of these, and the relative advantages and disadvantages, are discussed below. Note that the former is the procedure used during the SITE demonstration and similar validation studies to date.

Calibration Derived from Site Materials with In Situ Fluorescence Measurements

Method validation studies for LIF and other in situ sensors have generally used calibration standards

obtained directly from the ground by soil borings, which are then submitted for analysis by approved laboratory methods. The major advantage of this approach is that the influence of confounding variables such as weathering, soil moisture, soil matrix, and other changes, are eliminated. The concentrations are established with the standard analytical methods so regulatory agencies readily accept the results. The primary disadvantage of in situ calibration or validation methods is that it can be extremely difficult to obtain a sample for the conventional analysis from the same location as surveyed by ROST. The more homogeneously the contamination is distributed, the less this is a concern.

An option well worth considering is to subject any sample provided to a laboratory for analysis to an "above ground" ROST™ fluorescence measurement. This second reading provides a quality check on the soil sample to ensure it is representative of the soil measured in situ by the ROST™ system. Note, however, that the "uphole" measurement doesn't precisely replicate the conditions of the in situ push data, since the degree of soil compression is not the same.

Calibration Derived from Synthetic Standards with "Above Ground" Fluorescence Measurements

Another method, which closely resembles traditionally analytical methodology, uses standards for purposes of constructing the calibration curve. The synthetic calibration standard approach eliminates the need for any soil borings. The laboratory methods generally use solution standards, which are highly homogeneous and easily made by conventional weighing and volumetric procedures. The calibration samples for ROST™ are prepared by quantitatively spiking the petroleum product(s) of interest on to soil. Thus, for the most exacting requirements, the choice of the POL and soil for the calibration phase is crucial since the proportionality factor between fluorescence response and concentration depends on both the POL type and the soil matrix itself. The added material should match the target POL analyte as closely as possible. One of the difficulties in establishing the target POL analyte is that often many different petroleum products are present at a particular site. The actual contaminant may represent a combination of POL products. In addition, the contaminant will have weathered from long-term exposure at the site. Many other quantifying analytical methods also encounter this problem.

Depending on the objectives of the investigation, there are several approaches to designing a calibration procedure with synthetic standards:

Approach 1: Designation of POL and Soil Type

The client can assume that their contaminant is similar to a common product (gasoline, diesel fuel, coal tar, etc.) and their soil is similar to typical soil types (sand, silt, clay). If these assumptions are made, the conversion from the raw percent of fluorescence format to concentration units can be made using standard tables determined from laboratory studies. Note: These tables exist currently for common fuels on sand and are under construction for common fuels on clay and silt. This approach assumes a linear response of the instrument to the various contaminant concentrations.

Approach 2: Specific POL Material, Designated Soil Type

The client provides contaminant from the site that can be spiked in the laboratory onto reference soils and then analyzed by ROST. A set of standards is prepared by inoculating the soil samples with a series of increasing amounts of the target analyte. The spiked samples are tumbled for 24-48 hours to ensure uniform distribution of the fuel.

Approach 3: Specific POL Material and Soil from the Site

The client provides contaminant from the site and clean soil samples from the site. Contaminants from the site can then be spiked onto these soils and then analyzed by ROST. The soil is gathered from below the surface at a depth of 1-2 feet, to reduce hydrocarbon contamination from aerosols and other airborne particulates. This option is the most specific of the synthetic calibration standard approaches. However, please note that the calibration still assumes that the soil and product used in the calibration is representative of the site.

Section 8 References

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APPENDIX A

Qualitative, Quantitative, Geotechnical, and TOC Data

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TABLE A-1. QUALITATIVE REFERENCE LABORATORY DATA FOR TPH AND PAH—ATLANTIC SITE

Node Number	Depth (feet)	TPH (ppm)	PAH (ppm)
2	1 - 1.5	1,680	88.19
2	8 - 9	15	3.59
2	13 - 14	24.7	0
2	25 - 26	NS	0
2	35 - 36	19.3	.06
3	1 - 2	55.4	11.40
3	10 - 11	1,130	158.37
3	20.5 - 21.5	222	6.06
3	33.5 - 34.5	54.2	.99
4	2 - 2.5	149	13.39
4	6 - 6.5	330	.258
4	6.5 - 7	614	5.267
4	7 - 7.5	1,650	21.494
4	7.5 - 8	4,170	44.205
4	8 - 8.5	541	128.811
4	8.5 - 9	73.7	71.760
4	9 - 9.5	1,680	55.482
4	9 - 10	897	40.644
4	9.5 - 10	2,880	80.999
4	10 - 10.5	2,960	104.487
4	10.5 - 11	3,820	107.437
4	15 - 16	1,170	62.091
4	27 - 28	118	48.879
5	1 - 2	399	7.007
5	5 - 6	ND	0.020
5	7 - 8	275	18.496
5	27 - 28	146	3.481
5	33.5 - 34.5	ND	0.030

Notes:

PAH Polynuclear aromatic hydrocarbon.
 ppm Part per million.
 TPH Total petroleum hydrocarbon.
 NS Not sampled.
 ND Not detected.

TABLE A-2. QUALITATIVE REFERENCE LABORATORY DATA FOR TPH AND PAH—YORK SITE

Node Number	Depth (feet)	TPH (ppm)	PAH (ppm)
1	12 - 13	26.1	1.09
1	14 - 15	345	48.81
1	17 - 18	13.7	.88
1	22 - 22.5	ND	.01
2	8.5 - 9	ND	0
2	10.5 - 11	417	7.72
2	14 - 14.5	855	127.62
2	20 - 21	10.2	.060
3	10 - 11	10	0
3	12 - 13	259	37.62
3	16 - 16.5	2,570	134.67
3	16.5 - 17	3,650	313.97
3	17 - 17.5	57.5	1.90
3	17.5 - 18	12.7	0.23
3	18 - 18.5	27.8	0.20
3	21.5 - 22.5	ND	0.01
4	8 - 9	115	0.66
4	11 - 12	174	182.09
4	14 - 15	8,150	1,412.16
4	17 - 18	137	10.33
4	18 - 18.5	13,100	1,130.18
4	21.5 - 22	74.2	14.35
5	10 - 11	23.7	0
5	12 - 13	66	9.31
5	17 - 18	377	128.09
5	21 - 22	ND	0.165

Notes:

PAH Polynuclear aromatic hydrocarbon
ppm Part per million.
TPH Total petroleum hydrocarbon.
ND Not detected.

**TABLE A-3. QUALITATIVE REFERENCE LABORATORY DATA
FOR TPH AND PAH-FORT RILEY SITE**

Node Number	Depth (feet)	TPH (ppm)	PAH (ppm)
1	1- 1. 5	47. 1	0. 667
1	18- 19	482	12. 964
1	28. 5- 30	ND	0. 036
2	5- 6	37. 4	0. 108
2	6- 7	233	0. 142
2	15- 16	- 6, 720	137. 885
2	23. 5- 25	89. 3	1. 707
2	28. 5 - 30	96. 9	2. 713
3	1. 5 -2. 5	112	1. 358
3	5. 5 -6. 5	2, 670	118. 471
3	15- 16	1, 850	18. 730
3	23. 5 - 24	ND	0
4	15- 16	37	0
5	2. 5 - 3. 5	ND	0
5	5- 6	1, 280	1. 655
5	10- 10. 5	6, 730	143. 622
5	10. 5- 11	32, 800	338. 566
5	11 -11. 5	19, 300	344. 984
5	11. 5- 12	9, 360	206. 888
5	12- 12. 5	12, 700	190. 693
5	12. 5- 13	2, 830	87. 639
5	13- 13. 5	2, 550	64. 711
5	24- 25	9. 94	0
5	29- 30	ND	0

Notes:

PAH Polynucleararomati hydrocarbon
ppm Part per million.
TPH Total petroleum hydrocarbon.
ND Not detected.

TABLE A-4. QUANTITATIVE REFERENCE LABORATORY DATA - ATLANTIC SITE

Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 2 (21 to 22 feet)					Node 2 (24 to 25 feet)			
Ethyl-benzene	25,0W.W	42,000.W	34,000.00	7,035.62	250.00	39,000.00	14,690.00	16,663.45
TPH	8,850.00	15400.00	11,090.00	2689.89	36.00	9,880.00	4,004.40	4592.73
VPH	910.00	2,000.00	1,402.00	427.22	7.90	1,400.00	53758	579.81
Total PAH	70.42	918.32	672.69	354.08	3.99	691.99	290.96	324.69
Total BTEX	15400.00	293,000.00	221,200.00	53,049.03	1,250.00	260,000.00	93,950.00	109,210.58
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 3 (16 to 17 feet)					Node 4 (6.5 to 7.5 feet)			
Ethyl-benzene	3,600.00	4,600.00	3,900.00	469.04	250.00	3,600.00	1,410.00	1,897.71
TPH	104.00	1,290.00	425.25	577.00	20.70	412.00	254.93	166.39
VPH	88.00	130.00	112.00	21.35	10.00	110.00	43.33	57.74
Total PAH	4.43	6.84	5.75	1.05	3.91	13.73	8.30	4.63
Total BTEX	25590.00	33,550.00	28,330.00	3,728.07	320.00	37,300.00	10,435.00	17,931.46
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 4 (10 to 11 feet)					Node 4 (27.5 to 28.5 feet)			
Ethyl-benzene	29,000.00	35,000.00	31,600.00	2408.32	1,300.00	23,000.00	10,520.00	10,146.77
TPH	959.00	3,780.00	2,435.80	1,129.72	117.00	3,030.00	1,093.60	1,156.83
VPH	1,200.00	1,400.00	1,320.00	83.67	42.00	970.00	452.40	461.91
Total PAH	12.26	148.10	77.91	60.07	29.51	270.81	121.15	98.83
Total BTEX	218,700.00	307,000.00	273,740.00	34,028.49	13,700.00	193,000.00	96,740.00	85,721.28
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 5 (16 to 17 feet)					Node 5 (23.5 to 24.5 feet)			
Ethyl-benzene	390.00	2,100.00	1,198.00	811.80	940.00	1,700.00	1,174.00	301.30
TPH	87.80	516.00	201.38	177.36	48.20	893.00	238.50	366.76
VPH	36.00	160.00	96.00	59.36	52.00	160.00	77.20	46.38
Total PAH	0.48	4.72	2.39	1.79	1.96	5.11	2.99	1.26
Total BTEX	5,490.00	28,700.00	15,798.00	11,794.98	14,330.00	22,200.00	17,754.00	3,340.21

Notes:

~~XXXX~~ Values used in the final regression equations

TABLE A-5. QUANTITATIVE REFERENCE LABORATORY DATA - YORK SITE

Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 1 (15 to 16 feet)					Node 2 (13.5 to 14.5 feet)			
TPH	53.00	2,270.00	773.20	905.13	156.00	2,710.00	1,539.20	1,035.82
VPH					14.00	45.00	25.20	11.90
Total PAH	64.65	755.70	260.31	284.20	159.85	466.41	246.26	129.85
Total BTEX	580.00	4,700.00	2,026.67	2,317.79	1,800.00	23,280.00	7,556.00	8,853.57
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 2 (17 to 18 feet)					Node 3 (17 to 18 feet)			
Ethylbenzene	1,600.00	7,200.00	4,860.00	2,846.58	290.00	2,700.00	1,558.00	874.25
TPH	88.70	1,380.00	496.94	535.84	261.00	1,450.00	778.40	513.04
VPH	5.40	33.00	19.86	12.51	7.50	30.00	18.50	9.30
Total PAH	40.41	252.47	160.42	98.64	97.45	359.67	230.34	116.76
Total BTEX	1,900.00	14,100.00	8,946.00	5,131.92	1,090.00	4,900.00	2,948.40	1,641.76
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 4 (14 to 15 feet)					Node 4 (18 to 19 feet)			
Ethylbenzene	2,200.00	19,000.00	9,900.00	6,412.49	92.00	57,000.00	21,810.50	27,363.23
TPH	647.00	6,450.00	2,281.40	2,361.49	18.20	4,000.00	1,878.15	2,155.00
VPH	37.00	97.00	64.25	24.87	6.00	280.00	175.33	148.01
Total PAH	166.06	1,048.82	514.62	342.68	1.40	2,332.21	798.91	1,116.53
Total BTEX	4,540.00	36,300.00	19,542.00	11,891.11	274.00	128,800.00	42,528.80	59,970.23
Chemical	Minimum	Maximum	Mean	Standard Deviation				
Node 5 (1.5 to 2.5 feet)								
Ethylbenzene	ND	ND	ND	ND				
TPH	15.20	138.00	59.97	67.83				
VPH	ND	ND	ND	ND				
Total PAH	0.01	0.95	0.45	0.40				
Total BTEX	ND	ND	ND	ND				

Notes:

No data.

ND Not detected.

~~xxx.xx~~ Values used in the final regression equations.

TABLE A-6. QUANTITATIVE REFERENCE LABORATORY DATA - FORT RILEY SITE

Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 1 (2 to 3 feet)					Node 1 (13 to 14 feet)			
Ethyl-benzene	79.00	3,700.00	1,075.80	1502.51	100.00	20,000.00	8,595.00	10,009.87
TPH	27.50	15,800.00	5,727.98	6,698.52	32.90	3,110.00	1,416.00	1,607.95
VPH	6.00	110.00	47.50	44.90	9.20	320.00	183.55	152.78
Total PAH	0.97	260.60	89.15	105.57	0.02	96.62	31.44	44.47
Total BTEX	339.00	20,610.00	6,412.40	8,295.04	230.00	70,900.00	26,497.60	35,204.28
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 2 (6 to 7 feet)					Node 2 (17 to 18 feet)			
Ethyl-benzene	107.50	2,000.00	762.50	1,072.32	28,000.00	60,900.00	39,600.00	13464.77
TPH	48.60	7,720.00	2,169.32	3,186.75	7,050.00	16,900.00	13,150.00	4,182.11
VPH	9.00	98.00	41.83	48.87	530.00	1,200.00	790.00	259.71
Total PAH	0.05	42.05	10.98	18.15	60.66	224.76	153.55	72.14
Total BTEX	89.00	10,070.00	2,956.63	4,756.48	147,000.00	254,000.00	196,800.00	47,704.30
Chemical	Minimum	Maximum	Mean	Standard Deviation	Minimum	Maximum	Mean	Standard Deviation
Node 5 (10.5 to 11.5 feet)					Node 5 (16 to 17 feet)			
Ethyl-benzene	1,400.00	29,000.00	13,680.00	11,238.86	20,000.00	55,000.00	31,400.00	13,612.49
TPH	17,700.00	32,800.00	22,480.00	5,934.81	1,090.00	9,630.00	3,926.00	3,470.96
VPH	250.00	430.00	334.00	80.81	170.00	930.00	442.00	289.34
Total PAH	157.14	340.26	246.06	67.41	18.23	162.28	65.43	58.45
Total BTEX	23,270.00	96,300.00	59,854.00	27,580.73	63,100.00	219,700.00	108,680.00	62,975.05

Notes:

~~xxxx~~ Values used in the final regression equations.

TABLE A-7. GEOTECHNICAL AND TOC DATA - ATLANTIC SITE

Node/ Grid	Depth (feet)	TOC (mg/kg)	% > 2 mm	% Sand (0.5-2 mm)	% Silt (2-50 μm)	% Clay ($<2 \mu\text{m}$)	USDA Classification	USCS Classification
1/F	2 - 3	4,000	.03	12.43	58.33	29.21	Silty clay loam	Sandy lean clay (CL)
1/F	10 - 11	ND	0	38	43.78	20.22	Loam	Silt or clay (CL or ML)
1/F	20.5 - 21	600	1	50.84	34.17	13.99	Loam	Silt or clay (CL or ML)
1/F	30.5 - 31	200	28.38	62.78	4.72	4.12	Sand	Well to poorly graded sand (SW or SP)
1/F	35 - 35.5	400	0	24.72	44.73	30.55	Clay loam	Sandy loam or sandy silt (CL or ML)
4/c	9 - 10	3,800	0	19.34	51.24	29.42	Silty clay loam	Sandy lean silt or sandy lean clay (CL or ML)
4/C	15-16	3,200	0	44.79	30.57	24.64	Loam	Silt or clay (CL or ML)

Notes:

mg/kg Milligram per kilogram.
mm Millimeter.
 μm Micrometer.
USDA United States Department of Agriculture.
USCS Unified Soil Classification System, () two-letter classification code.
ND

TABLE A-8. GEOTECHNICAL AND TOC DATA - YORK SITE

Node/ Grid	Depth (feet)	TOC (mg/kg)	%>2mm	% Sand (0.5-2 mm)	% Silt (2-50 μm)	% Clay (<2 μm)	USDA Classification	USCS Classification
I/G	5 - 6	ND	0.00	13.66	58.94	27.40	Silty clay loam	Clay or silt with sand (CL or ML)
I/G	7 - 8	2,800	0.05	26.08	51.05	22.82	Silt loam	Clay or silt with sand (CL or ML)
I/G	15-15.5	1,400	0.23	60.24	20.93	18.60	Sandy loam	Silty to Clayey sand (SM or SC)
I/G	18.5 - 19	490	30.54	46.38	12.09	10.99	Sandy loam	Poorly graded sand with silt or clay (SW-SC or SP-SC)
3/C	12-13	3,200	0.00	8.90	80.43	30.67	Silty clay loam	Silt or lean clay with sand (CL or ML)
3/C	16.5 - 17	2,600	6.69	52.48	17.92	22.91	Sandy clay loam	Clayey or silty sand (SM or SC)

Notes:

mg/kg Milligram per kilogram.
mm Millimeter.
 μm Micrometer.
USDA United States Department of Agriculture.
USCS Unified Soil Classification System, () two-letter classification code.
ND Not detected.

TABLE A-9. GEOTECHNICAL AND TOC DATA - FORT RILEY SITE

Node/ Grid	Depth (feet)	TOC (mg/kg)	%<2 mm	% Sand (0.5-2 mm)	% Silt (2-50 μm)	% Clay (<2 μm)	USDA Classification
4/H	2 - 3	3,400	0.00	31.32	43.48	25.20	Loam
4/H	7.5 - 8.5	600	.16	60.76	22.08	17.00	Sandy loam
4/H	15-16	800	0.00	62.44	19.16	18.40	Sandy loam
4/H	29 - 30	300	20.36	57.48	10.46	11.70	Sandy loam
2/E	15-16	4,600	.11	55.13	25.87	18.89	Sandy loam
3/G	5.5 - 6.5	9,000	.10	47.61	36.02	18.27	Loam

Notes:

mg/kg Milligram per kilogram.
mm Millimeter.
 μm Micrometer.
USDA United States Department of Agriculture.
USCS Unified Soil Classification System, () two-letter classification code