The Rapid Optical Screening Tool (ROST™) Laser-Induced Fluorescence (LIF) System for Screening of Petroleum Hydrocarbons in Subsurface Soils

Innovative Technology
Verification Report

by

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and managed the extramural research described here. It has been peer reviewed by the Agency and approved as an EPA publication. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.

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 Office of Research and Development (ORD) provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The National Exposure Research Laboratory (NERL), ORD, is the Agency's center for the investigation of technical and management approaches for identifying and quantifying risks to human heath and the environment. One focus of the Laboratory's research program is to develop and evaluate technologies for the characterization and monitoring of air, soil, water and subsurface resources. This in turn, will provide the scientific information needed by EPA to support regulatory and policy decisions; and to provide the science support needed to ensure effective implementation of environmental regulations and strategies.

Effective measurement and monitoring technologies are needed to assess the degree of contamination at a site, to provide data which may be used to determine the risk to public health or the environment, to supply the necessary cost and performance data to select the most appropriate technology, and to monitor the success or failure of a remediation process.

Candidate technologies can originate from within the federal government or from the private sector. Through this program, developers are given the opportunity to conduct a rigorous demonstration of their technology's performance under realistic field conditions. By completing the evaluation and distributing the results, the Agency establishes a baseline for acceptance and use of these technologies. The Characterization and Monitoring portion of this program is administered by NERL's Characterization Research Division in Las Vegas, Nevada.

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List of Abbreviations and Acronyms

AEC	Army Environmental Center
ASTM	American Society for Testing and Materials
ATI	Analytical Technologies, Inc.
bbl	Barrel (Equivalent to 42 U.S. Gallons)
bgs	Below Ground Surface
Cal EPA-DTSC	State of California Environmental Protection Agency, Department of Toxic Substances Control
CAS	Chemical Abstracts Service
cm	Centimeter
CPT	Cone Penetrometer Testing
CSC	Computer Sciences Corporation
CSCT	Consortium for Site Characterization Technology
DFM	Diesel Fuel Marine
DHS	Department of Health Services (State of California)
DoD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
DQO	Data Quality Objective
EMMC	Environmental Monitoring Management Council
EPA	U.S. Environmental Protection Agency
ETI	Environmental Technology Initiative
ETV	Environmental Technology Verification
ft	Feet
FVD	Fluorescence Versus Depth
GC/FID	Gas Chromatograph/Flame Ionization Detector
HNTS	Hydrocarbon National Test Site
HSA	Hollow Stem Auger
Hz	Hertz
IDW	Investigation Derived Waste
IR	Infrared
IRP	Installation Restoration Program
ITVR	Innovative Technology Verification Report
LIF	Laser-Induced Fluorescence
LOD	Limit of Detection
m	Meter
μm	Micrometer
mg/kg	Milligrams per Kilogram
mg/L	Milligrams per Liter
m/min	Meters per Minute

List of Abbreviations and Acronyms (Continued)

mJ	Millijoules
mL	Milliliter
mm	Millimeter
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ms	Millisecond
msl	Mean Sea Level
NCBC	Naval Construction Battalion Center
NCCOSC RDT&E	Naval Command, Control, and Ocean Surveillance Center Research, Development, Test, and Evaluation (Division)
NERL-CRD	National Exposure Research Laboratory-Characterization Research Division
nm	Nanometer
ns	Nanosecond
PAH	Polycyclic Aromatic Hydrocarbons
PDA	Photodiode Array
PE	Performance Evaluation
PPE	Personal Protective Equipment
ppm	Parts per Million
PRC	PRC Environmental Management, Inc.
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
R^2	Correlation Coefficient
RI/FS	Remedial Investigation/Feasibility Studies
ROST	Rapid Optical Screening Tool™
RPD	Relative Percent Difference
SCAPS	Site Characterization and Analysis Penetrometer System
SNL	Sandia National Laboratories (Department of Energy)
SOP	Standard Operating Procedure
SPT	Standard Penetrometer Testing
TER	Technology Evaluation Report
TPH	Total Petroleum Hydrocarbons
TRPH	Total Recoverable Petroleum Hydrocarbons
TSF	Tons per Square Foot
U.S.	United States
USCS	Unified Soil Classification System
UV	Ultraviolet
WES	Waterways Experimental Station (Army Corps of Engineers)
WTM	Wavelength-Time Matrix

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We wish to acknowledge the support of all those who helped plan and conduct the demonstrations, interpret data, and prepare this report. In particular, for demonstration site access and relevant background information, Stephan McCarel and Ernest Lory (Naval Facilities Engineering Service Center), and David Miller (SNL); for implementation of the demonstration plan and data evaluation, Grace Bujewski, Brian Rutherford, Robert Knowlton, Robert Helgesen, and Peter Stang (PRC); for logistical and health and safety support, Michael Skelly (Roy F. Weston, Inc.) and Michael Strosinsky (SNL); for editorial and publication support, Merlyn Liberty (Tech Reps, Inc.); for peer and technical reviews, Jerry Peace (SNL); Bruce LaBelle (State of California Environmental Protection Agency, Department of Toxic Substances Control); and for U.S. EPA project management, Stephen Billets and Bob Lien (U.S. EPA). In addition, we gratefully acknowledge the participation of the ROST™ technology developers, Greg Gillispie and Randy St. Germain, Dakota Technologies, Inc. (701-237-4908); Mr. Andy Taer, Fugro Geosciences (713) 778-5580; and Mr. George Robitaille, Tri-Services SCAPS Program of the U.S. Army Environmental Center (410-612-6865).

Section 1

Executive Summary

The Consortium for Site Characterization Technology (CSCT) has established a formal program to accelerate acceptance and application of innovative monitoring and site characterization technologies that improve the way the nation manages its environmental problems. The CSCT is a partnership program involving the U.S. Environmental Protection Agency (EPA), the Department of Defense (DoD), and the Department of Energy (DOE). Its mission is to support the demonstration and verify the performance of new and emerging technologies.

In 1995 the CSCT conducted a demonstration of two *in situ* laser-induced fluorescence-based technologies using the Site Characterization and Analysis Penetrometer System (SCAPS) cone penetrometer testing (CPT) platform. The two technologies were the Rapid Optical Screening Tool™ (ROST™) developed by Loral Corporation and Dakota Technologies, Inc., and the SCAPS LIF, developed through a collaborative effort of the Army, Navy, and Air Force under the Tri-Services SCAPS program and by the Naval Command, Control, and Ocean Surveillance Center, Research, Development Test, and Evaluation (NCCOSC RDT&E) Division. 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 distinguish contaminated and noncontaminated areas. Results for the SCAPS LIF and CPT performance evaluation are presented in a separate report.

The purpose of this Innovative Technology Verification Report (ITVR) is to document the demonstration activities and present and evaluate the demonstration data in order to verify the performance of the ROST™ LIF sensing technology relative to developer claims as presented in the approved demonstration plan.

Technology Description

The ROST™ LIF sensor provides real-time field screening of the physical characteristics of soil and chemical characteristics of aromatic petroleum hydrocarbon contamination at hazardous waste sites. The current configuration is designed to quickly and cost-effectively distinguish aromatic hydrocarbon-contaminated areas from uncontaminated areas. The ROST™ system mounted on a standard cone penetrometer truck is also capable of acquiring geologic information and has the added benefit of reduced generation of investigation-derived waste. This capability allows further investigation and remediation decisions to be made more efficiently and reduces the number of samples that must be submitted to laboratories for analysis.

The ROST™ sensor evolved from the tunable laser instrumentation originally developed at North Dakota State University (NDSU) with U.S. Air Force research support. The NDSU tunable laser system was first deployed for LIF-CPT in 1992 in a demonstration project at Tinker AFB. The technology developers from NDSU then formed a small business, Dakota Technologies, Inc. (DTI) and participated in additional demonstrations of LIF-CPT projects. The technology has been commercialized and marketed by a consortium of government and industry led by Loral Corporation. ROST™ was acquired by Fugro Geosciences, Inc., in May 1996 and is now offered as an integrated service with their CPT systems worldwide. DTI provides ROST™ technical support to Fugro.

The ROST™ uses a wavelength tunable ultraviolet laser source coupled with an optical detector to measure fluorescence via optical fibers. The measurement is made through a sapphire window on a probe that is pushed into the ground with a truck-mounted CPT. The optical fibers are integrated with the geotechnical probe and umbilical of a standard truck-mounted CPT system. CPT and standard penetrometer testing (SPT) have been widely used in the geotechnical industry for determining soil strength and soil type from measurements of tip resistance and sleeve friction on an instrumented probe.

The ROST™ LIF method provides data on the *in situ* distribution of petroleum hydrocarbons from the fluorescence response induced in the polycyclic aromatic hydrocarbon (PAH) compounds that are components of the petroleum hydrocarbon. The methods detect PAHs in the bulk soil matrix throughout the vadose, capillary fringe, and saturated zones. The methods provide a screening of the relative petroleum hydrocarbon concentrations present. However, for the purposes of this demonstration, only the detect/nondetect capability of ROST™ was evaluated.

Demonstration Objectives and Approach

The primary objectives of the field demonstrations were to evaluate the ROST™ LIF technology in the following areas: (1) its performance compared to conventional sampling and analytical methods; (2) the logistical resources necessary to operate the technology; (3) the quality of the LIF data; (4) the applications of the technology as determined by its performance in the CSCT demonstrations; and (5) its performance relative to developer claims. Performance of the ROST™ LIF sensor was evaluated to determine the agreement between LIF "detect/nondetect" data and laboratory analyses for both total recoverable petroleum hydrocarbons by EPA Method 418.1 and total petroleum hydrocarbons by California Department of Health Services Method 8015-modified. A secondary objective for this demonstration was to evaluate the LIF technology for cost, range of usefulness, and ease of operation.

In the approved demonstration plan, the developers presented several performance claims against which they were evaluated. These claims included the ability to collect measurements up to 150 feet below the surface when the sensor is used with an industry-standard 20-ton CPT rig; the ability to integrate the sensor subassembly with the rig in the field within a few hours, a standard data collection rate of one sample every 1.2 seconds, providing a spatial resolution of less than 0.2 feet for a standard push rate of 1 meter per minute; the ability of the system to acquire multidimensional data representations such as wavelength time matrices (WTMs) to identify fuel or waste type (*e.g.*, creosote); and the ability of the crew to utilize WTM information to eliminate false positives from nonhydrocarbon fluorophores.

The demonstration was designed to evaluate the ROST™ technology as a field screening method by comparing the LIF data to data produced by conventional sampling and analytical methods. For both demonstrations, conventional sampling and analysis consisted of boring with a hollow stem auger, collecting split spoon samples as closely as possible to the push cavity, and analyzing discrete samples at an off-site commercial laboratory for petroleum hydrocarbons by EPA Method 418.1 and California Department of Health Services Method 8015-modified. The demonstrations were conducted at two geologically and climatologically different sites: (1) the Hydrocarbon National Test Site located at Naval Construction Batallion Center (NCBC), Port Hueneme, California, in May 1995, and (2) the Steam Plant Tank Farm at Sandia National Laboratories (SNL), Albuquerque, New Mexico, in November 1995.

Demonstration Results and Performance Evaluation

The ROST™ LIF technology was evaluated against the developer claims as presented in the demonstration plan for the Port Hueneme demonstration and subsequent addendum for the SNL arid site demonstration All developers' claims were met. The ROST™ technology was integrated with the SCAPS cone penetrometer platform and was operated in both static and dynamic modes. The data collection rate was measured to be 1 meter per minute with a vertical spatial resolution of less than 2 cm. In static mode, the system acquired multidimensional data representations to identify fuel or waste type. Wavelength-time matrices were used to eliminate false positives from nonhydrocarbon fluorophores, specifically carbonates at the SNL. The ROST™ system was demonstrated to be an effective, rapid *in situ* field screening method for characterizing the subsurface distribution of diesel no. 2 and diesel fuel marine to depths of 55 feet in a variety of soil textures in unsaturated and saturated zones.

Cost Evaluation

The ROST™ technology is available for use within the 48 contiguous United States for a cost of approximately $5,300 per day or site-specific footage rates, which includes a CPT rig provided by a commercial vendor such as Fugro Geosciences. Crew per diem and mobilization costs are additional and site specific. The ROST™ subassembly can be integrated with any commercially available industry-standard CPT rig. Typical crew members include a ROST™ system operator (at a minimum), CPT operator, and assistant. Under normal conditions, an average of 300 feet of pushes can be completed in a day. This translates to a cost of under $20 per foot. This compares to conventional drilling costs, which range between $15 to $20 per foot for drilling and installation of monitoring wells and between $50 and $100 per foot for drilling and sampling for site characterization. In addition, laboratory analysis costs, which range from $90 to $150 per sample for TPH and TRPH, respectively, must be considered.

The main savings attributable to the ROST™ LIF system is that it can substantially reduce the duration of the field investigation, quantity of costly sample collection and analyses, and ultimately the number of soil borings and monitoring wells drilled at a site. In a general site characterization effort, it can provide more data in less time and less expensively than conventional drilling and sampling. Investigation-derived wastes are minimal, and worker exposure to contaminants is reduced when using *in situ* technologies rather than conventional drilling and sampling methods.

Section 2

Introduction

The Site Characterization Technology Challenge

Rapid, reliable and cost effective field screening technologies are needed to assist in the complex task of characterizing and monitoring of hazardous and chemical waste sites. However, some environmental regulators and remediation site managers may be reluctant to use new site characterization technologies that have not been validated in an EPA-sanctioned testing program, since data from them may not be admissible in potential legal proceedings associated with a site or its cleanup. Until characterization technology claims can be verified through an unbiased evaluation, the user community will remain skeptical of innovative technologies, despite their promise of better, less expensive and faster environmental analyses.

The Consortium for Site Characterization Technology was established as a component of the Environmental Technology Innovation, Commercialization and Enhancement Program as outlined in 1993 in President Clinton's Environmental Technology Initiative to specifically address these concerns. The CSCT is a partnership between the EPA, the Department of Energy, and the Department of Defense. As a partnership, the CSCT offers valuable expertise to support the demonstration of new and emerging technologies. Through its organizational structure, it provides a formal mechanism for independent third-party assessment, evaluation, and verification of emerging site characterization technologies.

The mission of the CSCT is to identify, demonstrate, assess, and disseminate information about innovative and alternative environmental monitoring, measurement, and characterization technologies to developers, remediation site managers, and regulators. The Consortium is intended to be a principal source of information and support with respect to the availability, maturity, and performance of innovative environmental monitoring, measurement, and characterization technologies.

Technology Demonstration Process

The CSCT provides technology developers a clearly defined performance assessment, evaluation and verification pathway. The pathway is outlined in the following four components:

- technology selection;
- technology demonstration;
- technology performance assessment, evaluation, and verification, and
- information distribution.

These are discussed in more detail in the following paragraphs.

Technology Selection

The first step in the overall demonstration process is one of technology selection. The selection process comprises two components. Beyond the initial identification of potential technologies, a critical aspect of technology selection is an assessment of its *field deployment readiness*. Only pre-production and production instrumentation with a history of successful laboratory or field

operation are accepted into the program. Early, unproven prototype instrumentation systems requiring extensive testing and modification prior to field deployment are not acceptable demonstration candidates. The candidate technology must meet minimum technology maturity criteria in order to participate in a demonstration. The degree of technology maturity may be described by one to three levels:

Level 1
Technology has been demonstrated in a laboratory environment and ready for initial field trials.

Level 2
Technology has been demonstrated in a laboratory environment and in field trials.

Level 3
Technology has been demonstrated extensively both in the laboratory and in field trials and is commercially available.

A second aspect of the technology selection process involves a determination of *technology/field requirements match*. Because of limited resources, the Consortium must determine a technology's suitability for demonstration in light of the current needs of the environmental characterization and monitoring community. A technology may be given priority for demonstration and evaluation based on its environmental and fiscal impact and the likelihood that its demonstration will fill information gaps which currently impede cost effective and efficient environmental problem solving. The CSCT conducts surveys of EPA, DOE, DoD, state, local, tribal and industry agencies to assist in determining the degree of match between the candidate technology and the needs of the environmental restoration community.

Technology Demonstration

A technology demonstration plan is developed by the technology verification entity, according to document preparation guidance provided by the Consortium for Site Characterization Technology. The demonstration plan includes a technology description, the experimental design, sampling and analysis plan, methods for evaluating the technology, a quality assurance project plan, and a health and safety plan. After approval by the EPA and technology developers, the demonstration plan is implemented at an appropriate field location. The CSCT provides technical support to the technology developer during demonstration plan preparation and execution and also audits the demonstration and data collection processes.

Technology Performance Assessment, Evaluation, and Verification

In this important component of the demonstration process, an objective comparison of demonstration technology data is carried out against a reference data set generated using conventional analysis methodologies. The principal product of this phase of the project is the ITVR, prepared by an independent third party. The report documents the demonstration technology data along with an assessment of the technology's performance in light of the reference data. The degree of data analysis in the technology report is determined by the level of maturity of the technology under evaluation, with the more mature technologies receiving more thorough analysis. The CSCT provides Level 1 technologies with a fielding opportunity in which the system can be tested. Evaluation of the system performance and comparison of field data with reference laboratory data are the developer's responsibility. In the case of Level 2 technologies, the performance evaluation is performed by the CSCT. The most extensive evaluation is done for

the Level 3 technologies since these are considered market-ready. As part of the demonstration objectives, the CSCT evaluates the developer claims regarding the capabilities of the Level 3 technology and prepares a technology evaluation report containing an assessment of the technology's performance.

Information Distribution

Evaluation reports for Level 2 technologies are distributed to the technology developers, CSCT partners, and the general public. In addition, for Level 3 technologies performance verification statements are distributed to the developers for subsequent use in seeking additional developmental funding or marketing.

Technology reports for Level 1 technologies are distributed as EPA project reports. There is no technology evaluation contained in these documents. Results are compiled and reference data is provided so that the developer and reader can formulate an opinion regarding technology performance.

The CPT-LIF Sensor Demonstrations

The developer of the ROST™ LIF technology was Loral Corporation and Dakota Technologies, Inc. (DTI). PRC Environmental Management, Inc. (PRC), a contractor to the NCCOSC RDT&E Division (the developer of the SCAPS LIF technology), prepared the demonstration plan for both developers and conducted the predemonstration and demonstration field efforts, coordinated the analyses of the soil samples, and provided the raw data to Sandia National Laboratories-New Mexico (SNL), a DOE-owned laboratory operated by Lockheed Martin Corporation. SNL, as the EPA's verification entity, reviewed and approved the demonstration plan and amendments and reduced and analyzed the data generated during the two field demonstrations.

The ROST™ LIF is a CSCT Level 3 technology. For these demonstrations, the CSCT and the developers selected the demonstration sites, participated in the demonstration planning process, and jointly and separately evaluated the data generated during both demonstrations.

This report describes how the demonstration participants collected and analyzed samples, provides the results of the demonstration, and describes how the performance of the ROST™ LIF technology was verified. Section 5 discusses the experimental design for the demonstration. Section 4 presents the reference laboratory results and evaluation. Section 3 describes the ROST™ LIF technology. Section 6 presents the ROST™ LIF demonstration results and evaluation. Section 7 is an assessment of recommended applications of the technology. Section 8 is a forum wherein the developer has the opportunity to discuss the technology results and comment on the evaluation and future technology developments. Section 9 is a table summarizing selected ROST™ commercial projects. In addition, there are appendices containing the reference laboratory data, ROST™ LIF data, and proposed ROST™ LIF method.

Section 3

ROST™ LIF Technology Description

The description of the ROST™ LIF technology and verification of its performance has been divided into two sections, Section 3 and Section 6. Because this is an innovative technology, evaluating its performance and comparing it to conventional laboratory methods with well-established procedures is not as simple as the evaluation of the laboratory methods as presented in the preceding section. Section 3 describes the ROST™ LIF sensor technology and includes background information and a description of the equipment. General operating procedures, training and maintenance requirements, and some preliminary information regarding the costs associated with the technologies are also discussed. Much of this information was provided by the technology developer and presented in the demonstration plan (Loral, 1995). Any claims made in this section may or may not have been verified during this demonstration. Specifically, the subsections regarding technology applications and limitations and advantages of the technology were provided by the developer and may not have been verified. The verification of technology performance at the two demonstration sites and evaluation of developer claims for this program are presented in detail in Section 6.

ROST™ LIF Sensor

Petroleum-based fuels, such as gasoline, diesel, and kerosene, and other hydrocarbons, such as coal tar and creosote, contain compounds that fluoresce when excited by ultraviolet light. A soil sample contaminated with petroleum substances will exhibit fluorescence intensity that is proportional to the contaminant concentration. The concentration of the hydrocarbon fraction in an unknown sample can be determined by comparing its fluorescence intensity to that of calibration standards.

ROST™ detects the presence and quantitates the amount of aromatic petroleum hydrocarbons by the laser-induced fluorescence in the sample. The Rapid Optical Screening Tool is a tunable dye laser-induced fluorescence system designed as a field screening tool for detecting petroleum hydrocarbons in the subsurface. The ROST™ LIF system uses a pulsed laser coupled with an optical detector to make fluorescence measurements via optical fibers. The measurement is made through a sapphire window on a probe that is pushed into the ground with a truck-mounted cone penetrometer.

The ROST™ approach permits temporary or permanent installation of the LIF equipment on a CPT truck or other direct push vehicle, although a dedicated ROST™ unit could be permanently installed in a CPT. The CPT LIF system uses a steel probe containing the LIF sapphire optical window as well as the cone and sleeve strain gauges. The excitation and emission optical fibers are isolated from the soil system by a 6.35-mm diameter sapphire window located 60 cm from the probe tip and mounted flush with the outside of the probe. The ROST™ LIF system uses 600-μm diameter fibers that are up to 100 m in length.

Laser Source

The ROST™ LIF primary laser uses a neodymium-doped yttrium aluminum garnet pump (Nd:YAG) laser. It produces 532-nm light at 50 Hertz (Hz) with a pulse energy of 50 mJ. The light from the primary laser pumps a rhodamine 6G dye laser whose output is then frequency-doubled to produce ultraviolet (UV) light. The laser system used in the ROST™ is capable of generating wavelengths of light ranging from about 280 nm to about 300 nm, depending on the dye being used. The wavelength of light produced by the ROST™ LIF laser is tunable within this range. The ROST™ laser system is coupled to a silica clad silica ultraviolet/visible light transmitting optical fiber. This fiber and the collection fiber are integrated with the geotechnical probe and umbilical of a standard truck-mounted CPT system.

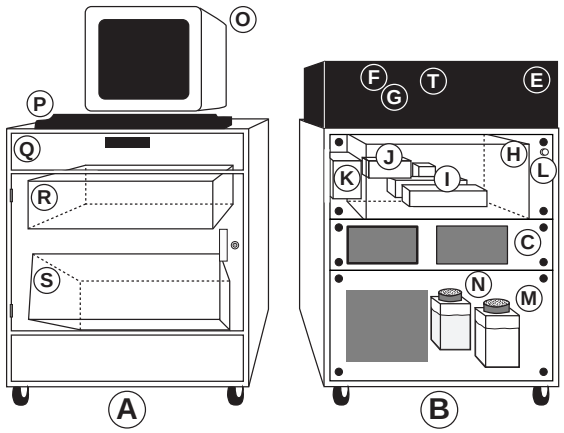
System Components

The Rapid Optical Screening Tool consists of the spectrometer rack and the control rack (Figure-3-1). The spectrometer rack holds all the spectroscopic instrumentation, including the Nd:YAG pump laser, tunable dye laser, emission monochromator, photomultiplier tube, and associated power supplies and motion controllers. The control rack contains the control computer and a digital oscilloscope signal processor. In operation the racks can be positioned independently and separated from each other by up to 25 feet. The racks themselves are standard industrial models with a 20-inch by 25-inch footprint and stand 25 inches high. The Nd:YAG pump laser and dye laser are arranged on an optical breadboard affixed to the top of the spectrometer rack. When the opaque plastic dye laser cover is in place, the total height of the spectrometer rack is 34 inches. The computer monitor can be conveniently placed on top of either the control rack or the dye laser cover.

Spectrometer Rack Components

The spectrometer rack holds modules for generation of pulsed ultraviolet light and detection of the return fluorescence signal. The fiberoptic cables leading to and from the cone penetrometer probe are interfaced at the back of the spectrometer rack through ST connectors. The generation of exitation light in the ROST is based on a two-stage dye laser pumped by the 532 nm harmonic of a compact pulsed Nd:YAG laser. The Nd:YAG laser head, Rhodamine 6G dye laser, and all related optics are arranged on a 19-in. by 23-in. aluminum breadboard, which is affixed to the top of the spectrometer rack. Light in the 280-300 nm wavelength range is generated via frequency doubling of the dye laser output. A 266-nm exictation wavelength capability is employed for direct detection of benzene, toluene, ethylbenzene, and xylenes (BTEX) and other single-ring aromatic hydrocarbons. In this case, the 532-nm Nd:YAG beam is diverted around the dye laser to the frequency doubling crystal for fourth harmonic generation (266 nm) To change between the tunable and 266-nm configurations requires insertion (or removal) of two mirrors on kinematic mounts.

All other mechanical operations are controlled through software. During normal operation, the only time the cover need be removed is to change between the 266-nm and 280-300-nm configurations. The frequency doubling crystal has been incorporated into a housing whose temperature is held at 40° C for isolation from any temperature drift in the truck. Pyroelectric power meters are built in for monitoring the 532-nm output of the Nd:YAG laser and the ultraviolet light emerging from the doubling crystal. If the ultraviolet output relative to the 532-nm pump input falls below specifications, an automated routine is initiated by the operator to re-optimize the frequency doubling crystal position.



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

Figure 3-1. ROST™ system components.

The ROST™ fluorescence detector consists of a monochromator and photomultiplier tube (PMT). The monochromator selects a narrow wavelength interval of the pulsed, polychromatic fluorescence light that is returned to it from the cone via the collection fiber. The normal wavelength range of the monochromator setting is 300 to 500 nm. The fluorescence light pulse lasts for tens to hundreds of nanoseconds. The photons emerging from the monochromator to a pulsed electrical signal in the PMT. The photoelectron stream is amplified during passage down the photomultiplier dynode chain to the anode. The time profile of the electron current that is collected at the dynode is slightly distorted in time by the time response characteristics of the PMT.

Control Rack Components

The principal components of the control rack are the control computer, the digital oscilloscope signal processor, and the slide-out computer keyboard. Signals passing from the computer to the spectrometer rack are used to set the monochromator slit width, the wavelength passed by the monochromator, the wavelength of the dye laser, and the position of the frequency doubling crystal for the chosen dye wavelength. Information passing from the spectrometer rack to the control computer includes the signal from the PMT, diagnostic information from the Nd:YAG laser, and the outputs from the power meters.

The pulsed electrical signal from the PMT is fed to a digital storage oscilloscope, which digitizes, averages, and displays the fluorescence intensity versus time waveform. The user may select the number of waveforms to be averaged in the digital storage oscilloscope. After completion of the specified number of acquisitions, the waveform is downloaded to the computer for permanent storage and post-processing of the data. The digital storage oscilloscope and computer communicate via a GPIB bus.

Dynamic Range

The linear dynamic range of the ROST™ LIF detector depends on the specific hydrocarbon analyte as well as the particular matrix. Generally, for *in situ* measurements, it has been found that the linear portion of the response curves extends well beyond three orders of magnitude. Nonlinearity tends to occur at concentrations greater than 10,000 mg/kg. In sandy soils, the nonlinearity occurs at lower concentrations than in clay rich soils, possibly due to self absorption or saturation. The linear dynamic range of the LIF sensor also depends on operator-controlled instrumental parameters. The linear dynamic range may be extended to higher concentrations by adjusting the slit width of the detector, but this results in decreased sensitivity at lower concentrations.

Sensitivity, Noise, and Background

Three quantities are needed to determine the fluorescence LOD and concentration LOD limit: noise, background, and sensitivity. Sensitivity is determined using the calibration samples prepared, in most cases, immediately prior to the site visit using soil from the site and standard analytical techniques. The noise is computed after the pushes have been performed and is generally computed on a push by push basis.

The fluorescence intensity for each calibration sample is measured in triplicate each day prior to the start of operations. The three measurements are averaged to provide a single measured intensity for each concentration. The fluorescence data are regressed using the known concentration values to establish a slope and intercept. The intercept is an estimate of the intensity of the unspiked calibration standard (0 mg/kg). The slope is an estimate of the "sensitivity" of the fluorescence measurement to changes in hydrocarbon contamination.:

intercept: b = intensity measured on 0 mg/kg calibration sample

slope : $$m = \frac{\Sigma(y_i - b)\,x_i}{\Sigma\, x_i^2}$$

where the sums are taken over the range of calibration samples. For these calibration soils, x is given by the concentration of the target fuel, while y is the measured fluorescence intensity adjusted to be a percentage of the M-1 standard.

Following each push, a histogram is provided for the LIF responses showing a percentage of the M-1 standard. A subjective decision is made based on the belief that background counts (again expressed as a percentage of M-1 standard) should be somewhat normally distributed. This decision results in an estimate of background noise and an estimate of the mean background fluorescence level, expressed as a percentage of M-1 standard and the background noise, the

standard deviation of the fitted normal distribution. For pushes in uncontaminated areas, the noise is directly reflected in the width of the histogram. It is possible to get a histogram that is bi-modal (or multi-modal), complicating the noise evaluation. A single mode will not be observed if different levels of background fluorescence are present, *e.g.*, from two different types of minerals, or if samples reflect information from uncontaminated regions and regions where hydrocarbons are present.

Calculated Fluorescence and Concentration Thresholds

The ROST™ LIF fluorescence threshold can be qualitatively interpreted as the minimum signal amplitude that is reliably associated with petroleum contamination. The fluorescence threshold is affected by any fluorescence background arising from the fiber, window, or soil matrix. The basis of the ROST™ fluorescence threshold determination is that the background signals should be normally distributed. The center of the normal (Gaussian) distribution gives the background value, and the standard deviation can be used to establish confidence intervals. For this demonstration a 99% confidence interval was used, such that:

$$\text{fluorescence threshold} = \text{mean background} + 2.58 \times \text{standard deviation of the background.}$$

The concentration threshold is determined directly from the fluorescence threshold using the estimated sensitivity provided by the calibration results. These results are based on the equation:

$$\text{concentration threshold} = 2.58 \times \text{standard deviation of the background/sensitivity}$$

For the Port Hueneme demonstration, the ROST™ data was integrated over a 6-inch interval. For the SNL demonstration, the data was averaged over a 3-inch interval. Any signal exceeding the fluorescence threshold was considered a "detect."

Mobilization and Installation of ROST™ for CPT LIF work

ROST™ is transported to job sites, installed in the CPT truck for the duration of the job, and then demobilized for transport to its next site. Several different transportation modes have already been tested and proved satisfactory. For transportation by commercial entities (motor freight or airlines), the spectrometer rack and control rack are placed in wooden shipping containers. During the shipment, the racks rest in the boxes on the shock mountings that are affixed to the floor of the CPT truck.

Deployment Costs

The daily rate for ROST™ is approximately $5300 per day, which includes the daily rate for the CPT rig. Footage rates may be proposed on a job-specific basis. Per diem costs vary with each deployment. Electronic data files are available to the client for $12 per push and color integrated CPT/ROST logs are available for $12.50 per push. Mobilization fees are quoted on a job specific basis. Additional crew members are available on an hourly basis.

Technology Applications

Fugro Geosciences' ROST™ LIF system was developed in response to the need for real-time *in situ* measurements of subsurface contamination at hazardous waste sites. The ROST™ LIF system performs rapid field screening to determine either the presence or absence or relative concentration of petroleum hydrocarbon contaminants within the subsurface of the site. The site can be further characterized with limited numbers of carefully placed borings or wells. In addition, remediation efforts can be directed on an expedited basis as a result of the immediate availability of the LIF and soil matrix data.

Advantages of the Technology

The LIF sensing technology is an *in situ* field screening technique for characterizing the subsurface distribution of petroleum hydrocarbon contamination before installing groundwater monitoring wells or soil borings. The method is not intended to be a complete replacement for traditional soil borings and monitoring wells, but is a means of more accurately placing a reduced number of borings and monitoring wells in order to achieve site characterization.

The LIF technology using a CPT platform provides real-time field screening of the physical characteristics of soil and chemical characteristics of petroleum hydrocarbons at hazardous waste sites. The current configuration is designed to quickly and cost-effectively distinguish petroleum hydrocarbon-contaminated areas from uncontaminated areas. This capability allows further investigation and remediation decisions to be made more efficiently and reduces the number of samples that must be submitted to laboratories for costly analysis. By achieving site characterization while expending a minimum amount of resources, remaining resources can be directed at studying the actual risks posed by the hazardous waste site and for remediation if warranted.

Table 3-1 compares the important attributes of the ROST™ technology with those of traditional laboratory methods. The major advantage of ROST™ is that it provides real-time data in the field without the need for sample manipulation and the accompanying risk of sample degradation. ROST™ also provides a qualitative fingerprinting capability in a fraction of the time required by gas chromatography. Under normal conditions, an average of 300 feet of pushes can be reasonably advanced in one day.

Table 3-1. Total petroleum hydrocarbon analysis methods.

Criterion	DHS Method 8015	EPA Method 418.1	ROST™
Basis of method	Gas chromatography	IR absorbance in C-H	Fluorescence
Applicability	Volatile organic compounds	Compounds with C-H bonds	Aromatic hydrocarbons (single, double, and multi-ring)
Possible interferences	Any volatile compound	Any species with C-H bonds	Fluorescent minerals
Sample preparation	Extract, filter	Extract, filter	None
Analysis time	5-30 minutes	Seconds	Seconds
Fingerprint capability	Yes	No	Yes
Real-time/*In situ*	No	No	Yes

Detectors and Data Acquisition Modes

ROST™ uses the digital oscilloscope to capture time-domain information about the pulsed fluorescence signal resulting from the pulsed laser excitation. The areas of the time-integrated waveforms are proportional to the total photon flux passed to the detector. The time dependence of the fluorescence contains significant additional information, particularly about oxygen quenching. Oxygen fluorescence quenching leads to a decrease in the emitted intensity at all wavelengths. The fluorescence response as a function of fuel concentration (sensitivity) is affected by variable oxygen levels in the soil matrix. Variability in the oxygen levels encountered during a push can cause small changes to the FVD profile. Measurements performed with continuous excitation sources, or with pulsed sources but not time resolved detection, are unavoidably affected by the phenomenon. ROST™ operators and data interpreters can make valid assessments of the extent of contamination even when oxygen content varies.

Limits of the Technology

This section discusses the limits of the ROST™ LIF as it is currently understood.

Response to Different Petroleum Hydrocarbons

The relative response of the ROST™ LIF sensor depends on the specific analyte being measured. The instrument's sensitivity to different hydrocarbon compounds such as gasoline, diesel fuel and jet fuel are comparable. The sensitivity is not as great for coal tar and creosote although they are readily detectable. These variations in sensitivity are primarily a reflection of the variations in the PAH distribution. Other contributing factors such as optical density, self absorption, and quenching are less important. The total observable fluorescence produced by any given petroleum hydrocarbon sample depends on the mole fraction of fluorescing PAHs along with the relative quantum efficiency of each of the fluorescing species. The fluorescence properties of a hydrocarbon mixture in soil may also change after long-term exposure to and interaction with the environment. A contaminant that has been in the ground for any period of time will undergo changes in chemical composition due to weathering, biodegradation, and volatilization.

The ROST™ LIF system often uses 290 nm as the excitation wavelength. This wavelength is short enough to excite the fluorescence of all aromatic hydrocarbons with at least two conjugated aromatic rings. Aliphatic species and single-ring aromatics do not contribute to the ROST™ LIF signal from 290 nm. The ROST™ can also be configured for 266 nm excitation. The attenuation of light passing through the optical fibers, however, is greater at 266 nm than at 290 nm or longer wavelengths, so the possible length of the push may be restricted.

Matrix Effects

The *in situ* fluorescence response of the LIF sensor to hydrocarbon compounds is sensitive to variations in the soil matrix. Matrix properties that affect LIF sensitivity include soil grain size, mineralogy, moisture content, and surface area. Each of these factors influences the relative amount of analyte that is adsorbed on or absorbed into the soil. Only the relative fraction of analyte that is optically accessible at the window of the probe can contribute to the fluorescence signal. Of the four influencing factors mentioned above, the dominant variable appears to be soil surface area. LIF sensitivity to petroleum hydrocarbons on soil has been shown to be inversely

proportional to the available surface area of the soil substrate. Sandy soils tend to have a much lower total available surface area than clay soils. Hydrocarbon compounds in sandy soils generally yield a correspondingly higher fluorescence response than they do in clay rich soils. In one study, soil samples were prepared as a series of sand/clay (illite) mixtures with progressively increasing clay content. The relative LIF response to DFM in each soil is essentially identical once the response curves were normalized to the available surface area of each of the soils. The moisture content of the soil matrix is another influencing factor. The LIF sensitivity to petroleum hydrocarbons generally increases with greater soil moisture content, although in some natural soils the effect appears to be small. LIF response curves representing the results of fluorescence measurements on a soil with varying water content have also been generated. These results suggest that the response is fairly insensitive to changes in moisture content. In another study it was demonstrated that increasing the amount of water in a soil tends to narrow the sensitivity difference between sandy and clay soils. It is thought that water physically displaces the hydrocarbons from within the pore spaces of the matrix, effectively reducing the surface area available to contaminants. The effects of soil grain size have also been examined in laboratory studies. LIF sensitivity generally increases with increased grain size. The measured fluorescence was shown to be substantially greater in the coarser mesh sizes.

Spectral Interferences

The ROST™ LIF sensor is sensitive to any material that fluoresces when excited by ultraviolet wavelengths. Although intended to specifically target petroleum hydrocarbons, the excitation energy produced by the LIF system's laser may cause other naturally occurring substances to fluoresce as well. At some investigation sites, it is possible that LIF sensors could respond to fluorescence originating from nonhydrocarbon sources. Many common fluorescent minerals can produce a measurable LIF signal. Other non-hydrocarbon fluorescent material introduced through human activity may be found in the subsurface environment. Deicing agents, antifreeze additives, and many detergent products are all known to fluoresce very strongly. The potential presence of fluorescence emission from nontarget (non-hydrocarbon) analytes within the soil matrix must be considered when assessing LIF field screening data. In some instances, the inability to discriminate between hydrocarbon fluorescence and nonhydrocarbon fluorescence can lead to false positives for the presence of hydrocarbons. Nonhydrocarbon fluorescence can mask the presence of hydrocarbon fluorescence, leading to reduced sensitivity or erroneous estimation of the relative amount of hydrocarbon present. In the worst case, spectral interference can lead to a false positive or false negative report of findings. However, because the LIF sensor collects full spectral information, it is almost always possible to discriminate between hydrocarbon and nonhydrocarbon fluorescence by analyzing the spectral features associated with the data.

Truck-Mounted Cone Penetrometer Access Limits

The CPT support platform used to deploy the ROST™ LIF is typically a 20-ton all-wheel drive diesel powered truck. The dimensions of the truck require a minimum access width of 10 feet and a height clearance of 15 feet. Some sites, or certain areas of sites, might not be accessible to a vehicle of this size. The access limits for a typical CPT truck are similar to those for conventional drill rigs and heavy excavation equipment.

Cone Penetrometer Advancement Limits

The CPT sensors and sampling tools may be difficult to advance in subsurface lithologies containing cemented sands and clays, buried debris, gravel units, cobbles, boulders, and shallow bedrock. As with all intrusive site characterization methods, it is extremely important that all underground utilities and structures be located using reliable geophysical equipment operated by trained professionals before undertaking activities at a site. Local utility companies should be contacted for the appropriate information and approval.

Section 4

Reference Laboratory Results and Evaluation

The purpose of this section is to address issues related to the reference laboratory used for these demonstrations. Section 4 is divided into four subsections. The first subsection provides details concerning the selection of ATI as the reference laboratory and the reference methods performed on the soil samples at ATI for the purpose of comparison with results from the LIF technology. The second subsection provides an assessment of data quality for the laboratory and gives a description of the quality control procedures for TRPH (total recoverable petroleum hydrocarbons by IR spectrophotometry) by EPA Method 418.1 and California DHS Method 8015-modified for TPH (total petroleum hydrocarbons by GC-FID). These methods will be referred to as TRPH and TPH throughout the remainder of this report. In the third subsection, the methods used to estimate accuracy, precision, and completeness are discussed and results provided. The final subsection provides a summary of the laboratory data quality evaluation and a brief discussion of how the laboratory results will be used for comparison with the results of the LIF technology.

Selection of Reference Laboratory and Methods

To assess the performance of the LIF technology as a field screening tool for petroleum hydrocarbons in the subsurface, the data generated using the LIF technology was compared to data obtained using conventional sample collection and analytical methods. The analytical laboratory selected to provide reference analytical services, ATI, is certified in the state of California. The laboratory is located in San Diego, California.

ATI was selected because of its experience with QA procedures, analytical result reporting requirements, data quality parameters, and previous involvement with the Navy SCAPS program. ATI is not affiliated with the U.S. Navy, Loral Corporation, DTI, or any of the demonstration team members. ATI provided copies of the analytical results directly to SNL in order to maintain independence of the data. Copies of all QA and analytical procedures were provided to SNL for review prior to the demonstration and were included in the approved demonstration plan.

After discussion between representatives of State of California EPA, SNL, and the U.S. EPA, EPA Method 418.1 for TRPH and California DHS Method 8015-Modified for TPH were selected as the reference methods for the LIF technologies. The TRPH and TPH methods were chosen because of their widespread and generally accepted use in delineating the extent of petroleum hydrocarbon contamination. The TRPH and TPH methods are currently used as indicators of petroleum contamination in leaking underground and aboveground fuel tank investigations; as such they are the most comparable analytical methods corresponding to the objective of demonstrating rapid field screening using LIF.

EPA Method 418.1 for total recoverable petroleum hydrocarbons (TRPH) is used for the measurement of Freon-113-extractable petroleum hydrocarbons from surface and saline waters, soil, and industrial and domestic wastes. The sample is acidified to a low pH (<2) and serially extracted with Freon-113 in a separatory funnel. Interferences from polar animal oils and greases

are removed with silica gel adsorbent. Infrared analysis of the extract is performed, and its absorption is directly compared to that measured on a standard mixture of hydrocarbons.

California Department of Health Services (DHS) Method 8015-modified for total petroleum hydrocarbons (TPH) is based on EPA SW-846 Method 8015 for determination of ketones, modified for determination of petroleum hydrocarbons in soil (EPA, 1995). It is used for the determination of gasoline and diesel in contaminated groundwater, sludges, and soil. After solvent extraction, a sample is injected into a gas chromatograph where compounds are separated. Compounds in the GC effluent are identified and quantified using a flame ionization detector. The chromatogram produced by this analysis covers the carbon range from C7 to C36 and can help to identify the product type using the n-alkane pattern distribution, pristane: phytane ratios, and the width of the unresolved complex mixture.

Assessment of Laboratory Data Quality

Audits

As part of the cooperative agreement between the U.S. EPA and the State of California EPA Department of Toxic Substances Control, a representative of the California EPA audited the ATI laboratory in April 1995 and provided audit results to SNL. The audit found no irregularities and verified the procedures used to homogenize and analyze the discrete soil samples. SNL reviewed the ATI Quality Assurance Manual and all related procedures prior to the demonstrations (ATI, 1995).

Sample Holding Times

The holding time specification for EPA Method 418.1 is 28 days from the sampling date. The holding time specification for California DHS Method 8015-modified is extraction within 14 days of sampling date. The required holding times per ATI SOP 105 from the date of sample receipt to the date of extraction and analysis were met for the samples from both sites. However, for the SNL samples, two samples (SNLDB11-5 and SNLDB11-10) were misplaced prior to homogenization and were left unrefrigerated in a sealed container for five days before being located. They were homogenized, extracted and analyzed per both methods within 14 days of the sampling date (CEIMIC, 1996). The results are shown in Table A-2. These samples had large concentrations (>10,000 mg/kg) of hydrocarbons that exceeded the LIF detection limit. For this verification study, the total concentration of the petroleum hydrocarbons in the sample was unimportant for the comparison; the fact that both samples showed contamination well above the LIF detection limit (qualifying the samples as “detect”) was important for the purpose of comparison to the LIF method. For this reason, they were not excluded from the data set.

Sample Preparation

All soils were homogenized for five minutes prior to extraction and analysis per ATI SOP 421. Preparation of soils for TPH analysis was performed per ATI SOP 400 by diluting in methylene chloride. Preparation of soils for TRPH analysis was performed by extraction with Freon-113 for 45 minutes prior to analysis per ATI SOP 803.

Sample Analysis

TRPH was determined by EPA Method 418.1 by calculating the linear regression of absorbance versus concentration. The concentration thus derived tells only the concentration of oils in the Freon-113 extract. This was then related back to the original sample. TPH was quantified by DHS Method 8015-modified by sample peak area using the mean response factor of the curve. The concentration was calculated using the response factor and the mean calibration factor obtained from prepared diesel fuel standards and adjusting for volume and dilution factors. FID was used for compound detection.

Detection Limits

The ATI method detection limit for TRPH is 1.0 mg/kg for soil. The method detection limit for TPH is 5.0 mg/kg for soil.

Quality Control Procedures

For TPH, quality control procedures included preparation of a calibration curve for instrument calibration using NIST-traceable standards. A reagent blank is extracted each time a batch of no more than 20 samples is extracted. An additional reagent blank is extracted for each batch of 20 samples in any given day. A blank spike is extracted with each batch of no more than 20 samples. Surrogates are run with each soil sample and quality control sample. Matrix spikes and matrix spike duplicates are also prepared and associated to no more than 20 samples of a similar matrix to check for precision and accuracy. Spiking is done directly into the sample prior to extraction. Spiking levels for fuel hydrocarbons are 100 mg/kg for soils.

For TRPH, a reagent blank, blank spike, matrix spike, and matrix spike duplicate were analyzed for each batch of 10 samples. Spiking level for petroleum hydrocarbons is 130 mg/kg for soils. A laboratory control sample was analyzed to verify the working curve, and a midrange check standard was run every tenth scan. The working calibration curve was prepared once per day.

Calibration standards were run at least every 10 samples to verify the calibration curve. In addition, a laboratory control sample (a midrange reference standard) was run at least once during each instrument run to verify the calibration curves. ATI did not report the actual results to the developers or SNL, but did report that all calibration and control standards were within acceptance limits.

Accuracy, Precision, and Completeness

This section discusses the accuracy, precision, and completeness of the reference method data. Tables 4-1 and 4-2 display the results of the quality control samples used to estimate accuracy and precision of the methods. The data from the reference laboratory were internally reviewed by ATI QC personnel before the data were delivered to SNL and NCCOSC RDT&E Division. SNL reviewed the raw data and quality control sample results and verified all calculations.

Accuracy

Accuracy and matrix bias of the reference methods were assessed using laboratory spiked samples and, in the case of DHS Method 8015-modified, surrogate additions. Results of past PE audits of ATI were also reviewed to verify laboratory performance for accuracy and precision.

Table 4-1. Quality control results for TPH[1].

QC Sample	ATI Acceptance Limits	Port Hueneme Demo Average Result	SNL Demo Average Result
Matrix Spike % Recovery	63-119% Recovery	88 (range 80-100)	100 (one sample)
MS Duplicate % Recovery	63-119% Recovery	86 (range 77-100)	110 (one sample)
MS Duplicate RPD	18%	3 (range 0-8)	4 (range 0-10)
Surrogate Spikes	69-132% Recovery	104 (range 97-126)	110 (range 100-126)
Blank Spike	61-125% Recovery	96 (range 90-100)	108 (range 100-110)
Reagent Blanks	<5.0 mg/kg	all < 5.0 mg/kg	all < 5.0 mg/kg

[1] (Total Petroleum Hydrocarbons by GC/FID, California DHS Method 8015-modified).

Table 4-2. Quality control results for TRPH[2].

QC Parameter	ATI Acceptance Limits	Port Hueneme Demo Average Result	SNL Demo Average Result
Matrix Spike % Recovery	74-126% Recovery	104 (range 79-118)	104 (range 98-106)
MS Duplicates RPD	20%	3 (range 0-20)	4 (range 0-13)
Blank Spike	88-118% Recovery	102 (range 90-118)	104 (rang 100-110)
Reagent Blank	< 1.0 mg/kg	all < 1.0 mg/kg	all < 1.0 mg/kg

[2] (Petroleum Hydrocarbons by IR Spectrophotometry, EPA Method 418.1).

To estimate accuracy, the percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{\text{Spiked sample result - Unspiked sample result}}{\text{Spike concentration}} \times 100\%$$

Diesel fuel standard was the spiking compound for the TPH method, and the surrogate is bis-2-ethylhexylphthalate. Surrogate recoveries were all well within laboratory acceptance limits (69-132% recovery). Blanks were prepared using sterilized silica sand as the "soil." The spiking compound for TRPH was a prepared mixture of fuel hydrocarbons containing hexadecane, isooctane, and benzene. Blanks for both methods were prepared using sterilized silica sand as the "soil."

The percent recoveries for the laboratory measurements of matrix spikes, blank spikes, and duplicate spikes for both methods are presented in Tables 4-1 and 4-2.

Cal EPA-DTSC also obtained splits of samples to independently verify ATI's results at the State of California Hazardous Materials Laboratory. There was excellent agreement between both laboratories for TPH and TRPH.

Precision

Precision of the reference method results can be estimated using the field duplicates by comparing the relative percent differences (RPD) for sample results and their respective field duplicates, or results of a laboratory spiked sample prepared and analyzed in duplicate, using the following equation:

$$\text{RPD} = \frac{\left|\text{Sample result} - \text{Duplicate result}\right|}{\text{Average result}} \times 100\%$$

Field duplicate samples were analyzed by both reference methods. After the soil samples were homogenized, nine of the samples from the Port Hueneme site and one of the samples (SNLDB11-40) from the SNL site were analyzed in duplicate (see Table A-1). This subset was selected randomly by the SNL verification entity in the field during the Port Hueneme demonstration, based on a visual assessment of the contamination of the sample; only the samples containing visually detectable hydrocarbon contamination were analyzed in duplicate. The sample for the SNL demonstration was selected after the demonstration based on inspection of the LIF results. The mean precision estimate (RPD) for the 10 total field duplicates was 10.7% for TPH and 16.4% for TRPH. Overall, these data show good agreement between the samples and their respective field duplicates, indicating a high degree of precision by the reference laboratory.

The precision for the laboratory duplicates (Table 4-1, 4-2) was estimated by comparing the results of 14 pairs of matrix spike/matrix spike duplicates for TPH and 23 pairs of matrix spike/matrix spike duplicates for TRPH. Overall, those data shows good agreement between the laboratory matrix spikes and their duplicates for both methods.

Completeness

Percent completeness is defined as follows for all measurements:

$$\%C = 100\% \times \left(\frac{V}{T}\right)$$

where

V = number of sample measurements judged to be valid
T = total number of discrete sample measurements

Results were obtained for all of the soil samples. A total of 130 analytical soil sample results plus nine field duplicate results using both TPH and TRPH methods were available from Port Hueneme. A total of 92 soil sample results for both TPH and TRPH plus one field duplicate sample result were available from the SNL Tank Farm demonstration data set. As mentioned earlier, two samples from SNL that were left unrefrigerated for 5 days at the laboratory were included in the data set because their suitability for comparison to the LIF measurements did not appear to be compromised. Based on these results, the completeness of the data set was 100 percent.

Use of Qualified Data for Statistical Analysis

As noted above, 100 percent of the reference laboratory results from Port Hueneme and SNL samples were reported and validated. The data review indicated that all data were acceptable for meeting the demonstration objectives. The results of these analyses are presented in tabular form in Appendix A, Tables A-1 and A-2, and graphically in Section 6.

Section 5

Demonstration Design and Description

Evaluation of ROST™ LIF Sensor Performance

The performance of the ROST™ LIF sensor was evaluated to determine the percentage agreement between LIF "detect/nondetect" data and both TPH and TRPH results. Conventional sampling and analysis consisted of boring adjacent to the push holes with a hollow stem auger, collecting split spoon samples as close as possible to the push cavity, and analyzing the discrete samples at the reference laboratory. The data from the laboratory analysis of soil samples which showed TRPH or TPH contamination above the LIF detection limit were considered to show a "detect." Similarly, if *in situ* LIF readings registered above the LIF site detection limit, they would also indicate a "detect." The number of matches (detect/detect plus nondetect/nondetect) were tallied and reported as percentage agreement. The misses were indicated as LIF "false positives" or "false negatives." Because of natural interferences and fluorescent subsurface minerals, a greater number of false positives than false negatives was expected during the operation of the LIF technologies. Because the false positive data could be investigated with additional data analysis, the goal was to keep the number of false negatives to no more than 5 percent.

Other ROST™ attributes evaluated included the ability to collect measurements up to 150 feet below the surface when the sensor is used with an industry-standard 20-ton CPT rig; the ability to integrate the sensor subassembly with the rig in the field within a few hours, a standard data collection rate of one sample every 1.2 seconds, providing a spatial resolution of less than 0.2 feet for a standard push rate of 1 meter per minute; the ability of the system to acquire multi-dimensional data representations such as wavelength time matrices (WTMs) to identify fuel type; and the ability of the crew to utilize WTM information to eliminate false positives from nonhydrocarbon fluorophores. These attributes were evaluated by observing them in the field during the demonstration.

Performance audits were conducted in the field to verify that the ROST™ LIF system was operated according to the procedures outlined in the demonstration plan.

Description of Demonstration Sites

Field demonstrations were conducted at two sites: (1) the Hydrocarbon National Test Site located at Naval Construction Battalion Center (NCBC) Port Hueneme, California, in May 1995, and (2) the Steam Plant Tank Farm at Sandia National Laboratories (SNL), Albuquerque, New Mexico, in November 1995.

Port Hueneme Site Description

The NCBC Port Hueneme site encompasses approximately 4,000 acres on the Pacific coast in Ventura County, California. NCBC Port Hueneme is approximately 60 miles northwest of Los Angeles and is located immediately to the west and northwest of the City of Port Hueneme (Figure 5-1). NCBC Port Hueneme is an active Navy facility where remedial investigation/ feasibility studies (RI/FS) under the Navy's Installation Restoration Program (IRP) are currently

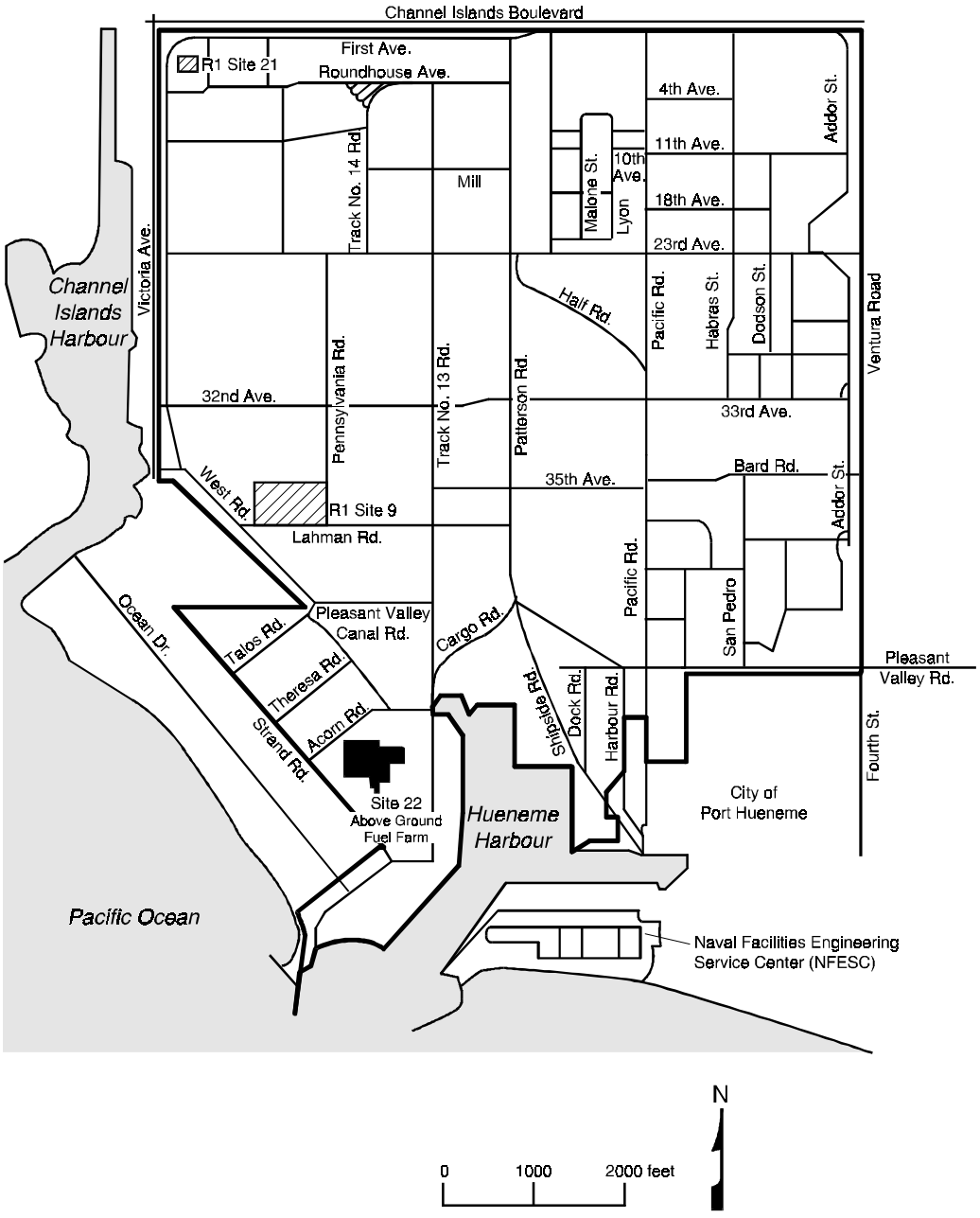


Figure 5-1. Site vicinity map, Port Hueneme; NCBC Port Hueneme area is delineated by the dashed perimeter.

in progress. The demonstration area is located at Site 22, the aboveground fuel farm. Site 22 is located in the southwestern portion of NCBC Port Hueneme, approximately 1,000 feet west of Hueneme Harbor and approximately 2,000 feet north of the Pacific Ocean.

Port Hueneme Site History

Site 22 includes five decommissioned aboveground fuel storage tanks numbered 5021, 5022, 5025, 5113, and 5114. The tanks are surrounded by a series of asphalt-paved earthen berms that restrict surface runoff and which were designed to contain the contents of each tank in the event of failure. Based on investigative findings during remedial investigation/feasibility study activities, it appears that all five tanks or their associated piping leaked.

Based on the contaminant type and distribution in the vicinity of Tank 5114, this area was selected for the demonstration. Tank 5114, a 10,500-barrel capacity tank, was constructed in 1969 and used to store diesel fuel marine (DFM).

Port Hueneme Site Geology and Hydrogeology

The uppermost 1 to 2 feet of soil at Site 22 typically consist of orange-brown silty sand or silt. Below this interval is a layer consisting of predominantly medium-grained sand, tan in color, with some coarse and fine-grained sand. This sand layer is approximately 18 feet thick. Site 22 has been built up several feet higher than the surrounding region; the elevation of the ground inside the berms averages about 17 feet above mean sea level (msl). A dark gray silt layer is present below the sand layer corresponding approximately to 18.5 feet below ground surface (bgs). Recent measurements of groundwater elevations in monitoring wells at Site 22 indicate a groundwater flow direction to the south-southeast. Depth to groundwater is 11 to 13.5 feet bgs.

Port Hueneme Site Contaminants and Distribution

The soils and groundwater in the area around Tank No. 5114 have been contaminated by petroleum hydrocarbons. The full extent of the contamination has not been assessed; however, previous site investigations have indicated TPH levels exceeding 70,000 mg/kg to a depth of 20 feet bgs. Predemonstration sampling as part of this effort indicated TPH contamination at 24,000 mg/kg at a depth of 16 feet bgs. Laboratory analysis confirmed that DFM is present in the soil. Contaminants appear to have migrated vertically and reached their greatest concentration near the water table.

Predemonstration Sampling and Analysis

A predemonstration sampling and analysis event was performed in accordance with the demonstration plan to evaluate the demonstration site and the standard analytical methods for verifying the LIF technologies. The developers conducted predemonstration sampling between April 4 and 12, 1995. Representatives of SNL, U.S. EPA, and State of California EPA Department of Toxic Substances Control (Cal EPA-DTSC) were present during the predemonstration event. During the sampling activities, a number of individual ROST™ pushes were advanced at the site. Following select pushes, a borehole was advanced adjacent to the penetrometer hole using a hollow stem auger with split spoon sampler, and discrete soil samples were collected. The soil samples were shipped to Analytical Technologies, Inc., (ATI) for

confirmatory analyses. Representatives of Cal EPA-DTSC collected duplicates for analysis at the State of California Hazardous Materials Laboratory for verification of contaminants.

In addition to the soil samples submitted to ATI and the State of California Hazardous Materials Laboratory for chemical analysis, one to two soil samples per boring were submitted to the Law/Crandall geotechnical laboratory in San Diego, California. These samples were subjected to mechanical soil analysis for grain size estimation using ASTM Method 422 and for moisture and density analysis using ASTM Method 2937.

The results of the predemonstration sampling and analysis were used by the developers to assess matrix effects or interferences, revise operating procedures where necessary, and finalize their performance claims. The developers and representatives of Cal EPA-DTSC, SNL, and U.S. EPA determined that the site and the contaminant type and distribution were acceptable for the purposes of this demonstration.

Demonstration Sampling Operations, Port Hueneme

The objective of the sampling design at Port Hueneme was to collect *in situ* LIF and conventional laboratory analytical data concurrently to demonstrate the ROST™ LIF sensor's capability to delineate the boundary (field screening) of a petroleum hydrocarbon plume. To accomplish this, a series of eight iterative pushes and comparison borings were advanced between Tank 5114 and the expected plume boundary. After each push, a boring was drilled adjacent to the push hole and sampled. The push and boring locations are depicted in Figure 5-2.

According to the demonstration plan, the SCAPS CPT platform alternatively pushed the SCAPS LIF probe and ROST™ LIF probe, producing a pair of pushes located approximately 8 inches apart, prior to the advancement of the comparison boring between the two push holes.

The SCAPS CPT platform was used to push the ROST™ LIF probe and acquire fluorescence data to a total depth of 16 to 20 feet bgs. Following the pair of pushes, the rig was moved completely away from the location and a hollow stem auger (HSA) drill rig was positioned with its stem center approximately 4 inches from the push hole. A hole was drilled using an 8-inch diameter hollow stem auger such that the internal diameter of the auger was parallel to, and approximately 2 inches offset from, the LIF probe cavity. Operating within this drilling geometry, the advancing auger flights destroyed the LIF probe's push hole while allowing for the collection of split spoon soil samples within approximately 3 inches (horizontally) of the push cavity. Soil samples were collected with a split spoon sampler lined with 6-inch long, 2.5-inch diameter stainless steel tubes. The sampler was driven in advance of the lead auger using a 140-pound slide hammer falling over a 30-inch distance, in accordance with the ASTM 1586 Standard Penetration Test.

Soil samples were collected from every 1 to 1.5 feet of boring starting at a depth of approximately 2 feet below ground surface. The sampler was overdrilled approximately 6 inches prior to retrieval to reduce the amount of slough soils typically in the bottom of the borehole. Only tubes containing sample soils that appeared relatively undisturbed were used.

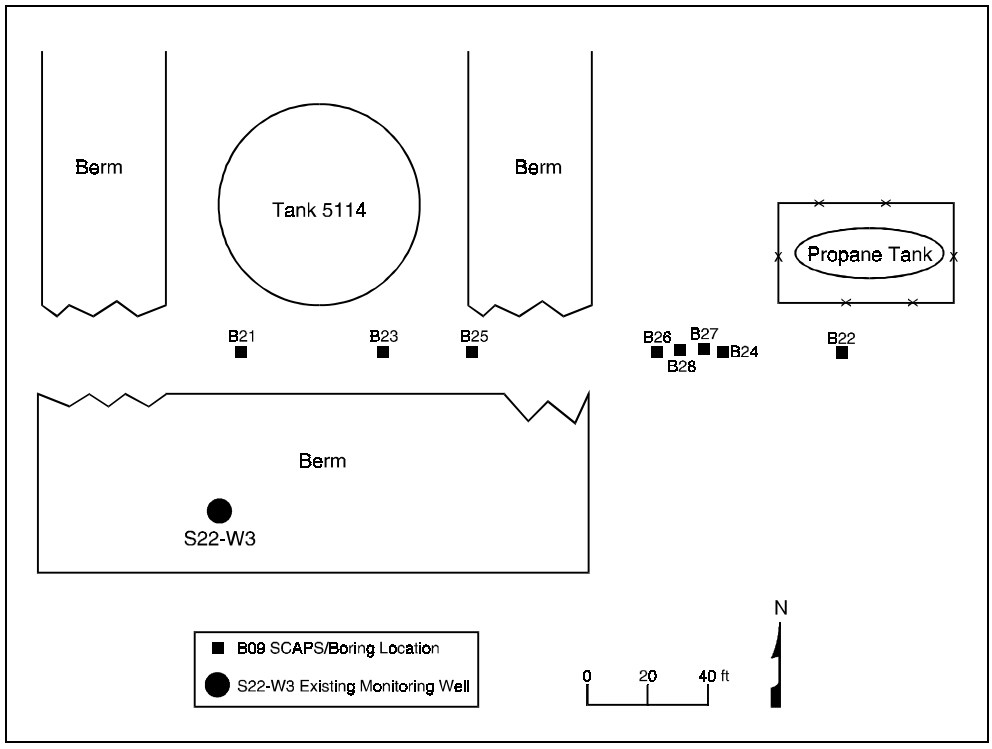


Figure 5-2. Demonstration site and sampling locations, Port Hueneme. B21-B28 are the locations of the HSA borings associated with the CPT pushes. For example, B21 is the boring associated with PHDR21, the initial ROST push.

The depth from which samples were collected was measured by lowering a weighted tape before and after sample retrieval. This permitted identification of the depth from which the samples were collected in the vadose zone to within approximately 3 inches. In the water saturated zone, however, sloughing and hydraulic soil movement (flowing or heaving sand conditions) were encountered which resulted in much greater uncertainty in identifying sample depth.

After each split spoon sampler was retrieved and the individual soil sample collection tubes were visually inspected, each soil sample was handled as follows:

- The soil sample tube was sealed with Teflon swatches and plastic end caps. The tube was labeled with the sample identification information.

- The end caps of the sealed, labeled soil sample tube were duct-taped in place. The samples were placed into an insulated cooler with ice, recorded onto the chain-of-custody form, and held for shipment to ATI for analysis. The PRC sample custodian and SNL verification entity verified the accuracy and completeness of the soil sample chain-of-custody forms and placed a custody seal on the cooler. Original field sheets and chain-of-custody forms accompanied all samples shipped to the reference laboratory.

- In addition to those soil samples submitted to ATI for chemical analysis, one to two soil samples per boring were submitted to Law/Crandall's geotechnical laboratory in San Diego, California. These samples were subjected to mechanical soil analysis to determine grain size distribution using ASTM Method 422 and for moisture and density analysis using ASTM

Method 2937. Those samples determined by grain size analysis to contain a substantial portion (>25 percent) of fine-grained material (defined as that passing through a #200 sieve) were subjected to hydrometer testing by ASTM Method 422. Although not part of the verification process, Law/Crandall, Inc., performed the geotechnical laboratory analyses on selected soil samples to confirm the visual logging of the borings in the field.

- Rinsate samples of the split spoon sampler were collected to check for cross-contamination after decontamination of the sampler. The rinsate samples were submitted to ATI for analysis.

Port Hueneme Sampling Locations

The sampling locations were in a line running west to east located south of Tank 5114 (Figure 5-2). The first ROST™ push was located in what was estimated to be an area within the plume and identified as PHDR21, at 6 feet east of the 0-foot location (Table 5-1). The first boring was advanced and sampled immediately after the probe was retrieved and the CPT rig was moved away. A second push, designated as PHDR22, was then advanced in an area estimated to be outside of the plume boundary. The second boring was advanced and sampled immediately after the probe was retrieved and the CPT rig was moved away. The strategy was to advance the first two pushes in locations that would bound the edge of the plume and then locate subsequent pushes, PHDR23-PHDR28, in an effort to close in on the horizontal extent of the plume. The distance between each successive push decreased until the edge of the subsurface hydrocarbon plume had been defined within 9 feet, for a total of 8 borings. The number of sampling locations was based on past use of the CPT and LIF technology to define hydrocarbon plume boundaries at other sites and on demonstration budget constraints.

Table 5-1. Port Hueneme boring and push summary table.

Push or Boring Identification	Date	Comments
PHDR21 PHDB21	5-17-95	R21 located 6 feet 8 inches east of zero point; B21 located 4 inches west of R21. Total of 15 samples collected; max depth 19 feet.
PHDR22 PHDB22	5-17-95	R22 located 200 feet east of zero point; B22 located 4 inches east of R22. Total of 17 samples collected; max depth 19.5 feet.
PHDR23 PHDB23	5-18-95	R23 located 53 feet 8 inches east of zero point; B23 located 4 inches west of R23. Total of 16 samples collected; max depth 19 feet.
PHDR24 PHDB24	5-18-95	R24 located 162 feet east of zero point; B24 located 4 inches east of R24. Total of 21 samples collected; max depth 19.5 feet.
PHDR25 PHDB25	5-19-95	R25 located 81 feet 8 inches east of zero point; B25 located 4 inches west of R25. Total of 16 samples collected; max depth 20 feet.
PHDR26 PHDB26	5-19-95	R26 located 142 feet east of zero point; B26 located 4 inches west of R26. Total of 17 samples collected; max depth 20 feet.
PHDR27A PHDB27	5-22-95	R27A advanced through 6 feet pilot hole of approximately 6 feet bgs. R27A located 156 feet 4 inches east of zero point. B27 located 4 inches east of R27A. Note that push R27 was refused in upper 5 feet due to gravel and cobble. Total of 19 samples collected; max depth 19.5 feet.
PHDR28 PHDB28	5-22-95	R28 advanced through 6-ft pilot hole 148 feet east of zero point. B28 located 4 inches east of R28. Total of 17 samples collected; max depth 18.5 feet.

Note: PHDR represents the ROST™ push at the Port Hueneme site. PHDB represents the hollow stem auger boring.

Each boring using the hollow stem auger and split spoon sampler was identified with a unique number assigned in the field. For example, PHDB21 identified the boring (B) that was collocated with the initial ROST™ (PHDR21) push. Individual samples collected from each boring were sequentially numbered as they were logged; for example, PHDB21-5 identified the fifth soil sample collected from boring B21. Each sample was submitted for analysis accompanied by the chain-of-custody documentation.

Note that PHDR27A represents the second ROST™ push attempted at the location indicated in Figure 5-2. The first push was refused due to an impenetrable gravel/cobble layer within 6 feet of the surface. PHDP27A was offset 8 inches from PHDR27 and was advanced without difficulty. It was attempted only after a pilot hole was advanced using an uninstrumented (dummy) probe. After extraction of the dummy probe, the ROST LIF probe was advanced though the pilot hole and LIF measurements were collected throughout the push. Because PHDR28 was located within 9 feet of PHDR27A and it was assumed that the subsurface gravel/cobble layer would be encountered, a dummy probe was also used to prepush this location.

SNL Tank Farm Site Description

The location for the second LIF demonstration was an active fuel tank farm for the Steam Plant at Sandia National Laboratories, Albuquerque, New Mexico (Figure 5-3). This site was selected because it represented a different climate, geology, and contaminant distribution than the Port Hueneme demonstration site. The Tank Farm site is an SNL Environmental Restoration Site that is currently being characterized and will begin a remediation feasibility investigation beginning in 1998. It is located in the southwest portion of Technical Area I on the northeast corner of the intersection of Hardin and Wyoming Boulevards (Figure 5-4). The 3-acre site is L-shaped and contains five tanks. The area west and north of Tank 5 was the area for this demonstration.

Site History, SNL Tank Farm

The Steam Plant Tank Farm was constructed in the 1940s. All tanks contained #2 diesel fuel to be used as a backup supply system for the Steam Plant when the primary fuel supply (natural gas) was unavailable. The backup supply system has never been used and the fuel currently in the tanks is the original product delivered. One documented release of fuel occurred in June 1991, when the main valve of Tank 5 was left open and more than 5,000 gal of fuel was discharged into a holding tank at the Steam Plant (approximately one-half mile north of the tank farm). During transfer operations from the holding tank to another storage tank south of Hardin Boulevard, a leaking pipe was discovered. The pipe was then cut and capped, and the impacted soils in the area were scheduled for excavation. A few weeks later during excavation operations, it became evident that the fuel release was much greater than previously thought. Although the full horizontal and vertical extent of the plume was not determined, the 50 foot by 35 foot by 15 foot deep excavation pit was backfilled with the original fuel-contaminated soil. Recent site investigations using a Geoprobe® identified petroleum contamination down to at least 30 feet bgs in the area of the excavation.

SNL Tank Farm Site Geology/Hydrogeology

SNL is located near the east-central ridge of the Albuquerque Basin. The basin is a rifted graben within the Rio Grande Rift that is bounded on the east and west by north-south trending faults. SNL lies on a partially dissected bajada formed by coalescing alluvial complexes. The deposits

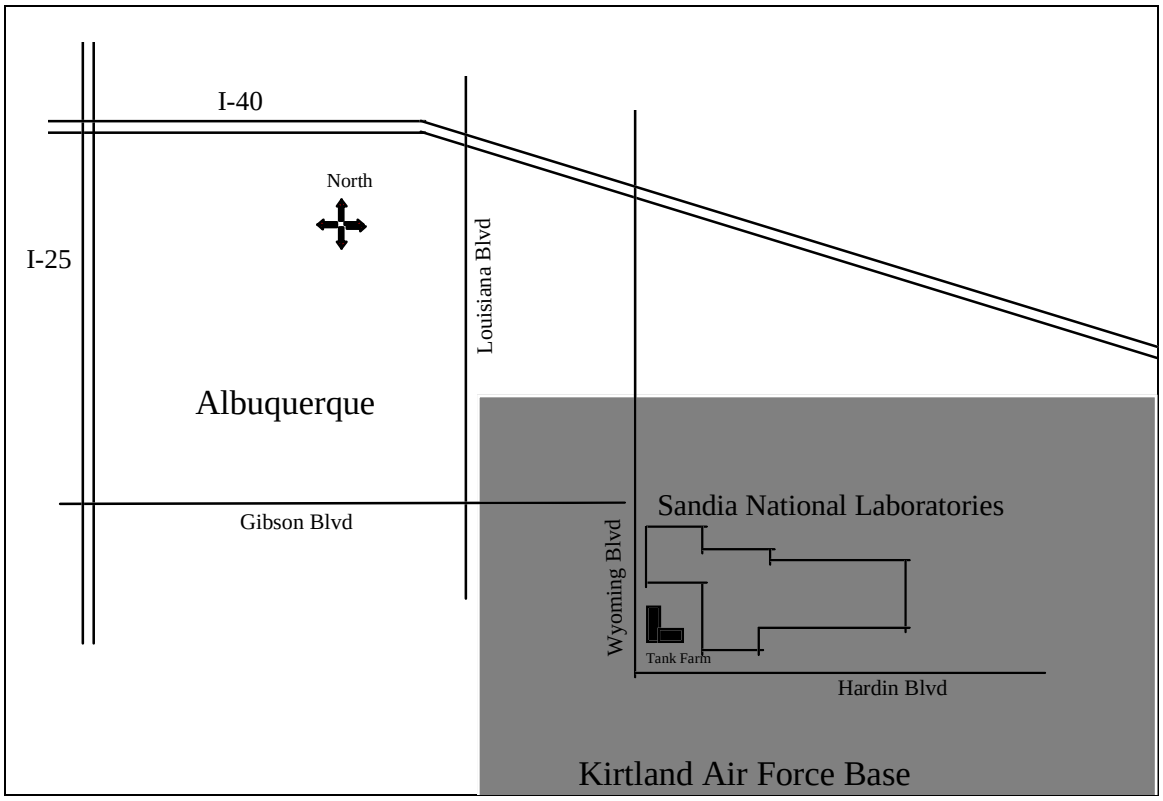


Figure 5-3. Site vicinity map, SNL Tank Farm

on the surface are composed of alluvial fan deposits shed from the eastern uplifts that interfinger with valley alluvium and consist of clayey to silty sands, with lesser amounts of silt, clay, and sand. Surficial deposits are underlain by a thick sequence (greater than 5,000 feet) of basin-fill deposits of interbedded gravels, sands, silts, and clays. Depth to groundwater is approximately 500 feet, with the potential for perched water at shallower depths. During the exploratory and informal predemonstration investigations, the SCAPS CPT consistently met with refusal at a depth of 52-57 feet, due to a consolidated gravel/caliche layer at this depth.

SNL Tank Farm Site Contaminants and Distribution

The SNL Geoprobe® investigations and the preliminary investigations using the SCAPS LIF sensor indicated diesel contamination greater than 1000 mg/kg in the vadose zone down to 56 feet. The area that was excavated down to approximately 15 feet and subsequently backfilled with the contaminated soil contains a somewhat homogenized mixture of diesel contaminated soil and uncontaminated soil. A high concentration of subsuface fluorescing minerals, most likely calcium carbonate, was identified prior to the demonstration. Calcium carbonate is present to some degree throughout the vadose zone in this area; it is more concentrated near the surface.

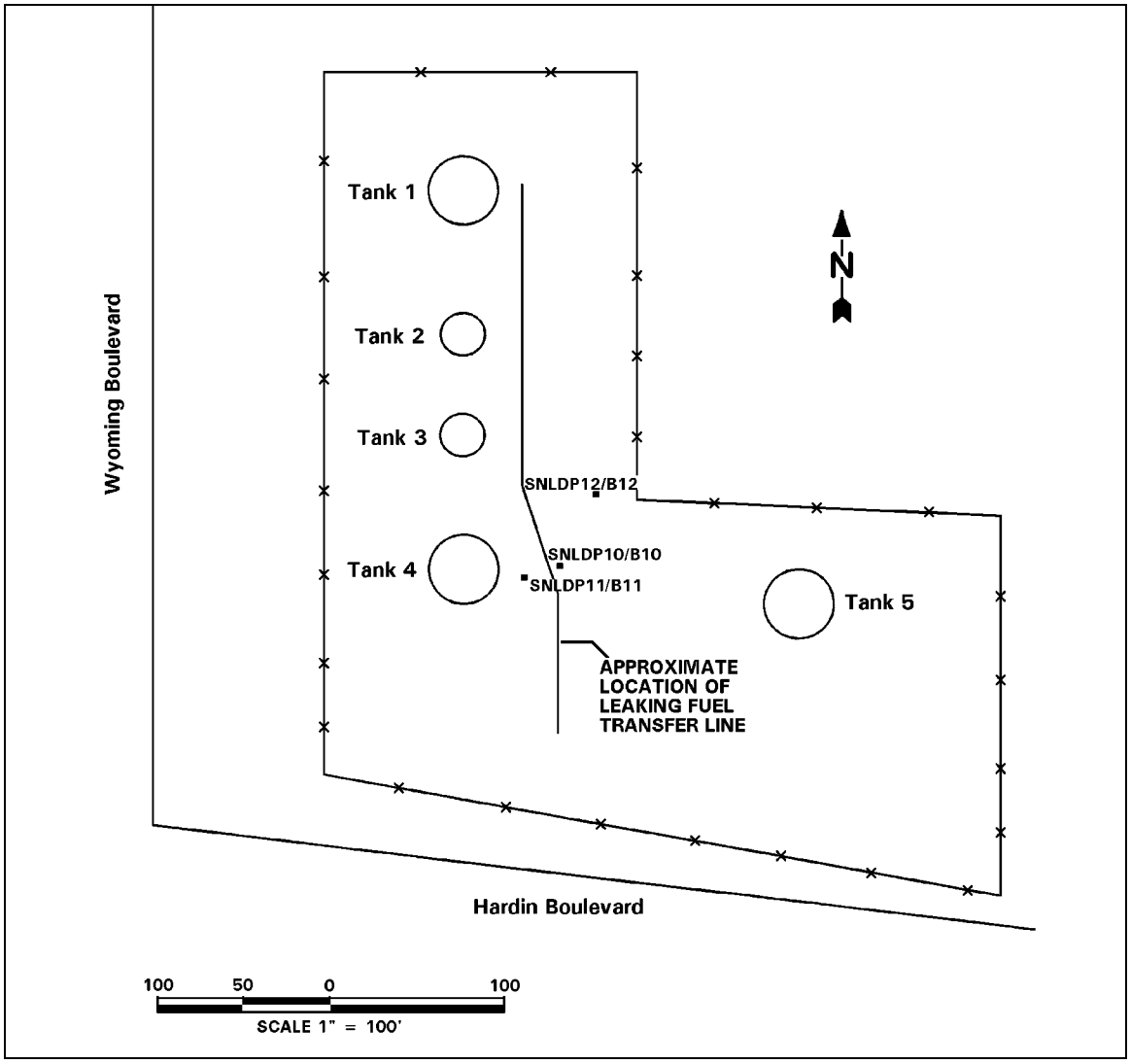


Figure 5-4. Demonstration site and sampling locations, SNL Tank Farm

SNL Tank Farm Predemonstration Sampling

A formal predemonstration event was not conducted at the SNL Tank Farm site. The site was evaluated for its suitability as a demonstration site during a site exploratory tour by the NCCOSC RDT&E Division in August 1995. Two other arid locations were evaluated at this time and determined to be unsuitable for this demonstration. Immediately prior to the field demonstration in November, NCCOSC RDT&E Division personnel performed informal sampling to determine sampling locations for the demonstration. Earthen berms had been removed to allow access to contaminated areas. Following select pushes, stab samples (discrete soil samples collected using the cone penetrometer soil sampling apparatus) were collected and shipped to ATI for overnight confirmatory TPH and TRPH analysis. Laboratory analysis of the stab samples indicated TRPH of 3380 mg/kg and TPH of 3300 mg/kg (as diesel) at a depth of 25 feet. Carbonate was observed in all the discrete soil samples in varying concentrations by the professional geologist

and confirmed by applying hydrochloric acid, causing release of carbon dioxide, to a few representative samples.

Demonstration Sampling Operations, SNL Tank Farm

The sampling operations at the SNL Tank Farm were similar to the operations at Port Hueneme, with the following changes.

Because the horizontal extent of the plume at Port Hueneme Site 22 had been delineated to within 9 feet with 8 pushes during the field demonstration, this capability of the ROST™ technology was not the primary focus of the second demonstration. For the SNL Tank Farm demonstration, the developers and representatives of SNL and U.S. EPA determined that it would be preferable to collect more samples from areas expected to be contaminated to compare the LIF technology with the results from the reference laboratory analysis of discrete soil samples. The addendum to the demonstration plan reflected this change to the sampling strategy. For the demonstration, three pairs of CPT pushes were advanced, followed by three overborings. Based on the results of the informal predemonstration, the first pair of CPT pushes and boring were located in an area that had contamination throughout the push, the second pair of pushes and boring were advanced in an area that had contamination from approximately the 40 to 50 feet depth, and the third pair of pushes and boring were advanced in an area expected to be uncontaminated.

During the Port Hueneme demonstration, samples were collected throughout the contaminated and uncontaminated areas at intervals of every 1 to 1.5 feet. The experimental design called for several pushes to be located in clean areas in order to delineate the horizontal extent of the plume. This resulted in a large quantity of clean samples in the data set (114 nondetects of 130 total samples as determined by the reference laboratory). For the demonstration at the SNL Tank Farm, the experimental design was modified to focus discrete sampling in the impacted areas and limit the number of samples in areas expected to be unimpacted. This conserved resources and allowed for more comparisons of hydrocarbon-impacted samples (68 detects of 92 total samples as determined by the reference laboratory).

During drilling operations, discrete soil samples for reference laboratory analysis were collected using a California modified split-spoon sampler lined with 2.5-in diameter by 3-in stainless steel tubes. The smaller size of the sample tube was selected to allow for a greater number of discrete samples to be collected during a single 24-inch sample drive and would also permit finer scale resolution of the comparison of the LIF response to the reference laboratory analytical results. In addition, fewer samples were collected in the unimpacted boring. A total of 92 soil samples were collected during this demonstration, compared to 130 for the Port Hueneme demonstration.

All demonstration samples were collected and documented as previously described. Each ROST™ push was identified with a unique number assigned in the field (Table 5-2). For example, the tenth ROST™ push was identified as SNLDR10 (SNL Demonstration, ROST™ push 10). Each boring was uniquely identified, such as SNLB10 for the boring (B) that was collocated with the SNLDR10 push. Individual samples collected from each boring were sequentially numbered as they were logged; for example, SNLDB10-5 identified the fifth soil sample collected from the tenth boring.

Table 5-2. SNL Tank Farm boring and push summary table.

Push or Boring Identification	Date	Comments
SNLDR10 SNLDB10	11-6-95	R10 located 2 feet 8 inches north and east of fuel transfer line. B10 located 4 inches offset from R10. Total of 53 samples collected; max depth 56.25 feet.
SNLDR11 SNLDB11	11-7-95	R11 located 9 feet 8 inches south and west of fuel transfer line. B11 located 4 inches offset from R11. Total of 28 samples collected; max depth 55.25 feet.
SNLDR12 SNLDB12	11-8-95	R12 located 50 feet north and east of R10. B12 located 4 inches offset from R12. Total of 20 samples collected; max depth 49.5 feet.

Note: SNLDR represents the ROST™ push at the SNL Tank Farm Demonstration. SNLDB represents the hollow stem auger boring.

Calibration Procedures, Quality Control Checks, and Corrective Action

Calibration procedures, method-specific QC requirements, and corrective action associated with nonconformance QC for the LIF technology are described in the following paragraphs.

ROST™ LIF Initial Calibration Procedures

The time window (typically 250 ns wide) on the digital oscilloscope is adjusted to compensate for the light transmit time through the optical fiber. For a 50-meter long push, the fluorescence signal is received at the detector about 500 ns after the laser has actually fired. Once set, the time delay needs to be adjusted only if the length of the fiber in the probe umbilical is changed. The position of the ROST™ time window can be determined automatically with routines built into the scope's software. The procedure was carried out prior to the demonstration.

A wavelength calibration for the emission monochromator was performed at the start of the demonstration and thereafter during troubleshooting procedures. The 532 nm Nd:YAG second harmonic light was used as a primary reference to verify the wavelength accuracy of the monochromator. A small amount of 532 nm light was directed into the monochromator at a narrow slitwidth, and the wavelength was scanned to verify that the signal maximizes at 532±0.2 nm. The monochromator can then be used as a secondary reference to calibrate the dye laser wavelength.

The concentration calibration was performed using a set of calibration standards (DFM-spiked site-specific soil samples) prepared by the serial addition method. The calibration standards were run in triplicate at the beginning of each day and again when equipment was changed. These samples were sequentially presented to the sapphire window for measurement. After measurement, the average and standard deviation was computed for each sample. If the standard deviation exceeded 20 percent for replicate analyses of any single sample, that sample was rerun. If deviation remained excessive, the system check standard was measured. If the check standard was out of compliance, system checkout and debugging was required. A calibration curve was generated by regressing fluorescence peak intensity expressed as a percentage of a reference solution versus the concentration of fuel product added to the calibration soil sample.

ROST™ LIF Continuing Calibration Procedures

A fluorescence reference measurement was performed before and after each push for normalization purposes and to check system performance. The reference material, referred to as M-1

reference solution, is a selected mixture of hydrocarbons in solution. The M-1 reference solution is contained in a standard fluorescence cuvette that can be reproducibly strapped onto the cone outside the sapphire window. If the reference intensity at the conclusion of the push differed by more than 25 percent of the value immediately before the push, system troubleshooting procedures were initiated.

Method Blanks

A clean sand blank was measured pre- and post-push as part of the standard data collection procedure. If the clean sand blank LIF measurement varied beyond 50 percent of its pre-push calibration value, troubleshooting procedures were initiated.

Spike Samples

Spiked samples were not used for monitoring the performance of the ROST™ LIF system. *In situ* measurement precludes the presentation of spiked samples to the LIF measurement system.

Instrument Check Standards

A system check using the M-1 reference solution was performed before and after ROST™ LIF data collection. Both wavelength and intensity of the standard were monitored. If the wavelength differed by greater than 5 nm from the known value, a wavelength calibration was performed. If the intensity changed by more than 20 percent, system troubleshooting was required.

Performance Evaluation Materials

Performance evaluation (PE) samples were not used for this demonstration. Because the LIF technologies are *in situ* measurement techniques, PE samples cannot be inserted into these dynamic measurement processes.

Duplicate Samples

Due to the nature of the *in situ* measurement, duplicate samples cannot be measured by LIF. In an homogeneous environment, nearby pushes are a near duplicate measurement. Soil heterogeneity and variation in contaminant distribution can be significant over short distances both horizontally and vertically. Therefore, the quality assurance plan included no *in situ* duplicate measurements.

Equipment Rinsate Samples

To assess whether cross contamination was being introduced during equipment decontamination, an equipment rinsate sample was collected daily. The source of the water for the equipment rinsate sample was the deionized water used for the final rinse step of the equipment decontamination process. Deionized water was poured over the sampler and into vials equipped with Teflon seals in a manner so that headspace was minimized. The equipment rinsate samples were sealed, labeled, and placed into an insulated cooler, logged on the chain-of-custody form, and

submitted to ATI for analysis of TRPH and TPH using the reference analysis methods previously described.

Data Reporting, Reduction, and Verification Steps

To maintain good data quality, specific procedures were followed by the developer and the SNL verification entity during data reduction, validation, and reporting. These procedures are detailed below.

Data Reporting

The following data were reported to SNL:

1. Data logs from all pushes, including ROST™ fluorescence as a percentage of M-1 fluorescence with respect to depth. Also provided were wavelength time matrices for select positions along each push.
2. System check and calibration sample concentrations; tabulated raw system check and calibration sample fluorescence data; average system check intensity and system check ratio for each push; background, noise, and sensitivity calculated from calibration data.
3. Borehole logs indicating soil sample collection information, including sample numbers, depth of samples, location of water table, and other relevant information concerning the collection of the soil samples, and chain-of-custody documentation associated with soil samples.
4. Laboratory results for TPH and TRPH measurements of soil samples, including the reference method analytical results and quality control data.

Data Reduction and Verification Steps for the ROST™ LIF Data

The LIF system records the fluorescence as a percentage of the M-1 standard as a function of depth as the probe is pushed into the ground. This raw data is calibrated using the system check standard measured before and after each push, and the series of calibration samples measured on a daily basis during the site operations. The raw data and daily calibration procedures were used to make decisions in the field. Following the conclusion of site operations, the raw fluorescence measurements were adjusted by a normalization factor, and a site-wide regression slope was computed to the detection limits. This procedure is detailed below.

1. Each day, calibration curves were established using the DFM-spiked samples prepared prior to the demonstration. The resulting sensitivity (the slope of the line estimated using all calibration data) was used to determine the limit of detection (LOD) in mg/kg.
2. Each fluorescence versus depth (FVD) log was analyzed to determine if depth data from the depth encoder were correct.
3. Each FVD was analyzed to determine the background signal for each push. Background signals are assumed to generate a bell-shaped curve at the low end of the histogram centered around the mean of the background generated signal. The calculated mean of the bell shaped curve is then used to represent the background for that push. The background is subtracted from each percent fluorescence measurement to produce a background-corrected data set. The standard deviation is used as an estimate of noise. The LOD is calculated as 2.58 standard deviations (the 99th percentile) added to the background.

4. To compare the *in situ* data with the soil sample analysis results, the percent fluorescence measurements taken at depths from which the soil samples were gathered were tabulated. Because the spacing between LIF data points is approximately 2.4 inches, the fluorescence data from all points corresponding to the 6-inch interval of soil from Port Hueneme were averaged to produce a single fluorescence intensity for a given sample. For the SNL demo, the sample interval was 3 inches. Therefore, the percent fluorescence data corresponding to the 3-inch sample interval were averaged to produce a single percent fluorescence measurement to compare with the analytical results.
5. Fluorescence data were reduced to a detect or nondetect reading using the limit of detection (LOD) determined in Step 3 above. The average percent fluorescence reading corresponding to each soil sample was compared to the fluorescence threshold. Those exceeding the LOD were recorded as detects; those falling below the LOD were recorded as nondetects.
6. Results from the reference laboratory were also reduced to a detect or nondetect reading. The laboratory analytical result (TPH and TRPH) for each soil sample was compared to the LOD in mg/kg. Those exceeding the LOD were recorded as detects; those falling below the LOD were recorded as nondetects. This LOD in units of mg/kg was computed using the fluorescence LOD (less background) divided by the sensitivity as described in Step 1 above.
7. Field notes and photographs were reviewed to verify that procedures outlined in the demonstration plan were followed.
8. On-site system audits for field operations and procedural quality assurance audits were conducted by SNL in the field while the demonstration was being conducted. Audit results are reported in Section 6. Specifically, the ROST™ system and operators were audited for compliance with the draft ROST™ method provided in Appendix C.

Changes to the Demonstration Plan

During the Port Hueneme demonstration, it was agreed that the developers would use the daily calibration results from Port Hueneme and reduce the data after the demonstration according to their standard procedure (as described above), which was slightly different than described in the demonstration plan, to arrive at a site-specific detection limit for Port Hueneme. They used the above-described method for data reduction for the SNL data set.

Information from single point tests (SPTs) on homogenized soil samples following reference laboratory analysis were allowed for both developers for both demonstrations. SPTs are measurements taken by placing a homogenized portion of a discrete sample (after laboratory analysis was complete) on the LIF probe and recording the fluorescence intensity. This intensity can be compared to the reported laboratory result for the original sample and to the *in situ* fluorescence intensity to determine if the sample analyzed by the laboratory was collected at a different depth than the depth of the *in situ* sensor measurement. The SPTs for the Port Hueneme demonstration were performed by NCCOSC RDT&E Division. Results from the SPTs were used to adjust sample depths for discrete samples; adjustments affected the results from both technologies similarly.

For both demonstrations, calibration standards were prepared using site-specific soil. The standards were measured daily at the start of operations. During the SNL Tank Farm demonstration, it was determined that the soil collected at the surface for preparation of the standards was not representative of the nonimpacted soil at the site. The soil down to a depth of 10-15 feet had been excavated near the leaking fuel transfer line in order to repair the line, and then had been returned without remediation. In addition, the soil near the surface had a large concentration of calcium carbonate, which fluoresces quite strongly under UV light. Because the

calibration standards prepared prior to the demonstration showed a strong fluorescence signal, it was agreed by all parties that a revised set of calibration standards would be prepared using soil more representative of the subsurface environment. This soil was collected at a depth of 36 feet bgs using the split spoon sampler during advancement of boring SNLDB12, the nonimpacted location. The developer reported that the background signal produced using the newly prepared calibration standards did not appreciably affect their data set, and elected not to use the new calibration standards.

Section 6

Technology Results and Evaluation

The purpose of this section is to present and evaluate the ROST™ LIF results from the two demonstrations performed as part of this program. First, the developer claims are presented. Second, the accuracy, precision, and completeness of the ROST™ LIF data set are provided. Third, the ROST™ LIF results are compared to the laboratory results, and the performance of the technology is evaluated against the developer claims. Finally, a summary of the performance evaluation is given at the end of this section.

The *in situ* LIF results from both demonstrations are presented in Appendix B. The raw LIF data have been analyzed by SNL and presented in this section in a variety of formats to compare them with the reference laboratory results and to determine if the developer claims were met. The graphical depictions of the ROST™ LIF data were developed from the original data set.

Developer Claims Presented

As stated in Section 5, the purpose of the demonstration was to generate appropriate field data to verify the performance of the technology as a field screening tool for identifying petroleum hydrocarbons in the subsurface. To accomplish this, two different sites were selected for demonstration locations: a shallow, coastal site and a deep, arid site. The LIF data were evaluated to determine the technology's performance relative to developer claims made in the demonstration plan. The LIF sensor data were compared to the data from laboratory soil analyses and the ROST™ CPT platform was compared to conventional sampling methods.

Specific claims for the ROST™ LIF sensor presented in the demonstration plan were:

1. The ROST™ system can be integrated with cone penetrometer trucks from all major manufacturers. Field integration is routinely accomplished in a few hours.

2. Standard data collection rate is one sample every 1.2 second, providing a vertical spatial resolution of 0.2 feet for a standard push rate of 1 meter per min.

3. The system can acquire multidimensional data representations, such as WTMs, to identify fuel type or to eliminate false positives from non-hydrocarbon fluorophores.

4. Target of 80 percent agreement with conventional laboratory analysis of samples and 5 percent false negatives.

These claims were evaluated individually and collectively throughout the demonstration and in post-demonstration data analysis. Results are summarized at the end of Section 6.

Technology Data Quality Assessment

Data generated by the ROST LIF technology were compared to the data generated from analysis of soil samples using the two analytical methods. The quality of the reference laboratory data has been previously discussed, and all laboratory data were determined to be acceptable for comparison to the LIF technology data. The following LIF data quality indicators were closely examined to determine if the technology data were of sufficient quality to be compared to the

reference laboratory data. The indicators evaluated for the ROST™ LIF technology were precision and completeness. The accuracy of the data was assessed upon comparison to the laboratory results.

Precision

Precision refers to the reproducibility of measurements of the same characteristic, usually under a given set of conditions. Unfortunately, the conditions can vary in environmental data to an extent that leaves the term ambiguous. Differences from site to site, sample to sample within a site, and differences in results from repeated measurements from a single sample provide examples. Because the ROST™ LIF sensor's primary utility is for *in situ* sensing as the probe is pushed into the ground, it was not possible to obtain precision data for the sensor under conditions that exactly duplicated the manner in which *in situ* measurements are made in the subsurface.

During the Port Hueneme demonstration, an estimate of the instrumental precision was obtained by placing a standard cuvette containing M-1 reference standard in front of the sapphire window and measuring the sample 20 times (50 laser shots for each analysis). This is the same as the system check procedure used before and after each push. Because the system check standard is a liquid, it was considered to be homogenous. This procedure provided an estimate of the precision of the instrument. The standard deviation of the 20 measurements was 2.2% of the mean count.

Completeness

Completeness refers to the amount of data collected from a measurement process compared to the amount that could be obtained under ideal conditions. For this demonstration, completeness refers to the proportion of valid, acceptable data generated using each method. It was anticipated that less than 100 percent completeness of both the LIF data and discrete sample analysis results would occur. For LIF data collection, a push that was refused due to contact with cobbles or other obstructions was disqualified. A substitute push was advanced in these cases, within 8 inches horizontally of the disqualified push. This occurred on ROST™ push 27 at Port Hueneme. At this site, the refusals occurred near the surface, so the subsequent push (PHDR27A) allowed for LIF data to be collected near the same location. As long as the substitute push was located within 8 inches, the disqualified push was not counted against the completeness goal. Therefore, the completeness was 100 percent for Port Hueneme. At SNL, preliminary pushes had indicated an impenetrable gravel/caliche layer at approximately 50-58 feet bgs. While this was able to be penetrated by the HSA rig, the cone penetrometer was not advanced past this depth. The pushes were considered to be complete at the point of refusal. Therefore, the LIF data set was considered 100 percent complete for the SNL site.

Accuracy

Accuracy refers to the degree of agreement of a measurement to the true value. For an *in situ* field screening measurement technique such as LIF, determining the accuracy of the technique presents a particular challenge. This is because it is not a simple matter to confidently assign a “true” value to a subsurface contaminant distribution. When compared to conventional laboratory-based measurements, the accuracy of the method is a function of both the sampling errors and errors associated with the measurement method.

Because there is no independent measure of the subsurface value of contaminant concentration, the accuracy of the *in situ* measurement was assessed by comparing it to results from conventional laboratory measurements. The percent agreement between TRPH or TPH and fluorescence data and percent false negatives was calculated using the equations that follow.

$$\%\ Agreement = \frac{x_{--} + x_{++}}{x_T} \bullet 100\%$$

Where:

x_{--} = Number of samples where fluorescence is less than the detection threshold and the corresponding lab result is also less than the corresponding detection limit;

x_{++} = Number of samples where fluorescence is greater than the detection threshold and the corresponding lab result is also greater than the corresponding detection limit; and

x_T = Total number of samples collected for comparison.

$$\%\ False\ Negatives = \frac{x_{-+}}{x_T} \bullet 100$$

Where:

x_{-+} = Number of samples where fluorescence is less than the detection threshold and the corresponding lab result is greater than the corresponding detection limit.

The average of the ROST™ LIF measurements corresponding to a 6-inch interval (Port Hueneme) or a 3-in interval (SNL Tank Farm) were compared to TRPH and TPH results for a discrete sample collected at the same depth. The results of the comparison are shown in Table 6-1. The laboratory result for TPH and TRPH from each homogenized soil sample was compared to the corresponding limit of detection established by the developer in the field. If the laboratory result was above the LOD and the average LIF data from the push at the corresponding depth exceeded the LIF fluorescence LOD, the result was a “detect/detect.” If the average LIF data were below the threshold and the corresponding analytical data were above the corresponding LOD, the result was a "false negative." If the average LIF data were above the LOD and the laboratory results were below the corresponding concentration LOD, the result was a "false positive." If the average LIF data and laboratory results were below the fluorescence LOD and corresponding concentration LOD, the result was “nondetect/nondetect” agreement. This process was performed on each sample. The results provided the determination if the developer’s claims of 1) 80 percent agreement and 2) less than 5 percent false negatives were achieved.

For the Port Hueneme demonstration, the accuracy achieved by the LIF technology was 87.7 percent agreement of LIF data with TRPH data, with 10 percent false negatives and 2.3 percent false positives. Compared to TPH results, the technology achieved 89.2 percent agreement with TPH results, with 5.4 percent false negatives and 5.4 percent false positives. For the SNL Tank Farm demonstration, the accuracy achieved by the technology was 93.4 percent agreement with either TRPH or TPH data, with 3.3 percent false negatives and 3.3 percent false positives when compared to either TRPH or TPH.

Port Hueneme Site Data Presentation and Results

The data presented in this section are used to assess of the ability of the ROST™ LIF to provide field screening and mapping of subsurface contaminants in a shallow, coastal site with contamination in the vadose zone, capillary fringe, and saturated zone. The percentage agreement with the laboratory results of soil samples from the Port Hueneme demonstration site is reported in this section.

Port Hueneme Detection Limit

As described in Section 5, the LOD was determined on a push-by-push basis in the field during the demonstration, and a composite site sensitivity was calculated for determination of agreement with the laboratory results. For the Port Hueneme site, the ROST™ site LOD was 5 mg/kg. Because the soil samples were 6 inches long, the fluorescence for the 6-inch interval associated with each sample was averaged and compared to the LOD. The reference method data were considered to show a detect when the value exceeded the Port Hueneme LIF site detection limit of 5 mg/kg. When the average *in situ* fluorescence result exceeded the fluorescence LOD, this was designated a "detect." The actual results for the Port Hueneme demonstration are presented in Table 6-1. The results indicate that the LIF data correlate better with the TPH results, which may be due to the humic interferences common to TPRH analysis. The instances where matches or misses occurred are listed in Appendix A, Table A-1.

Table 6-1. Summary of comparison of Port Hueneme LIF data with laboratory data.

Category LIF/Lab	Compared to TRPH result	Compared to TPH result
Nondetect/Nondetect Match	91	97
Detect/Detect Match	23	19
Nondetect/Detect Miss ("FN")	13	7
Detect/Nondetect Miss ("FP")	3	7
Total Samples	130	130
Percent ND/ND of Total	70%	74.6%
Percent D/D of Total	17.7%	14.6%
Percent Matches of Total	87.7%	89.2%
Percent ND/D Misses ("FN") of Total	10%	5.4%
Percent D/ND Misses ("FP") of Total	2.3%	5.4%

Downhole Results for Port Hueneme

The LIF results obtained during five contaminated pushes at Port Hueneme have been plotted in Figure 6-1. These five plots indicate the pushes and associated borings along the transect near Tank 5114. The corresponding soil sample collection locations and results are also indicated. The square symbols indicate the locations and results of the single point tests. As discussed in Section 5, during the predemonstration event there was a depth discrepancy observed with the hollow stem auger and split spoon sampling operation, believed to be due to sloughing of sands in the saturated zone. This was also observed during the demonstration. The reference laboratory provided splits of the homogenized samples from the demonstration to NCCOSC

RDT&E Division to perform single point tests (SPTs) at their facility after the demonstration. NCCOSC RDT&E Division personnel placed portions of the homogenates on the LIF probe window. and the fluorescent intensity was measured. SPT results were compared to the *in situ* measurements obtained during the demonstration.

On review of the SPT measurements and *in situ* results for both technologies demonstrated, SNL determined that on two holes, a slight offset was apparent that affected the results of the laboratory measurements when compared to the data from both technologies. Field notes were reviewed to determine where sloughing of soils was most prominent. SNL determined that for holes 23 and 28, depth adjustments of 6 inches and 4 inches, respectively, for the laboratory samples collected in the saturated zone was appropriate. This adjustment supported (*i.e.*, improved) the percentage agreement results from both LIF technologies. All downhole results, including the adjusted data for holes 23 and 28, are presented in Figure 6-2.

Port Hueneme Subsurface Contaminant Mapping

The test area at Port Hueneme and the transect along which LIF pushes and hollow stem auger borings were advanced to collect data for the performance evaluation are illustrated in Figure 6-3. Each symbol along a hole indicates a location where a soil sample was collected. The TPH result of each data point was compared to the LIF measurement at the corresponding depth interval. The area of the plume was estimated based on the laboratory measurements. This figure illustrates several points:

- the contaminant plume was narrow, and the false positives and false negatives, in general, were located at the plume boundaries,
- the LIF field screening technology was able to determine the horizontal extent of the plume within 9 feet, based on the results of 8 pushes, and
- soil samples were collected at 1- to 1.5-foot intervals and often missed the boundaries of the plume.

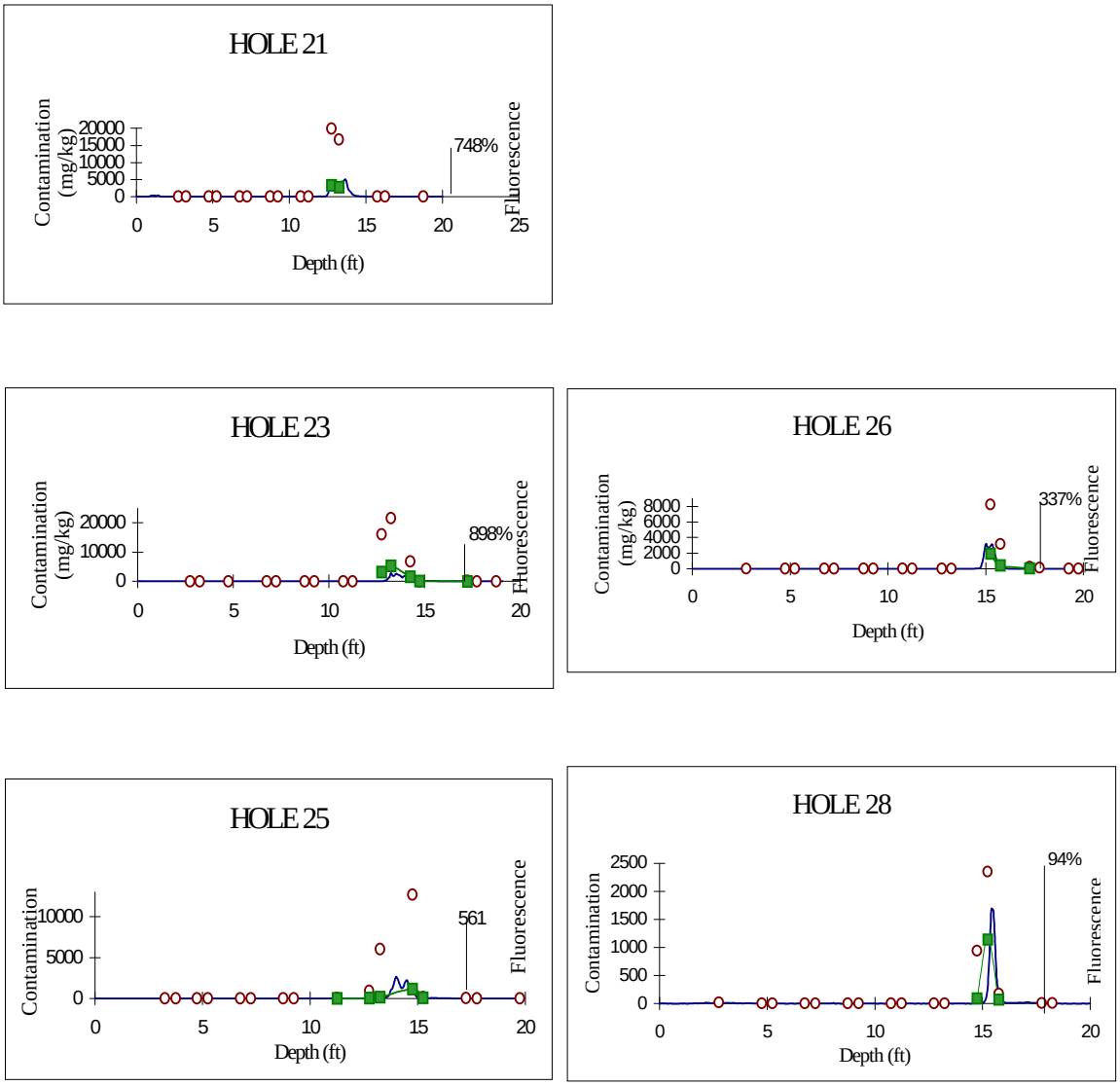


Figure 6-1. Downhole results for Port Hueneme. Results from the five drilling locations where single-point tests were evaluated are illustrated above. The laboratory measurements are indicated by the circles, the single point test measurements are indicated with the square symbols, and the LIF results are indicated by the continuous solid line. The horizontal axis is indexed by both concentration in mg/kg as measured by the average of the analytical methods and in % fluorescence measured by the ROST™ LIF technology. Note: It is inappropriate to compare the relative magnitude of the laboratory concentration to the LIF peaks as the LIF results are not linear at higher concentrations.

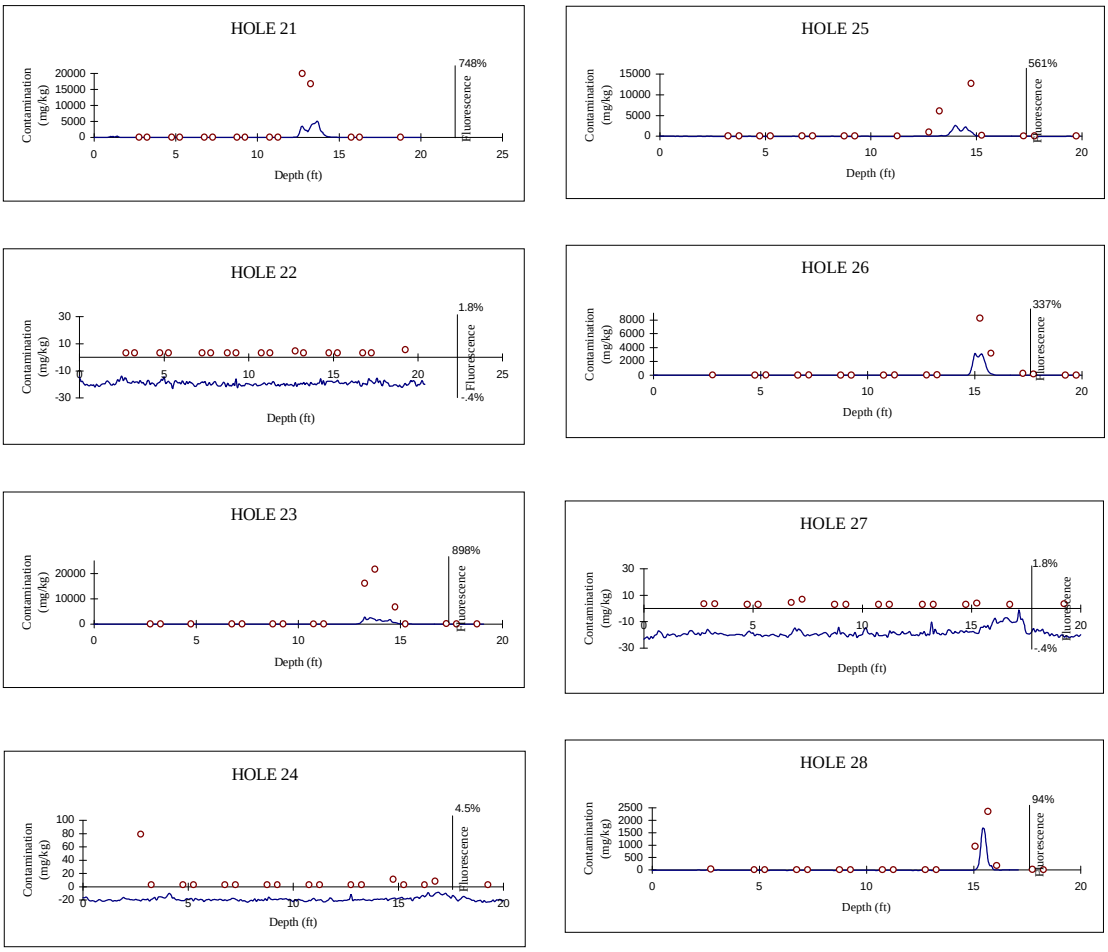


Figure 6-2. Adjusted downhole results for Port Hueneme. This figure provides a summary of all downhole results after adjustment for depth measurement inaccuracies due to sloughing that appears to have affected the measurements in the saturated zone at boring locations 23 and 28. Note that the vertical axes for the holes beyond the plume boundary, holes 22, 24, and 27, have a smaller scale than holes 21, 23, 25, 26, and 28, where contamination was detected.

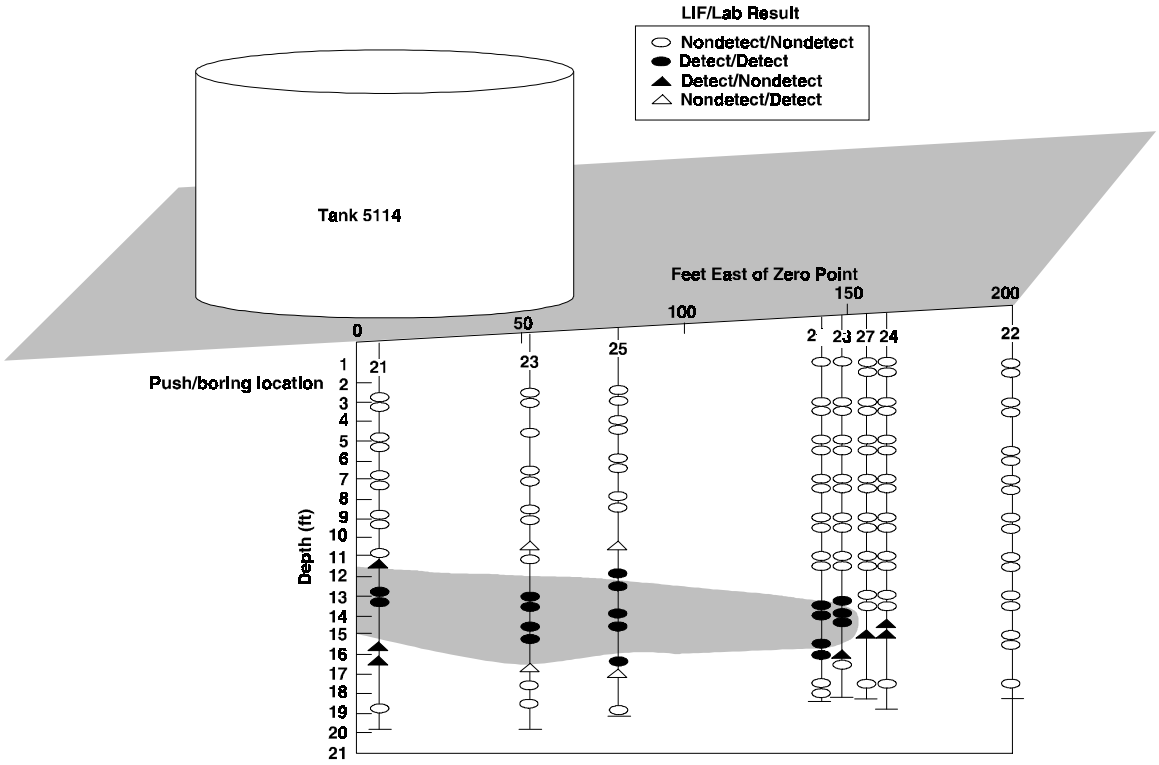


Figure 6-3. Cross-sectional map of transect near Tank 5114 at Port Hueneme. A contour view of the results shown in Table 6-1, comparing the TPH results to those of the ROST™.

SNL Tank Farm Site Data Presentation and Results

As described in the addendum to the demonstration plan, the purpose of the SNL Tank Farm demonstration was to demonstrate the capabilities of the LIF technology at an arid site with a deeper hydrocarbon plume in the vadose zone. Again, the percentage agreement of the LIF technology data set with the laboratory analytical results of soil samples from the SNL Tank farm site provides the basis for evaluation.

SNL Tank Farm Detection Limit

For the SNL Tank Farm site, a detection limit was determined on a push-by-push basis in the field during the demonstration. For the SNL Tank Farm site, the LODs for the three pushes were 102.4 mg/kg (PHDR10), 77.8 mg/kg (PHDR11), and 41.0 mg/kg (PHDR12). The TRPH and TPH measurements for each push were considered to show a detect when their values exceeded these limits.

During the demonstration, it was realized that the site-specific background soil to be used for preparation of calibration soils had been collected from the area that had been previously excavated. This soil had a high concentration of fluorescent minerals and a high background

reading. A second set of calibration soils was collected at 36 feet bgs from boring 12 (the uncontaminated push/boring). This second set showed a more typical fluorescent response. It was agreed by SNL and the developers that this soil could be used to prepare a second set of calibration standards after the demonstration. However, the ROST™ developers elected not to use this second set of calibration standards as their performance did not improve when using the new calibration standards.

The results of the comparison are presented in Table 6-2. This table summarizes how well ROST™ LIF qualitative results (detect or nondetect) matched those of the laboratory methods. The table indicates better results than those of the Port Hueneme demonstration, in terms of match and miss percentages. This is most likely due to the higher detection limits for this site, which reflect the higher background fluorescence at SNL. The discrepancies are in regions that are impacted at levels close to the ROST™ LIF detection limit and in the areas where high carbonate fluorescence was observed. In the case of boring/push 10, the regions are separated from the plume because of the excavation, which redistributed hydrocarbon contamination near the surface.

Table 6-2. Summary of comparison of SNL LIF data with laboratory data.

Category LIF/Lab	Compared to TRPH result	Compared to TPH result
Nondetect/Nondetect Match	22	22
Detect/Detect Match	64	64
Nondetect/Detect Miss ("FN")	3	3
Detect/Nondetect Miss ("FP")	3	3
Total Samples	92	92
Percent ND/ND of Total	23.9%	23.9%
Percent D/D of Total	69.5%	69.5%
Percent Matches of Total	93.4%	93.4%
Percent ND/D Misses ("FN") of Total	3.3%	3.3%
Percent D/ND Misses ("FP") of Total	3.3%	3.3%

At the Sandia Tank Farm demonstration, naturally occurring fluorescent minerals in the soil (*i.e.*, carbonates) caused some false positive results for this test. Although carbonates occur naturally throughout the vadose zone in desert environments and were observed in soil samples at all depths, they were especially concentrated within 14 feet of the ground surface.

As a standard practice, in order to separate regions of mineral fluoresence from those of hydrocarbon contamination, the ROST™ LIF operators evaluate the wavelength-time matrices (WTMs) collected at several locations during the push. In addition, the on-site geologist examines discrete samples collected from several additional locations. The discrete samples may be collected with the CPT stab sampler or, in the case of this demonstration, with the hollow stem auger and split spoon sampler. The carbonates can be distinguished from nonfluorescent soil by examining the soil sample (carbonate-based minerals appear as white crystalline material) and confirmed by pouring hydrochloric acid on the soil and observing release of carbon dioxide.

For this demonstration, the ROST™ LIF operators, relying on the evaluation of WTMs and fluorescence lifetimes, determined that two locations in SNLDR12 had a high fluorescent response from a nonhydrocarbon source. In order to evaluate their procedures, the verification entity evaluated the WTMs independently and reviewed field notes to see if there was any

difference in results. After independent analysis, the verification entity agreed with the Loral results. This improved the matching percentage to 96.5% and reduced the false positives to 1.1% when compared to either TPH and TRPH. WTMs and FVDs for all pushes are presented in Appendix B.

Downhole Results for SNL Tank Farm

Figure 6-4 shows the downhole fluorescence measurements for pushes 10, 11, and 12. Again, the developers determined that the area near the surface in SNLDR12 exhibited nonhydrocarbon fluorescence, and the on-site geologist confirmed this by examining the soil samples collected with the HSA after the push was completed.

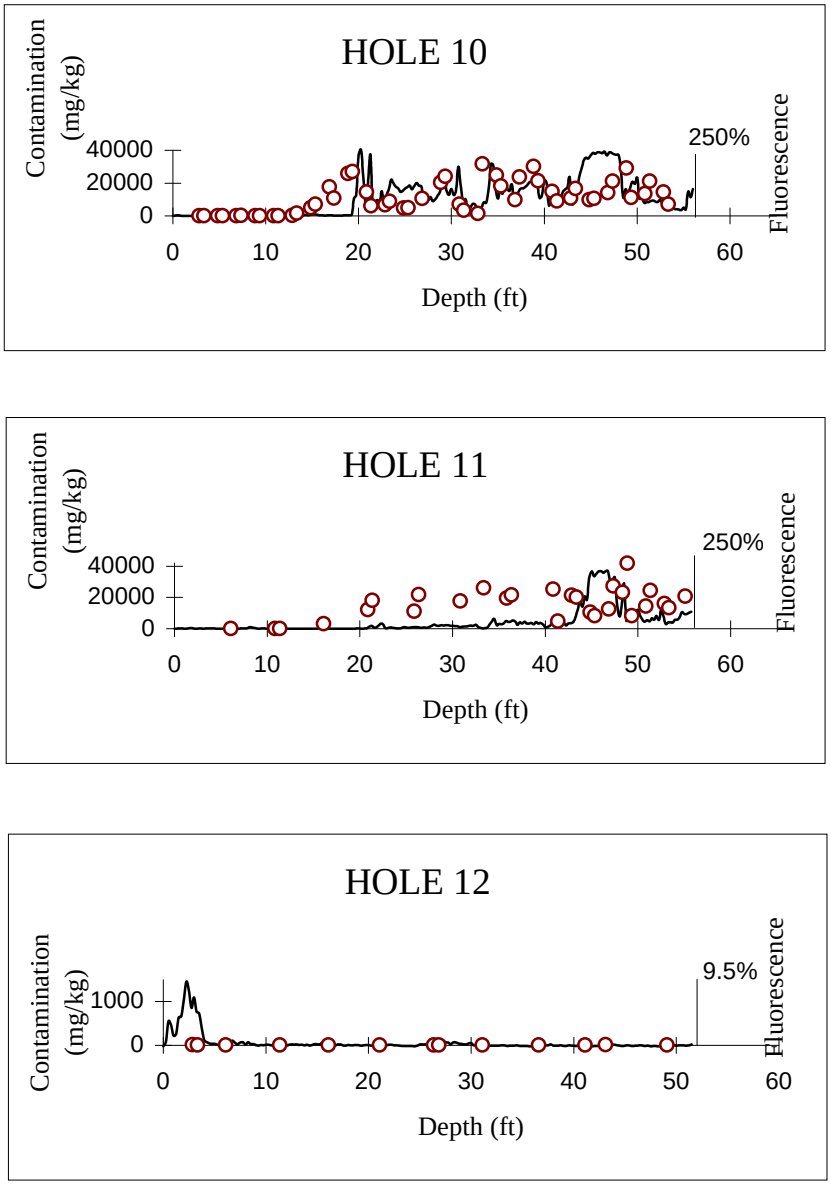


Figure 6-4. Downhole results for SNL Tank Farm.

SNL Tank Farm Subsurface Contaminant Mapping

The test area at the SNL Tank Farm and the three collocated ROST™ LIF pushes and hollow stem auger borings are shown in Figure 6-5. Each symbol along a hole indicates a location where a soil sample was collected. The result of each sample was compared to the LIF measurement at the corresponding depth interval. The horizontal boundary of the plume cannot be estimated from the information obtained from the three pushes and borings; however, the areas of strong carbonate fluorescence and hydrocarbon contamination are evident based on the LIF and laboratory results. This figure shows several points:

- the contaminant plume was thick and migrated downward rather than laterally;
- the false negatives were confined to areas where the strong carbonate fluorescence signal masked the hydrocarbon fluorescence signal; and
- the point of refusal for the CPT pushes was the gravel/caliche layer at 50-57 feet bgs.

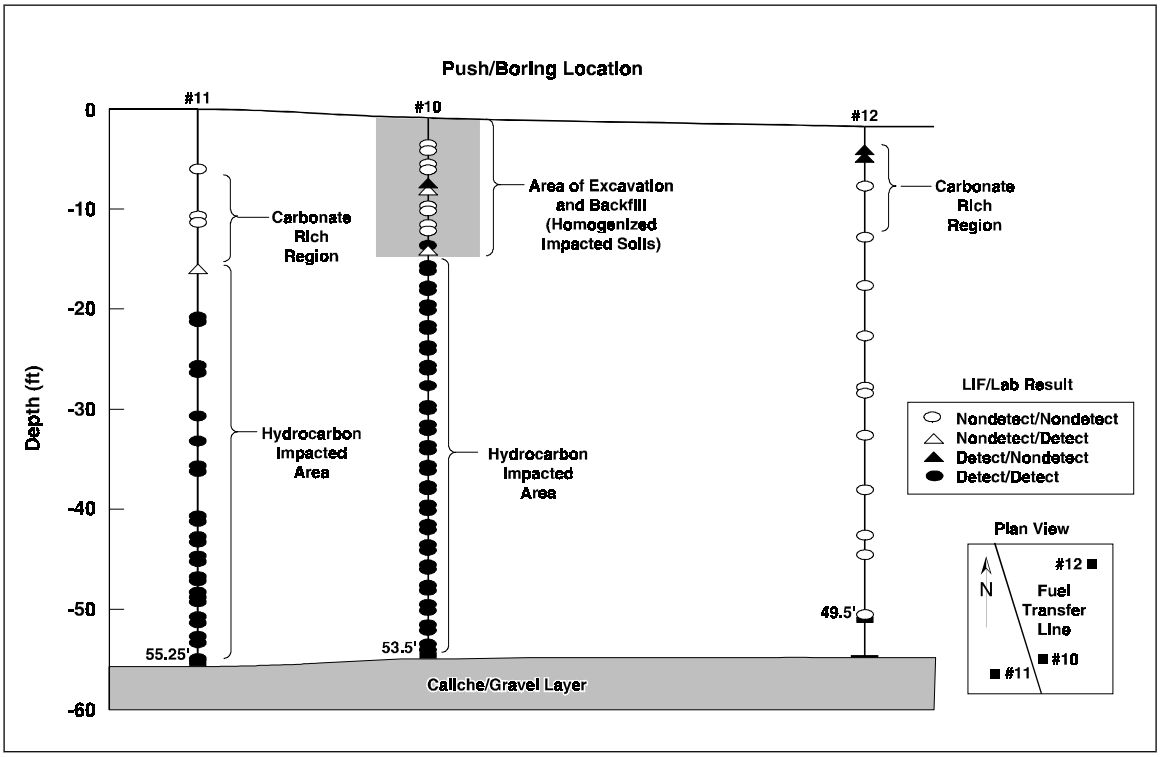


Figure 6-5. Subsurface contaminant map for SNL Tank Farm. Cross-section view of the results given in Table 6-2, comparing the ATI TPH results to those of the ROST™ LIF.

Cost Evaluation

Table 6-3 provides a comparison of deployment costs for 1) the ROST™ LIF system, 2) conventional drilling and sampling with a hollow stem auger drilling rig outfitted with a split spoon sampler, and 3) a Geoprobe® for a typical POL investigation.

Table 6-3. Cost comparison.

Scenario: Define the lateral and horizontal extent of free-phase volatile organic petroleum hydrocarbons and residual hydrocarbons. Depth to groundwater is 30 feet bgs. Soils will be continuously sampled from the surface to 35 feet bgs. The soil samples will be logged for soil classification and screened for petroleum hydrocarbon contamination in the field. The two soil samples from each boring that exhibit the greatest response to the field screening will be submitted for laboratory analysis.		
Hollow Stem Auger		
Assumptions: 10 borings to 35 feet bgs Production rate with continuous sampling, logging, and grouting is 70 feet per day		
Drilling	5 days @ $1500/day	$7500
Consultant Geologist	50 hrs @ $65/hr	3250
Organic Vapor Meter	5 days @ $75/day	375
Truck Rental	5 days @ $50/day	250
Disposal of Cuttings	8 drums @ $100/drum	800
Analytical Testing	20 samples @ $60/sample	1200
Total		$13,375
Geoprobe®		
Assumptions: 10 borings to 35 feet bgs Production rate with continuous sampling, logging, and grouting is 100 feet per day		
Geoprobing	3.5 days @ $1200/day	$4200
Consultant Geologist	35 hrs @ $65/hr	2275
Organic Vapor Meter	4 days @ $75/day	300
Truck Rental	4 days @ $50/day	200
Analytical Testing	20 samples @ $60/sample	1200
Total		$8,175
ROST™/CPT		
Assumptions: 10 pushes to 35 feet bgs Production rate is ten locations per day (10 hr day) Includes basic data report		
ROST™/CPT	1 day @ $5300/day	$5300
Per Diem/3 crew members	1 day @ $225/day	225
Per Diem/Consultant Geologist	15 hrs @ $65/hr	975
Sampling (CPT)	0.5 day @ $2500/day	1250
Analytical Testing (confirmatory samples from impacted zone)	5 samples @ $60/sample	300
Total		$8,050

Overall Performance Evaluation

In summary, the results of the demonstrations satisfy the requirements set forth in the demonstration plan and addendum for the ROST™ LIF system. The system located the plume accurately with higher matching percentage than the developer claimed. Matching percentages for the Port Hueneme demonstration were nearly 90 percent when compared to TPH and TRPH. Matching percentages for the SNL demonstration were 93.4% when compared to either laboratory method. The false negative rate for the Port Hueneme demonstration was 10 percent when compared to TRPH and 5.4 percent when compared to TPH. The false negative rate for the SNL demonstration was 3.3 percent when compared to either TRPH or TPH. Disagreements with the laboratory results were primarily confined to regions where contaminant concentration levels were close to the detection threshold. At Port Hueneme, an unusually low ROST™ detection threshold of 5 mg/kg may have contributed to the large percentage of false negatives. A portion of the ROST™ false negatives could be the result of variability in laboratory results where random errors are estimated to be in the range of 10 to 15 percent in general and are quite possibly higher near the TPH and TRPH detection limits.

As stated earlier, the performance of the ROST™ LIF was evaluated against the developer claims made in the demonstration plan. Evaluation of the developer claims for the LIF system is presented in Table 6-4.

Table 6-4. ROST™ LIF claims evaluation.

Claim	Result	Evaluation
The ROST™ system can be integrated with cone penetrometer trucks from all major manufacturers. Field integration is routinely accomplished in a few hours.	ROST™ system was integrated easily with the SCAPS CPT truck and has been successfully deployed on other CPT trucks. Field integration was accomplished in 2 hrs at Port Hueneme.	Met
Standard data collection rate is one sample every 1.2 sec, providing a vertical spatial resolution of 0.2 ft for a standard push rate of 1 m/min.	Data was collected every 0.2 ft or less if cone slowed or stopped. Push rate is dependent upon CPT.	Met
System can acquire multidimensional data representations, such as WTMs, to 1) identify fuel type or 2) eliminate false positives from nonhydrocarbon fluorophores.	1) Only one class of hydrocarbon was available at each site; therefore, the first claim was not evaluated. 2) WTMs and fluorescence lifetimes were used to distinguish hydrocarbon and nonhydrocarbon fluorophores.	1) not evaluated 2) met
Target of 80 percent agreement with conventional laboratory analysis of samples and 5 percent false negatives.	Result for Port Hueneme: 87.7% correlation with TRPH and 10% false negatives; 89.2% correlation with TPH and 5.4% false negatives. Result for SNL site: 93.4% correlation with either TRPH or TPH; 3.3% false negatives.	Both claims met when TPH data is used for comparison. Both claims met

Section 7

Applications Assessment

The ROST™ LIF technology is emerging as a supplement to and possible replacement for conventional drilling and sampling methods. As demonstrated, the ROST™ LIF technology has advantages and limitations. These advantages and limitations are described in the following sections.

Advantages of the Technology

Real-Time Analysis

Through the use of a cone penetrometer system, the ROST™ LIF provides real-time analysis of site conditions. This approach is faster than any competitive technology, and therefore quite useful for real-time decision making in the field. This is especially important in guiding soil sampling activities. For conventional field characterization, soil samples are collected using a standard drill rig and sent to a commercial laboratory for analysis. It can take weeks, and sometimes months, to get results. When the results are reviewed, a return trip to the field for further drilling and sampling may be indicated. Real-time sampling and data analysis often eliminates the expense and time delays of laboratory analysis and return trips to the field.

Continuous LIF Data Output

The ROST™ LIF has an advantage over conventional drilling and sampling methods in its ability to provide nearly continuous spatial data. It is common practice in environmental investigations to select a sampling interval (*e.g.*, every 5 feet) to collect samples for analysis at a commercial laboratory. Characterization of the contaminant zone may be severely impaired when the data density is sparse as it commonly is with conventional drilling and sampling approaches due to budget constraints. Areas of contamination may go wholly unnoticed in extreme cases. ROST™ allows a continuous record of possible contaminant locations and a more complete delineation of the area of contamination. In addition, some drilling and sampling operations can be hindered by an inability to produce core samples, due to flowing sands or limited cohesiveness of the soils to be sampled, whereas an *in situ* method such as ROST™ could potentially retrieve readings from these horizons.

Continuous Lithological Logging

The cone penetrometer affords continuous logging of the subsurface lithology with on-board geotechnical sensors used in conjunction with the LIF sensor. This allows a user to target stratigraphy of interest, which may influence contaminant flow and transport or have potential interfering influences on the LIF readings. A conventional drilling and sampling program would require continuous core collection and a dedicated geologist to get the same level of detail. The geologist may be able to define finer scale attributes of the media, but only through a much more labor-intensive effort. Compared to the conventional approach of sampling at regular intervals (*e.g.*, every 5 feet), the CPT offers much greater resolution. Although the CPT was not the focus

of this evaluation of the ROST™ technology, the features of the cone penetrometer enhance the usefulness of any sensor used with the CPT.

Cost Advantages

The ROST™ provides nearly continuous data at a fraction of the cost of discrete sampling and analysis of the same area. The cost effectiveness of the Department of Energy SCAPS (without LIF) compared to conventional drilling and sampling techniques has been evaluated independently by Booth et al. (LANL, 1991). They concluded that the SCAPS technology has a 30 to 50 percent cost savings for various scenarios analyzed.

Enhanced Operator Safety

The ROST™ LIF used in conjunction with a standard CPT rig is safer than a conventional drilling and sampling program. There is little chance of contacting contaminated soils, because soil samples are only occasionally brought to the surface and the sensor is driven into the subsurface to take measurements. CPT and ROST™ operators are located in the CPT truck, and generally are not in contact with the subsurface soil. Grouting of the push hole can be done to minimize any potential cross-contamination of geologic units in the subsurface. With drilling and sampling methods, the soil cuttings are brought to the surface and potentially come in contact with workers and also must be disposed of as investigation-derived waste. The samples are handled by multiple individuals for packaging and transport, and for subsequent laboratory analysis, again providing an opportunity for exposure. Decontamination of the sampling and drilling equipment is most often done manually by drilling personnel rather than automated. The ROST™ LIF and CPT offer a clear advantage over conventional drilling and sampling in the area of health and safety of the crew.

Performance Advantages

The ROST™ LIF technology works well in both the unsaturated and saturated zone. This may be important at sites with a relatively shallow water table or perched zone to delineate the continuity of the contamination across the interface.

The developer's performance claims were generally met in these demonstrations. Table 7-1 summarizes the performance statistics for the technology relative to the ability of the LIF to locate the presence of hydrocarbons. The developer claimed an overall detect/nondetect success rate of 80 percent. The technology exceeded this claim in all instances. The developer also claimed a false negative rate of no more than 5 percent. They met this claim with one exception, when the data were compared to TRPH data for the Port Hueneme demonstration resulting in 10 percent false negatives. A probable cause is the differences in analytical methods and matrix interferences.

Table 7-1. Performance statistics.

Demonstration Site	Percent Agreement Claim (≥80%)	Percent False Positive (implicit claim <20%)	Percent False Negative (claim <5%)
Port Hueneme	87.7% (TRPH) 89.2% (TPH)	2.3% (TRPH) 5.4% (TPH)	10% (TRPH) 5.4% (TPH)
SNL	93.4% (TRPH and TPH)	3.3% (TRPH and TPH)	3.3% (TRPH and TPH)

The ROST™ LIF system should meet the expectations of regulators or site owners interested in compliance with EPA sampling guidance (U.S. EPA, 1989b). In designing sampling strategies, the EPA has acknowledged the concepts of uncertainty and potential errors in analysis. They have incorporated these expectations in their guidance on allowable false positive and negative rates when comparing confirmatory sampling data to screening data. The EPA guidance on statistical sampling typically accepts a 5 to 10 percent false negative rate, which is within the range of the ROST™ LIF based on the results of these demonstrations. In addition, they allow a higher percentage of false positives, typically up to 20 percent. The ROST™ LIF system appears to be capable of meeting EPA's guidance of performance criteria for comparison of laboratory versus screening data.

Limitations of the Technology

Applicability

The ROST™ LIF system is applicable only to fuels and wastes containing nonchlorinated multi-ring aromatic hydrocarbon molecules. The detection capabilities for ROST™ include, but are not limited to, jet fuel, gasoline, diesel, lubricating oils, coal tar, and creosote. Other common compounds such as chlorinated hydrocarbons would require separate sensors.

ROST™ has been used to detect two-ring aromatic compounds (naphthalenes) on commercial projects involving jet fuel. In addition, ROST™ can readily detect mixtures of fuels and other materials; however, the technology may not distinguish them in the presence of the other. These capabilities were not evaluated as part of the CSCT demonstrations.

Quantitation and Speciation

The ROST™ LIF does not allow for the direct quantitation of specific constituents in the petroleum contaminant. The regulatory requirements for determining cleanup requirements for RCRA or CERCLA sites are established on the basis of individual constituent concentrations (*e.g.*, naphthalene concentrations) through comparisons with background, or established through the use of risk assessment techniques.

ROST™ has been calibrated to TPH in soil, which is appropriate for underground storage tank investigations. For RCRA or CERCLA investigations, it is best used as screening measure to pinpoint optimal locations for conventional sampling and analysis. The RCRA and CERCLA requirements are based on constituent-specific concentration thresholds and not aggregate measures of a total class of products such as TPH. TPH is affected by many interferants and is not readily correlated to individual constituents. For leaking underground fuel tank applications,

the guidance often refers to an action level of 100 mg/kg TPH for delineation of areas of potential concern. The ROST™ detection limits are site dependent and may exceed the 100 mg/kg action level at a given site, as shown in the SNL Tank Farm demonstration.

Push Limitations of CPT

A cone penetrometer system is limited in its ability to hydraulically push through certain stratigraphies (*e.g.*, boulders, cobbles, caliche). The maximum depth is governed by site-specific stratigraphy and the method is limited to sites where the cone penetrometer can be pushed to the depth of concern through primarily unconsolidated sedimentary deposits or formations. This can limit the applicability of the ROST™ LIF deployment to sites which have less severe geo-technical characteristics. It should also be noted that the sensor location for the LIF is some distance above the cone tip (*i.e.*, 36.5-60 cm, depending on the probe used), and when refusal occurs due to a stratigraphy change, the sensor does not actually get to that depth horizon. This can be problematic if the stratigraphic layer is also an impedance to flow and transport of the contaminants, thereby offering an opportunity for the contaminant to become concentrated at the interface boundary. In this case, the LIF sensor would not be able to address the issue unless the constituent concentrations were elevated 60 cm above the interface or refusal depth.

Interferences

The LIF system is subject to interferences which can make data reduction complicated, and limit the real-time nature of data analysis and decision making. Moisture in the soil, oxygen, and fluorescing compounds or minerals (*e.g.*, carbonates) are examples of naturally occurring constituents which affect the LIF readings and influence performance statistics. In many cases, if site-specific interferences are identified prior to or during the field investigation, the WTMs can provide information to distinguish fluorescent artifacts from actual hydrocarbon contaminants in the subsurface.

Conclusions

The ROST™ LIF system is an emerging technology worthy of pursuit in site investigations where polycyclic aromatic hydrocarbons (*e.g.*, petroleum, oils, and lubricants, coal tars, and creosote) are suspected. The technology offers a number of advantages over conventional drilling and sampling technologies for the purpose of screening a site for the nature and extent of contamination. It does not entirely take the place of a conventional sampling program, but adds significant benefits in terms of cost savings and more thorough characterization. This information, when used properly, could provide a more complete picture of the contamination and can be used to predict optimal sampling locations. As noted above, there are some limitations of which a prospective user should be aware when designing an environmental investigation. Stratigraphy and unidentifiable fluorescent interferences are issues that could prevent the sole use of the ROST™ LIF system. The technology has been used to identify lighter fuels but this capability was not evaluated in these demonstrations. Because the technology does not provide species-specific quantitation, it should be used in conjunction with conventional sampling and analysis if risk assessment or cleanup criteria must be met. As a screening technology to identify the nature and extent of polycyclic aromatic hydrocarbon contamination, this technology has many advantages over conventional techniques.

Section 8

Developer Forum

The following information was provided by Fugro Geosciences.

Fugro Geosciences acquired the technology from Loral (now Lockheed Martin) in May 1996. Since ROST™'s introduction in 1994, Fugro has worked closely with Loral, providing CPT services on the majority of Loral's ROST™ projects. Fugro now provides ROST™ worldwide directly to consultants and site owners as an integrated service with our extensive direct push capabilities.

Overall, Fugro Geosciences is pleased with the design and conclusions of the EPA CSCT evaluation of ROST™. However, some significant features of ROST™ were not fully evaluated by CSCT, due to ROST™,s deployment from the Navy's SCAPS CPT truck, the presence of only a single contaminant in test site soils, and the detect/nondetect evaluation criteria. Specifically, the features not evaluated are the high mobility and productivity rate of Fugro's CPT/ROST™, ROST™'s contaminant applicability and product identification capability, and ROST™,s delineation capabilities. Each of these important features are detailed in the following sections.

High Mobility and Productivity Rate of Fugro CPT/ROST™

Deployment of ROST™ from Fugro Geosciences' truck or all-terrain vehicle-mounted CPT rigs would have allowed demonstration of our high site mobility and productivity rate. Fugro's production rate on ROST™/CPT projects typically exceeds 300 linear feet per day for pushes averaging 30 feet or greater in depth. Typically, 10 to 12 ROST™/CPT pushes per day can be completed for projects involving shallower push depths.

Contaminant Applicability and Product Identification Capability

ROST™'s application to a wide range of petroleum contaminants and the technology's product differentiation capability make it a powerful site characterization tool. However, these capabilities were not demonstrated, since diesel fuel was the only contaminant present at both evaluation sites. ROST™ has been used successfully on commercial projects to delineate and differentiate materials including jet fuel/kerosene, gasoline, diesel fuel, lubricating oil, crude oil, bunker oil, coal tar, and creosote. The ability to differentiate between these materials in real-time using ROST™'s WTM function allows multiple sources to be recognized and delineated.

ROST™'s Delineation Capabilities

The demonstration only evaluated the detect/nondetect agreement between ROST™ and the reference method. However, ROST™ provides significantly more value than simply a detect/nondetect field screening tool. Since fluorescence intensity is generally proportional to *in*

situ concentration, ROST™ can effectively delineate not only the presence, but the relative concentration of contaminants. Our commercial clients typically use this proportional feature of ROST™ data to pinpoint the zones of highest contaminant concentration and screen the variation in concentration as they map the three-dimensional extent across a site.

CPT/ROST™ Data Presentation

CPT/ROST™ data are typically presented in a basic data report containing integrated logs illustrating fluorescence intensity versus depth, stratigraphy, and contaminant WTM fingerprints. As an option, the data may also be delivered to clients on a floppy disk in spreadsheet format. This method of data delivery provides significant benefit to consultants and site owners planning to input the data into three-dimensional graphic or modeling programs. Important zones can be readily selected for interpretation and graphic presentation with minimal effort.

ROST™ Upgrades

Dakota Technologies, Inc. (DTI), co-developers of ROST™, provide research and development and technical support to Fugro. DTI has developed a ROST™ upgrade that will allow simultaneous monitoring of fluorescence versus depth at four separate wavelengths during a push. The systems will be upgraded to the multi-wavelength function in the near future. This feature will allow detection of a wider range of contaminants simultaneously and will provide continuous product differentiation without the need to pause and collect WTMs. Fugro and DTI will continue to evaluate and upgrade the ROST™ system to make it as robust as possible.

Fugro's Existing and Emerging Technologies

Specialized CPT sensors and sampling tools developed by Fugro for site characterization include:

- Standard Cone Penetrometer - identifies stratigraphy
- Piezocone - identifies stratigraphy and measures saturated pore pressure. Allows identification of water table and estimation of hydraulic conductivity and refined interpretation of fine-grained soils
- Conductivity Cone - identifies stratigraphy and soil/groundwater conductivity
- Supercone - combined standard, piezo, and conductivity cone
- Natural Gamma Probe
- Seismic Cone
- Depth Discrete Groundwater and Soil Samplers
- CPT Installed piezometers from 1/2-inch to 2-inch diameter

Fugro is currently an active participant in the development of the next generation of laser-induced fluorescence *in situ* technology under the Advanced Applied Technology Demonstration Facility sponsored by the U.S. Department of Defense in partnership with Tufts University and Rice University. Fugro is also pursuing development of new sensors including probes for *in situ* metals and chlorinated hydrocarbon screening. Following development, we anticipate participating in evaluation of each of these tools under EPA's CSCT verification program.

Section 9
Previous Commercial Projects

The following information was provided by Fugro. The investigations included industrial plants, oil production facilities, refineries, railyards, and military bases in both the United States and Europe. Further information on these deployments may be obtained from Fugro Geosciences.

Table 9-1. Summary of Selected CPT/ROST™ Commercial Projects.

Facility Type	Site Location	Contaminant of Concern	CPT/ROST Soundings Completed	Total Linear Footage of Testing
Refinery Landfarm	Texas City, TX	Petroleum Hydrocarbons	23	485
Industrial Plant	Everett, MA	Naphthalene	72	640
Industrial Plant	Tennessee	Petroleum Hydrocarbons	29	1100
Oil Production Field	Guadalupe, CA	Kerosene, Diesel, Crude Oil	319	7,458
Oil Production Field	Lost Hills, CA	Compressor Lubricants	10	430
Natural Gas Production Plant	Refugio, TX	Natural Gas Condensate	17	625
Refinery	Beaumont, TX	Polyaromatic Hydrocarbons	21	845
Petrochemical Plant	Seadrift, TX	Petroleum Hydrocarbons	19	549
Manufactured Gas Plant	England, Wales, and Scotland	Coal Tar	54	623
Degasification Plant	Paris, France	Petroleum Hydrocarbons	13	115
Refinery Stormwater Impoundment	Beaumont, TX	Petroleum Hydrocarbons	56	635
Air Force Base	San Bernadino, CA	Gasoline, Diesel, Jet Fuel	105	1,610
Refinery	Westville, NJ	Petroleum Hydrocarbons	30	1,075
Industrial Plant	Vernon, CA	Petroleum Hydrocarbons	41	2,101
Industrial Plant	Indianapolis, IN	Diesel, Fuel Oil, Lubricants, Naphtha, Gasoline, Kerosene	47	1,372
Paint Manufacturing Plant	Anaheim, CA	Petroleum Hydrocarbons	11	624
Wood Preserving Plant	Green Spring, WV	Creosote	40	653
Retail Service Station	Valencia, CA	Gasoline	6	188
Wood Preserving Plant	Visalia, CA	Creosote	30	3433
Railroad Yard	California	Diesel, Bunker Oil	41	858

Facility Type	Site Location	Contaminant of Concern	CPT/ROST Soundings Completed	Total Linear Footage of Testing
Wood Preserving Plant	Seattle, WA	Creosote	18	2,082
Railroad Yard	Arizona	Kerosene, Bunker Oil	10	679
Department of Energy	Aiken, SC	Diesel Fuel	23	970
Refinery	Germany	Petroleum Hydrocarbons	151	4,218
Refinery	Carson, CA	Cat Cracker Feed, Petroleum Hydrocarbons	8	430
Retail Service Station	Escondido, CA	Gasoline	15	128
Oil Production Field	Casmalia, CA	Kerosene, Diesel, Crude Oil	68	2,268
Naval Station	China Lake, CA	Multiple Petroleum Products	33	1,553
Oil Production Field	Los Angeles, CA	Crude Oil	256	6,031
Refinery	Ponca City, OK	Gasoline	31	1,401
Pipeline	Albert Lea, MN	Jet Fuel	28	458
Railroad Yard	Los Angeles, CA	Lubricating Oil, Diesel	37	1,238
Oil Production Field	Guadalupe, CA	Kerosene, Diesel, Crude Oil	42	2,056
Refinery	Houston, TX	Benzene	17	410
Refinery	Wilmington, CA	Petroleum Hydrocarbons	7	482
Wood Preserving Plant	Houston, TX	Creosote	46	2,188
Refinery	Cincinnati, OH	Gasoline	18	548
Refinery	Carson, CA	Petroleum Hydrocarbons	15	1,127
Army Base	Rock Island, IL	Diesel	37	882
Refinery	Wales, UK	Petroleum Hydrocarbons	41	129
Refinery	Shreveport, LA	Petroleum Hydrocarbons	28	753
Refinery Stormwater Impoundment	Lockport, IL	Petroleum Hydrocarbons	27	293
Refinery	Toledo, OH	Petroleum Hydrocarbons	66	1,344
Air Force Base	Edwards AFB, CA	Gasoline, Diesel, Jet Fuel	31	1,400

Section 10

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Appendix A

Reference Laboratory Data

Table A-1
Reference Laboratory Results of Soil Samples
NCBC Port Hueneme

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH mg/kg	LIF/TRPH Result	LIF/TPH Result
PHDB21-1	2.5-3.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB21-2	3.0-3.5'	5/17/95	4	<5.0	ND/ND	ND/ND
PHDB21-3	4.5-5.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB21-4	5.0-5.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB21-5	6.5-7.0'	5/17/95	4	<5.0	ND/ND	ND/ND
PHDB21-6	7.0-7.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB21-7	8.5-9.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB21-8	9.0-9.5'	5/17/95	2	<5.0	ND/ND	ND/ND
PHDB21-9	10.5-11.0'	5/17/95	2	<5.0	ND/ND	ND/ND
PHDB21-10	11.0-11.5'	5/17/95	2	<5.0	D/ND	D/ND
PHDB21-11	12.5-13.0'	5/17/95	21900 (Dup 22500)	18000 (Dup 18000)	D/D	D/D
PHDB21-12	13.0-13.5'	5/17/95	18500 (Dup 17400)	15000 (Dup 4000)	D/D	D/D
PHDB21-13	15.5-16.0'	5/17/95	28	<5.0	D/D	D/ND
PHDB21-14	16.0-16.5'	5/17/95	18	<5.0	D/D	D/ND
PHDB21-15	18.5-19'	5/17/95	11	<5.0	ND/D	ND/ND
PHDB22-1	2.5-3.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-2	3.0-3.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-3	4.5-5.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-4	5.0-5.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-5	7.0-7.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-6	7.5-8.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-7	8.5-9.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-8	9.0-9.5	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-9	10.5 -11.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-10	11.0-11.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-11	12.5-13.0'	5/17/95	4	<5.0	ND/ND	ND/ND
PHDB22-12	13.0-13.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-13	14.5-15.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-14	15.0-15.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-15	16.5-17.0'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-16	17.0-17.5'	5/17/95	<1	<5.0	ND/ND	ND/ND
PHDB22-17	19.0-19.5'	5/17/95	6	<5.0	ND/D	ND/ND
PHDB23-1	2.5-3.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-2	3.0-3.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-3	4.5-5.0'	5/18/95	14	<5.0	ND/D	ND/ND
PHDB23-4	6.5-7.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-5	7.0-7.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-6	8.5-9.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-7	9.0-9.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-8	10.5-11.0'	5/18/95	53	9.6	ND/D	ND/D
PHDB23-9	11.0-11.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB23-10	12.5-13.0'	5/18/95	16200 (Dup 18300)	16000 (Dup 16000)	D/D*	D/D*
PHDB23-11	13.0-13.5'	5/18/95	24200 (Dup 26500)	19000 (Dup 23000)	D/D*	D/D*
PHDB23-12	14.0-14.5'	5/18/95	6460 (Dup 6160)	7000 (Dup 5800)	D/D*	D/D*
PHDB23-13	14.5-15.0'	5/18/95	22	29	D/D*	D/D*

Table A-1 (continued)
Reference Laboratory Results of Soil Samples
NCBC Port Hueneme

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH mg/kg	LIF/TRPH Result	LIF/TPH Result
PHDB23-14	17.0-17.5'	5/18/95	224	89	ND/D	ND/D
PHDB23-15	17.5-18.0'	5/18/95	2	<5.0	ND/ND	ND/ND
PHDB23-16	18.5-19.0'	5/18/95	5	<5.0	ND/ND	ND/ND
PHDB24-1	2.5-3.0'	5/18/95	81	77	ND/D	ND/D
PHDB24-2	3.0-3.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-4	4.5-5.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-5	5.0-5.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-7	6.5-7.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-8	7.0-7.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-9	8.5-9.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-10	9.0-9.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-12	10.5-11.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-13	11.0-11.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-14	12.5-13.0'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-15	13.0-13.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-17	14.5-15.0'	5/18/95	17	<5.0	ND/D	ND/ND
PHDB24-18	15.0-15.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB24-19	16.0-16.5'	5/18/95	<1	<5.0	D/ND	D/ND
PHDB24-20	16.5-17.0'	5/18/95	11	<5.0	D/D	D/ND
PHDB24-21	19.0-19.5'	5/18/95	<1	<5.0	ND/ND	ND/ND
PHDB25-1	3.0-3.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-2	3.5-4.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-3	4.5-5.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-4	5.0-5.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-5	6.5-7.01	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-6	7.0-7.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-7	8.5-9.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-8	9.0-9.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB25-9	11.0-11.5'	5/19/95	25	51	ND/D	ND/D
PHDB25-10	12.5-13.0'	5/19/95	748	1100	D/D	D/D
PHDB25-11	13.0-13.5'	5/19/95	5620	6400	D/D	D/D
PHDB25-12	14.5-15.0'	5/19/95	9340 (Dup 13600)	16000 (Dup 15000)	D/D	D/D
PHDB25-13	15.0-15.5'	5/19/95	172 (Dup 264)	150 (Dup 190)	D/D	D/D
PHDB25-14	17.0-17.5'	5/19/95	28	16	D/D	D/D
PHDB25-15	17.5-18.0'	5/19/95	1	11	ND/ND	ND/D
PHDB25-16	19.5-20.0'	5/19/95	9	<5.0	ND/D	ND/ND
PHDB26-1	2.5-3.0'	5/19/95	31	11	ND/D	ND/D
PHDB26-2	4.5-5.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-3	5.0-5.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-4	6.5-7.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-5	7.0-7.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-6	8.5-9.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-7	9.0-9.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-8	10.5-11.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-9	11.0-11.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-10	12.5-13.0'	5/19/95	<1	<5.0	ND/ND	ND/ND

Table A-1 (continued)
Reference Laboratory Results of Soil Samples
NCBC Port Hueneme

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH Concentration mg/kg	LIF/TRPH Result	LIF/TPH Result
PHDB26-11	13.0-13.5'	5/19/95	36	41	ND/D	ND/D
PHDB26-12	15.0-15.5'	5/19/95	8600	7900	D/D	D/D
PHDB26-13	15.5-16.0'	5/19/95	3540	2800	D/D	D/D
PHDB26-14	17.0-17.5'	5/19/95	229	250	D/D	D/D
PHDB26-15	17.5-18.0'	5/19/95	145	170	D/D	D/D
PHDB26-16	19.0-19.5'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB26-17	19.5-20.0'	5/19/95	<1	<5.0	ND/ND	ND/ND
PHDB27-1	2.5-3.0'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB27-2	3.0-3.5'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB27-3	4.5-5.0'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-4	5.0-5.5'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-5	6.5-7.0'	5/22/95	4	<5.0	ND/ND	ND/ND
PHDB27-6	7.0-7.5'	5/22/95	9	<5.0	ND/D	ND/ND
PHDB27-7	8.5-9.0'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-8	9.0-9.5'	5/22/95	1	<5.0	ND/ND	ND/ND
PHDB27-10	10.5-11.0'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-11	11.0-11.5'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-12	12.5-13.0'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-13	13.0-13.5'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-15	14.5-15.0'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB27-16	15.0-15.5'	5/22/95	3	<5.0	ND/ND	ND/ND
PHDB27-17	16.5-17.0'	5/22/95	1	<5.0	D/ND	D/ND
PHDB27-19	19.0-19.5'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB28-1	2.5-3.0'	5/22/95	34	9.8	D/D	D/D
PHDB28-2	4.5-5.0'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB28-3	5.0-5.5'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB28-4	6.5-7.0'	5/22/95	3	<5.0	ND/ND	ND/ND
PHDB28-5	7.0-7.5'	5/22/95	4	<5.0	ND/ND	ND/ND
PHDB28-6	8.5-9.0'	5/22/95	3	<5.0	ND/ND	ND/ND
PHDB28-7	9.0-9.5'	5/22/95	3	<5.0	ND/ND	ND/ND
PHDB28-8	10.5-11.0'	5/22/95	5	<5.0	ND/ND	ND/ND
PHDB28-9	11.0-11.5'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB28-11	12.5-13.0'	5/22/95	2	<5.0	ND/ND	ND/ND
PHDB28-12	13.0-13.5'	5/22/95	<1	<5.0	ND/ND	ND/ND
PHDB28-13	14.5-15.0'	5/22/95	1100 (Dup 800)	780 (Dup 920)	D/D*	D/D*
PHDB28-14	15.0-15.5'	5/22/95	1800 (Dup 2100)	2900 (Dup 3400)	D/D*	D/D*
PHDB28-15	15.5-16.0'	5/22/95	100	250	D/D*	D/D*
PHDB28-16	17.5-18.0'	5/22/95	13	<5.0	D/D	D/ND
PHDB28-17	18.0-18.5'	5/22/95	9	<5.0	ND/D	ND/ND

Notes:
1. TRPH indicates total recoverable petroleum hydrocarbons, analyzed by EPA method 418.1. **2.** TPH indicates total petroleum hydrocarbons, analyzed by the Calif. DHS method 8015-modified. **3.** mg/kg = milligrams per kilogram. **4.** Dup indicates duplicate analysis performed by separate analysis of split sample following homogenization. **5.** Accuracy in depth is estimated to be within 3 inches in the vadose zone, and 6 inches in the saturated zone. **6.** * indicates samples for which single point test measurement results were used to determine depth discrepancy between discrete soil samples and *in-situ* measurements. Depth of discrete samples was adjusted 4 inches to correlate with *in-situ* LIF measurements.

Table A-2
Reference Laboratory Results of Soil Samples
SNL Tank Farm

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH Concentration mg/kg	LIF/TRPH Result	LIF/TPH Result
SNLDB10-1	2.75-3.0'	11/6/95	60	23	ND/ND	ND/ND
SNLDB10-2	3.25-3.5'	11/6/95	25	<5	ND/ND	ND/ND
SNLDB10-3	4.75-5.0'	11/6/95	89	99	ND/ND	ND/ND
SNLDB10-4	5.25-5.5'	11/6/95	42	54	ND/ND	ND/ND
SNLDB10-5	6.75-7.0'	11/6/95	71	70	D/ND	D/ND
SNLDB10-6	7.25-7.5'	11/6/95	162	150	ND/D	ND/D
SNLDB10-7	8.75-9.0'	11/6/95	17	<5	ND/ND	ND/ND
SNLDB10-8	9.25-9.5'	11/6/95	11	14	ND/ND	ND/ND
SNLDB10-9	10.75-11.0'	11/6/95	27	24	ND/ND	ND/ND
SNLDB10-10	11.25-11.5'	11/6/95	22	27	ND/ND	ND/ND
SNLDB10-11	12.75-13.0'	11/6/95	206	270	D/D	D/D
SNLDB10-12	13.25-13.5'	11/6/95	1470	1500	ND/D	ND/D
SNLDB10-13	14.75-15.0'	11/6/95	4870	5000	D/D	D/D
SNLDB10-14	15.25-15.5'	11/6/95	7600	6600	D/D	D/D
SNLDB10-15	16.75-17.0'	11/6/95	14300	21000	D/D	D/D
SNLDB10-16	17.25-17.5'	11/6/95	8500	13000	D/D	D/D
SNLDB10-17	18.75-19.0'	11/6/95	25600	26000	D/D	D/D
SNLDB10-18	19.25-19.5'	11/6/95	25800	28000	D/D	D/D
SNLDB10-19	20.75-21.0'	11/6/95	14700	14000	D/D	D/D
SNLDB10-20	21.25-21.5'	11/6/95	5790	6300	D/D	D/D
SNLDB10-21	22.75-23.0'	11/6/95	6530	6900	D/D	D/D
SNLDB10-22	23.25-23.5'	11/6/95	8560	9100	D/D	D/D
SNLDB10-23	24.75-25.0'	11/6/95	5100	4200	D/D	D/D
SNLDB10-24	25.25-25.5'	11/6/95	5400	4500	D/D	D/D
SNLDB10-25	26.75-27.0'	11/6/95	11200	9800	D/D	D/D
SNLDB10-26	28.75-29.0'	11/6/95	20400	20000	D/D	D/D
SNLDB10-27	29.25-29.5'	11/6/95	24900	23000	D/D	D/D
SNLDB10-28	30.75-31.0'	11/6/95	7330	6600	D/D	D/D
SNLDB10-29	31.25-31.5'	11/6/95	3520	3100	D/D	D/D
SNLDB10-30	32.75-33.0'	11/6/95	1340	1400	D/D	D/D
SNLDB10-31	33.25-33.5'	11/6/95	28400	35000	D/D	D/D
SNLDB10-32	34.75-35.0'	11/6/95		24000	D/D	D/D
SNLDB10-33	35.25-35.5'	11/6/95	18200	18000	D/D	D/D
SNLDB10-34	36.75-37.0'	11/6/95	9620	10000	D/D	D/D
SNLDB10-35	37.25-37.5'	11/6/95	26200	21000	D/D	D/D
SNLDB10-36	38.75-39.0'	11/6/95	32200	28000	D/D	D/D
SNLDB10-37	39.25-39.5'	11/6/95	21700	21000	D/D	D/D

Table A-2 (continued)
Reference Laboratory Results of Soil Samples
SNL Tank Farm

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH Concentration mg/kg	LIF/TRPH Result	LIF/TPH Result
SNLDB10-38	40.75-41.0'	11/6/95	15800	14000	D/D	D/D
SNLDB10-39	41.25-41.5'	11/6/95	8440	9700	D/D	D/D
SNLDB10-40	42.75-43.0'	11/6/95	9,500 (Dup 9,160)	12,000 (Dup 12,000)	D/D	D/D
SNLDB10-41	43.25-43.5'	11/6/95	15000	18000	D/D	D/D
SNLDB10-42	44.75-45.0'	11/6/95	7500	12000	D/D	D/D
SNLDB10-43	45.25-45.5'	11/6/95	11000	9900	D/D	D/D
SNLDB10-44	46.75-47.0'	11/6/95	13000	15000	D/D	D/D
SNLDB10-45	47.25-47.5'	11/6/95	19000	23000	D/D	D/D
SNLDB10-46	48.75-49.0'	11/6/95	26000	32000	D/D	D/D
SNLDB10-47	49.25-49.5'	11/6/95	8200	14000	D/D	D/D
SNLDB10-48	50.75-51.0	11/6/95	13000	14000	D/D	D/D
SNLDB10-49	51.25-51.5'	11/6/95	15000	27000	D/D	D/D
SNLDB10-50	52.75-53.0'	11/6/95	17000	12000	D/D	D/D
SNLDB10-51	53.25-53.5'	11/6/95	5500	8500	D/D	D/D
SNLDB11-1	6.0-6.25'	11/7/95	9.7	19	ND/ND	ND/ND
SNLDB11-2	10.75-11.0'	11/7/95	9	<5	ND/ND	ND/ND
SNLDB11-3	11.25-11.5'	11/7/95	< 1	<5	ND/ND	ND/ND
SNLDB11-4	16.0-16.25'	11/7/95	3470	2700	ND/D	ND/D
SNLDB11-5	20.75-21.0'	11/7/95	13000	11000	D/D	D/D
SNLDB11-6	21.25-21.5'	11/7/95	15200	21000	D/D	D/D
SNLDB11-7	25.75-26.0'	11/7/95	12000	10000	D/D	D/D
SNLDB11-8	26.25-26.5'	11/7/95	22300	21000	D/D	D/D
SNLDB11-9	30.75-31.0'	11/7/95	18200	17000	D/D	D/D
SNLDB11-10	33.25-33.5'	11/7/95	31000	21000	D/D	D/D
SNLDB11-11	35.75-36.0'	11/7/95	19800	19000	D/D	D/D
SNLDB11-12	36.25-36.5'	11/7/95	22200	21000	D/D	D/D
SNLDB11-13	40.75-41.0'	11/7/95	26200	24000	D/D	D/D
SNLDB11-14	41.25-41.5'	11/7/95	5160	4200	D/D	D/D
SNLDB11-15	42.75-43.0'	11/7/95	20600	22000	D/D	D/D
SNLDB11-16	43.25-43.5'	11/7/95	18300	22000	D/D	D/D
SNLDB11-17	44.75-45.0'	11/7/95	7030	14000	D/D	D/D
SNLDB11-18	45.25-45.5'	11/7/95	6240	10000	D/D	D/D
SNLDB11-19	46.75-47.0'	11/7/95	11900	13000	D/D	D/D
SNLDB11-20	47.25-47.5'	11/7/95	25400	29000	D/D	D/D
SNLDB11-21	48.25-48.5'	11/7/95	17200	29000	D/D	D/D
SNLDB11-22	48.75-49.0'	11/7/95	44600	39000	D/D	D/D
SNLDB11-23	49.25-49.5'	11/7/95	7340	8900	D/D	D/D
SNLDB11-24	50.75-51.0'	33548	14700	14000	D/D	D/D
SNLDB11-25	51.25-51.5'	33548	23600	25000	D/D	D/D
SNLDB11-26	52.75-53.0'	11/7/95	16100	16000	D/D	D/D
SNLDB11-27	53.25-53.5'	11/7/95	13600	13000	D/D	D/D
SNLDB11-28	55.0-55.25'	11/7/95	21400	20000	D/D	D/D

Table A-2 (continued)
Reference Laboratory Results of Soil Samples
SNL Tank Farm

Sample Number	Depth	Date	TRPH Concentration mg/kg	TPH Concentration mg/kg	LIF/TRPH Result	LIF/TPH Result
SNLDB12-1	2.75-3.0'	11/8/95	3	<5	D/ND	D/ND**
SNLDB12-2	3.25-3.5'	11/8/95	2	<5	D/ND	D/ND**
SNLDB12-3	6.0-6.25	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-5	11.25-11.5'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-7	16.0-16.25'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-9	21.0-21.25'	11/8/95	2	<5	ND/ND	ND/ND
SNLDB12-11	26.25-26.5'	11/8/95	2	<5	ND/ND	ND/ND
SNLDB12-12	26.75-27.0'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-13	31.0-31.25'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-15	36.5-36.75'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-17	41.0-41.25'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-19	43.0-43.25'	11/8/95	<1	<5	ND/ND	ND/ND
SNLDB12-20	49.0-49.5'	11/8/95	<1	<5	ND/ND	ND/ND

1. TRPH indicates total recoverable petroleum hydrocarbons, analyzed by EPA method 418.1.
2. TPH indicates total petroleum hydrocarbons, analyzed by the Calif. DHS Method 8015-modified.
3. mg/kg = milligrams per kilogram.
4. ** indicates where WTM review indicated a nonhydrocarbon fluorophore.

Appendix B

ROST™ LIF Field Data Logs

Appendix C

ROST™ LIF Draft EMMC Method

DRAFT METHOD

FIELD SCREENING OF SUBSURFACE PETROLEUM HYDROCARBONS WITH THE RAPID OPTICAL SCREENING TOOL (ROST™)

1.0 SCOPE AND APPLICATION

1.1 This field screening method provides rapid determination of the location and distribution of subsurface petroleum hydrocarbon contamination. The method can be used to detect contaminants in the vadose, capillary fringe, and saturated zones to depths greater than 50 meters below ground surface. The measurements are performed *in situ* and physical sampling is not required. The list of the petroleum products for which this method is appropriate includes, but is not limited to:

mineral oil	gasoline	tar	jet fuel
kerosene	diesel fuel	asphaltum	aviation fuel
fuel oil	lubricating oil	hydraulic oil	petroleum distillates

1.2 The method detection limit depends on several factors including soil matrix properties, excitation source wavelength, length of fiber optic probe, optical collection efficiency, and petroleum product type. The detection limits can be as low as a few parts-per-million (ppm) and the method can be applied up to contamination levels of 10 percent or greater.

1.3 The method yields qualitative (type) and quantitative (amount) information on subsurface petroleum, oil, and lubricant (POL) contamination, making it appropriate for preliminary assessments of contaminant distribution as in environmental field screening applications.

2.0 SUMMARY OF METHOD

2.1 This method provides an overview and guidelines for the use of Laser Induced Fluorescence/Cone Penetrometer Testing (LIF/CPT) with the ROST system to obtain *in situ* measurements of hydrocarbon contamination in soil. Procedures for calibration and data analysis are also provided.

2.2 The ROST instrument senses POLs via the fluorescence response to ultraviolet wavelength laser excitation of their aromatic hydrocarbon constituents. The fluorescence measurements are carried out remotely over fiber optic cables. Excitation light is delivered by an optical fiber to a sapphire window located in a sub-assembly near the penetrometer tip. One or more collection fibers transmit the return fluorescence signal back to the surface for analysis.

2.3 The ROST is deployed on a standard cone penetrometer truck, which provides a mobile platform for moving from one push location to another. The ROST system has been integrated with cone penetrometer trucks from all major manufacturers. Fluorescence measurements can be obtained at depths as great as 50 meters below ground surface when the sensor is used in conjunction with a standard 20-ton penetrometer vehicle.

2.4 Geotechnical sensors are normally integrated with the LIF sensor probe to facilitate geotechnical and statigraphic analyses of the soil matrix.

3.0 Definitions

3.1 LIF: laser induced fluorescence.

3.2 Penetrometer: an instrument in the form of a conically-tipped cylindrical rod that is hydraulically advanced into soil to acquire subsurface measurements of penetration resistance. Used for cone penetrometer testing (CPT). Also called cone penetrometer, friction-cone penetrometer.

3.3 POL: petroleum, oil, lubricant. Used in reference to any petroleum product or derivative.

3.4 Push rods: cylindrical rods with threaded tips that are joined to advance the penetrometer probe into the ground.

3.5 UV: ultraviolet

3.6 PMT: photomultiplier tube

3.7 DSO: digital storage oscilloscope

4.0 INTERFERENCES

4.1 In addition to the aromatic hydrocarbon constituents of the specifically targeted petroleum hydrocarbons, other substances may fluoresce when excited by the laser light source and interfere with the POL determination. Possible interfering species include fluorescent minerals, naturally occurring organic material, de-icing agents, antifreeze additives, and detergent products.

4.2 The possibility of fluorescence emission from nontarget (non-POL) analytes, leading to false positive assignment of POL contamination, must be considered. The fluorescence of the POL species of interest can be distinguished from non-POL fluorescence on the basis of spectral and temporal (fluorescence decay) information acquired at selected (or all) depths during the push. Past experience indicates that POL species have characteristic fluorescence patterns (wavelength-time matrices) that allow them to be identified and distinguished from potential interferents.

4.3 There are several background sources caused by the laser light separate from the petroleum or soil matrix fluorescence. Their signal amplitudes occur on the same time scale as the petroleum fluorescence and can therefore contribute to the total intensity. The possibilities include window fluorescence, cladding/buffer fluorescence, Raman signals generated within fiber, stray light in monochromator. These can be distinguished from the true fluorescence signals by appropriate control experiments.

5.0 SAFETY

5.1 The ROST LIF sensor involves high-power pulsed laser beams that represent a potential eye hazard. Eye protection precaution similar to those which apply to the use of pulsed lasers in laboratory situations must be observed.

5.2 Components of the ROST system are at sufficiently high voltage to present a shock hazard. However, these components are not accessible during normal operation.

6.0 EQUIPMENT AND SUPPLIES

6.1 The main ROST components are the Nd:YAG pump laser, tunable dye laser, fiber optic cable, monochromator, photomultiplier tube (PMT), digital storage oscilloscope (DSO), control/analysis computer and software. The system components in the current version of ROST fit into two half-height instrumentation racks, each of which is approximately 26" high x 20" wide x 24" deep. The pulsed laser excitation source operates either at a selected wavelength in the range 280-300 run or at 266 nm. The fluorescence emission which is transmitted back to the surface is spectrally analyzed with a monochromator. The intensity of the emission signal passed by the monochromator is quantitatively measured by a photomultiplier tube detector and digital oscilloscope. ROST records voltage-time waveforms created by pulsed fluorescence light striking a photomultipher tube detector. Typically, waveforms are averaged over 50 laser shots, which requires one second at the standard 50 pulses/second repetition rate. Approximately 0.2 seconds is required to transfer the waveform to the host computer in preparation for acquisition of the next waveform.

6.2 The industry standard CPT systems employ a hydraulic ram mounted to a truck chassis so that a series of attached threaded rods can be advanced into the ground through an opening in the floor of the vehicle.

6.3 For ROST measurements, a sub-assembly is positioned between the standard penetrometer cone and the first push rod. A sapphire window view port is mounted on the side of the sub-assembly. An optical module that holds the ends of the optical fibers and other optics is inserted firmly within the sub-assembly. The electrical cables for the geotechnical sensors pass around the optical module to the cone penetrometer. Field integration is routinely accomplished in a few hours.

6.4 The ROST system can be integrated with and deployed on commercially available CPT vehicles. ROST has a depth encoder system independent of the CPT depth measurement device so the fluorescence data can be acquired independently of the CPT measurements. One person operates the LIF sensor, taking measurements of the calibration and control standards, and monitoring the actual real-time push data.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 A check standard is used to verify satisfactory instrument performance on a continuing basis. The check standard should fluoresce in the same wavelength range as the target species. Other desirable attributes of the check standard are that it possess a high quantum efficiency, be chemically stable, easily prepared, and exhibit minimal photdegmdation. The appropriate concentration of the check standard will depend on system sensitivity.

7.3 A method blank may be prepared from a sample of clean dry soil. Fine to medium-grain sea sand is appropriate.

8.0 PROCEDURE

8.1 Before the LIF/CPT system is deployed, the site is visited to determine location of obstructions that would limit access by the CPT truck. These obstructions may include buildings, cement platforms, and fence lines. The site is also surveyed for possible underground obstructions such as utilities, pipelines, and existing storage tanks. At this time, information on possible contaminants and prior efforts at characterization or remediation is also obtained. Soil samples can be collected for preparation of site-specific calibration standards.

8.2 The CPT truck is positioned over the push location and then elevated and leveled on hydraulic jacks. Following a short series of measurements to establish ROST quality control, the sensor is pushed into the ground at a rate of 1 meter/minute. The push rods are 1 meter in length, and rods are added approximately once a minute as the sensor is advanced. A 30-meter push will typically require about 40 minutes to reach full depth. Approximately 300 linear feet of push data can be accomplished in a routine day's operation.

8.3 The ROST sensor measures fluorescence signal as a function of depth as the penetrometer is pushed into the ground, thereby providing a fluorescence vs. depth (FVD) log. The ordinate of the FVD is presented relative to the check reference intensity.

8.4 As the next push rod is being added, a wavelength-time matrix can be acquired for contaminant identification purposes. Alternatively, the ROST operator can signal to the hydraulics operator to temporarily interrupt the push for WTM measurement.

9.0 QUALITY CONTROL AND SYSTEM CHECKOUT

9.1 The fluorescence intensity value is typically reported relative to the fluorescence intensity of a reference solution, which is measured just prior to the initiation of each push. The M-1 reference solution, a selected fluid hydrocarbon mixture, is contained in a standard 1-cm pathlength cuvette, which can be strapped onto the sapphire window. The procedure 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.

9.2 If the reference check intensity varies by more than 25 percent from the average of the previous values, the probe window and sample cuvette should be cleaned and the measurement repeated. If compliance cannot be achieved, the system operator should begin troubleshooting procedures as per the system's maintenance manual.

9.3 The time window (typically 250 ns wide) on the digital oscilloscope is adjusted to compensate for the light transit time through the optical fiber; for a 50 meter long fluorescence signal is received at the detector about 500 ns after the laser has actually fired. Once set, the time delay need by adjusted only if the length of fiber in the probe umbilical is changed. The position of the ROST time window can be determined automatically with routines built into the scope's software.

9.4 A wavelength calibration for the emission monochromator is performed at the start of the job and thereafter during troubleshooting procedures. The 532 nm Nd:YAG 2nd harmonic light is used as a primary reference to verify the wavelength accuracy of the monochromator. A small amount of 532 nm light is directed into the monochromator at a narrow slitwidth and the wavelength is scanned to verify that the signal maximizes at 532 ± 0.2 nm. The monochromator can then be used as a secondary reference to calibrate the dye laser wavelength.

10.0 CALIBRATION OF CONTAMINANT CONCENTRATION

10.1 At present, there is no standard procedure for calibrating the LIF sensor. Depending on data objectives, fluorescence intensity alone may be reported as a relative indicator of POL presence. The reference fluorescence intensity 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.

10.2 When called for, a calibration curve can be generated to establish the LIF sensor response, dynamic range, and limit of detection. Depending on the objectives of the investigation, the following options should be considered:

10.2.1 A common POL contaminant (gasoline, diesel fuel, coal tar, etc.) and soil type (sand, silt, clay) that is though most representative of the site conditions is designated. Then the relative fluorescence intensities can be converted to concentration units with response tables determined in laboratory studies. These tables exist currently only for common fuels on sand.

10.2.2 A contaminant from the site is spiked onto a specified reference soil type and 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.

10.2.3 The contaminant from the site is spiked onto clean soil samples from the site. 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, but still assumes that the soil and product used in the calibration is representative of the site.

10.3 The calibration standards can be obtained directly from the ground by soil borings, which are submitted for analysis for approved laboratory methods. The influence of confounding variables such as weathering, soil moisture, soil matrix, and other changes, are eliminated. The disadvantage of the *in situ* calibration standard is the difficulty in obtaining a sample for the conventional analysis from actually the same spot as surveyed by ROST. There are two options: 1) use the ROST data as measured during the active pushes; 2) place the sample material on the window and rerun.

11.0 SAMPLE COLLECTION

This is an *in situ* method. Spectroscopic measurements are obtained directly without physical sampling. Sample collection is not a part of the normal method procedure. The vertical spatial resolution is less than 4 cm when the penetrometer is driven at the standard 1 m/min push rate.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The amplitude of the logs is the area under the voltage vs. time waveforms, which is proportional to the total light received (within the wavelength interval set by the monochromator) per laser pulse. The standard display format is to plot the area under the fluorescence intensity vs. time waveform as a function of depth. This is referred to as a Fluorescence vs. Depth (FVD) log or plot.

12.2 The raw voltage-time waveforms (voltage proportional to fluorescence light intensity) are subjected to various data processing and analysis procedures. The first type of manipulation is to remove any DC offset from current leakage through the amplifiers of the scope input stages, from ambient light (not induced by the laser) that reaches the detector, or dark current from the photomultiplier tube. The basis for removing the DC offset is that true light-induced signals, cannot occur in advance of the laser pulse itself. The DC offset which is automatically subtracted from the averaged waveforms before they are transferred to the system computer.

12.3 The light-induced background signals are eliminated by an analysis of the baseline. One expects the true background (including noise components) to be normally distributed, *i.e.*, to follow a Gaussian distribution. The

center of the Gaussian falls at the true background amplitude and the width corresponds to the noise level (uncertainty). We generate a histogram of the intensities measured during the course of a push.

13.0 METHOD PERFORMANCE

13.1 The detection limit, accuracy, and precision obtained through use of the method are dependent on the soil matrix, target analyte, and choice of laser wavelength, as well as instrumental conditions such as fiber length and monochromator slitwidth. They must be established on a case-by-case basis.

14.0 REFERENCES

References are to be provided by Loral.