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6. AUTHOR(S)
Bruce J. Nielsen, Dr. Greg Gillispie, David A. Bohne, David R. Lindstrom

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Armstrong Laboratory, Environics Directorate
Tyndall AFB, FL 32403-5323

Dakota Technologies, Inc.
Fargo, ND 58102-1809

Unisys Corp., Environmental Systems
St. Paul, MN 55164-0525

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The cost of characterizing and monitoring U.S. government hazardous waste sites could exceed $100 billion utilizing traditional methods and technology. New sensor technologies are being developed to meet the nation's environmental remediation and compliance programs. A consortia consisting of the CRDA partners, Dakota Technologies Inc., and NDSU submitted a proposal to the Advanced Research Projects Agency, Technology Reinvestment Project and won an award to fund the commercialization. The result, Rapid Optical Screening Tool or ROST is a state-of-the-art laser spectroscopy system for analysis of aromatic hydrocarbon-contaminated soil and groundwater. With ROST, environmental investigators are able to find, classify, and map the distribution of many hazardous chemicals in the field instead of waiting for reports to come back from the analytical laboratory. The research and development program leading to prototype laser spectrometers is summarized along with results from laboratory and field demonstrations illustrating system performance and benefits for site characterization. The technology has recently been demonstrated in Germany, the Netherlands, and several sites in the United Kingdom having light, medium, and heavy aromatic hydrocarbon contamination from fuel spills and refinery or chemical plant operations.

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A NEW SITE CHARACTERIZATION AND MONITORING TECHNOLOGY

14 June, 1995

Bruce J. Nielsen
Armstrong Laboratory, Environics Directorate
Tyndall AFB, FL 32403-5323

Dr. Greg Gillispie
Dakota Technologies, Inc.
Fargo, ND 58102-1809

David A. Bohne, David R. Lindstrom
Loral Corp., Environmental Systems
St. Paul, MN 55164-0525

ABSTRACT

The cost of characterizing and monitoring U.S. government hazardous waste sites could exceed $100 billion utilizing traditional methods and technology. New sensor technologies are being developed to meet the nation's environmental remediation and compliance programs. In 1993, Armstrong Laboratory and Loral Defense Systems, Eagan (formerly a division of Unisys Corporation) signed a Cooperative Research and Development Agreement (CRDA) to commercialize fiber optic laser-induced fluorescence technology that had been developed with Air Force funding at North Dakota State University (NDSU). A consortia consisting of the CRDA partners(USAF and Loral), Dakota Technologies Inc., and NDSU submitted a proposal to the Advanced Research Projects Agency, Technology Reinvestment Project and won an award to fund the commercialization. The result, Rapid Optical Screening Tool or ROST[1] is a state-of-the-art laser spectroscopy system for analysis of aromatic hydrocarbon-contaminated soil and groundwater. With ROST, environmental investigators are able to find, classify, and map the distribution of many hazardous chemicals in the field instead of waiting for reports to come back from the analytical laboratory. The research and development program leading to prototype laser spectrometers is summarized along with results from laboratory and field demonstrations illustrating system performance and benefits for site characterization. The technology has recently been demonstrated in Germany, the Netherlands, and several sites in the United Kingdom having

light, medium, and heavy aromatic hydrocarbon contamination from fuel spills and refinery or chemical plant operations.

INTRODUCTION

The vision of U.S. Department of Defense (DOD), Tri-Service (Air Force, Army and Navy) scientists has become a reality as a partnership between DOD, academia, and private industry evolves into a combined technology that can save millions of dollars in long-term hazardous waste site cleanup costs. The DOD has about 20,000 contaminated sites, most of which will require further characterization and many may require monitoring for 20 or more years, costing millions of dollars per year. The cost of site characterization and monitoring has traditionally been one-third or more of the total remediation costs.

Traditional methods employed during environmental site characterizations are time-consuming, yet often lead to insufficient or inadequate soil and groundwater data. The typical or phased approach involves many steps, often widely separated in time, including: investigation design; grid layout; geophysics; soil boring; sampling (soil, soil gas, and groundwater); off-site analysis; and data evaluation. Due to the expense and time involved, sampling programs are usually conservative, typically providing the minimum amount of data necessary to complete the investigation. The understanding of hydrogeology and contaminant distribution is often poor and remediation designs fail. Too many times, steps must be repeated until the extent of contamination is satisfactorily defined.

To address this problem, the Tri-Services integrated laser spectroscopy with a cone penetrometer. The combination provides an opportunity to significantly expedite the characterization process by providing in situ, real-time data of both petroleum contaminant distribution and soil hydrogeology. This technology has been field-tested at numerous sites and is now being commercially deployed. Ongoing research will extend sensitivities, expand capabilities to detect other contaminants such as solvents, metals, and explosives; and make system operation more user-friendly for operating technicians. The end result is a technology that can significantly reduce the cost of site characterization and monitoring.

BACKGROUND

Development

The Site Characterization and Analysis Penetrometer System (SCAPS), developed jointly by the Tri-Services, has proven to be an effective technology for characterizing contaminated sites. The Tri-Services are cooperating on the development and implementation of cone penetrometers and associated technologies. The Army has provided leadership on developing SCAPS; the Waterways Experiment Station conceived the idea of combining optical measurements with cone penetrometers to determine chemical information about the soil. A patent, entitled "Device for Measuring Reflectance and Fluorescence of In Situ Soil," has been licensed. SCAPS includes the truck-mounted cone penetrometer; physical and chemical sensors; environmental samplers; data acquisition, analysis, and graphical presentation hardware and software; and probe hole grouting.

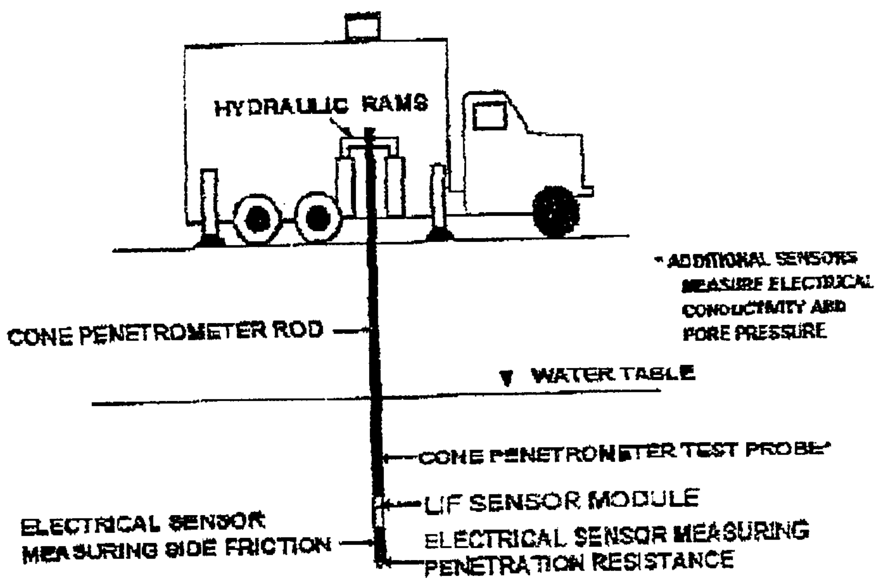

Figure 1. Cone Penetrometer

Cone Penetrometry

The typical cone penetrometer is mounted on a 20-ton truck and driven to the site requiring characterization (Figure 1). Using the truck as a reaction mass, the penetrometer hydraulically pushes an instrumented conical rod into the ground to be characterized. The cone is pushed into the subsurface continuously at a rate of 2 centimeters per second. Signals from the cone are conveyed to the surface through cables located within the center of the push rods. The signals are processed by a computer located in the cone penetrometer truck. The cone penetrometer may characterize several aspects of the subsurface, depending on the types of sensors integrated into the penetrometer. Strain gauges measure the forces against the tip and sleeve of the cone tool allowing determination of soil type; i.e., sand, silt, clay, etc.; and stratification. Electrodes on the rod allow measurement of the electrical conductivity of the soil which are indicative of changes in soil type or moisture and can often indicate the presence of contamination. Other sensors provide additional hydrogeological and chemical information regarding soil and contamination.

Soil, soil gas, and groundwater sampling can be performed using the cone penetrometer. To collect samples, the instrumented cone is removed from the push rods and specially designed sampling tools are attached. The sampling devices are also hydraulically pushed to the desired depth and a sample is collected. The sample is brought to the surface for subsequent analysis in the field or at an off-site laboratory. The cone penetrometer sensors provide information on hydrogeology and contamination; the samplers verify it. The real-time ability to receive and assess monitoring data on-site, without laboratory analysis, is critical. It facilitates decision-making during site investigation projects, while ensuring accurate and efficient completion of site investigations and optimized site remediation. Cone penetrometer technology can also be used to provide baseline data for intrinsic bioremediation modeling studies, to define excavation limits, and to monitor the progress of site remediation. Sampling, monitoring point installation, and many other capabilities exist when deploying a cone penetrometer for environmental investigations.

Laser Spectrometer Systems

One of the key sensors deployed for use with the cone penetrometer involves the use of laser systems to induce fluorescence of fuel products as the cone penetrometer probe is advanced into soils. Laser-Induced Fluorescence (LIF) has been shown to be useful in identifying petroleum contamination such as deisel, gasoline and JP-4 jet fuel. The first cone penetrometers fielded by the Army and the Navy made use of a fixed-frequency nitrogen laser developed by the Navy, but now tunable or multiple-wavelength laser systems are available. Armstrong

Laboratory's Environics Directorate, working with North Dakota State University (NDSU), developed a transportable, laser spectrometer system using a Nd:YAG (neodymium:yttrium aluminum garnet) laser to pump a dye laser. The tunable, laser-generated ultraviolet light is transmitted through optical fibers to the subsurface contaminant. Optical fibers are also used to return the resulting light (fluorescence) for spectroscopic analysis. The detection system consists of either a monochromator, photomultiplier tube, and digital oscilloscope or a gated optical multichannel analyzer. A personal computer is used for system control, automated data collection, and data analysis. The system detects aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), naphthalene, and polycyclic aromatic hydrocarbons (PAHs) by fluorescence. It can identify contamination from gasoline, diesel fuel, fuel oils, jet fuel, creosote and coal tars, all of which contain aromatic hydrocarbons by their fluorescent spectra.

The basic detection approach takes advantage of the fact that certain substances fluoresce when particular wavelengths of light are absorbed. The transportable laser system is unique because its output may be tuned to select the optimum wavelength to stimulate fluorescence of the pollutants while minimizing potential interferences. The resultant spectral emission including fluorescent lifetime is somewhat like a fingerprint, useful for identifying the contaminant. The fluorescent intensity indicates concentration of the contaminant. This technology provides semiqualitative and semiquantitative information, on site, in minutes. The LIF response can be correlated to the total petroleum hydrocarbon (TPH) concentration within the soil using standard or site specific calibration curves. The system has been tested in the field with TPH detection limits as low as parts-per-million levels on soil when used with a cone penetrometer and in the laboratory at parts-per-billion levels for naphthalene in water using fiber optic probes.

Combined Technologies

The combined cone penetrometer and transportable laser spectrometer has been used at a variety of sites having aromatic hydrocarbon contamination. Sites characterized include fuels (jet, gasoline, kerosene, diesel, etc.), naphthalene, benzene, creosotes and coal tars. The tunable laser system is optimized for stimulating contaminants and detecting the fluorescence. Laboratory fluorescence spectra from fuels suggest that naphthalene often produces the maximum fluorescence; consequently, a laser excitation wavelength appropriate for naphthalene is commonly utilized during field investigations.

The system is designed to collect data in two different modes: "push" or "static." In the push mode, laser excitation frequency is fixed and LIF signal is monitored as the cone penetrometer probe is advanced, acquiring a fluorescence intensity-versus-depth (FVD) profile. Operation in the static mode, or with the probe stopped, allows collection of LIF multidimensional data sets, typically the fluorescence emission wavelength, intensity, and time of decay matrices (WTM). WTMs have proven to be useful in identifying various fuel types. The commercial product of this technology, known as ROST, is now available for state-of-the-art fuel-contaminated site characterization services (Fig. 2).

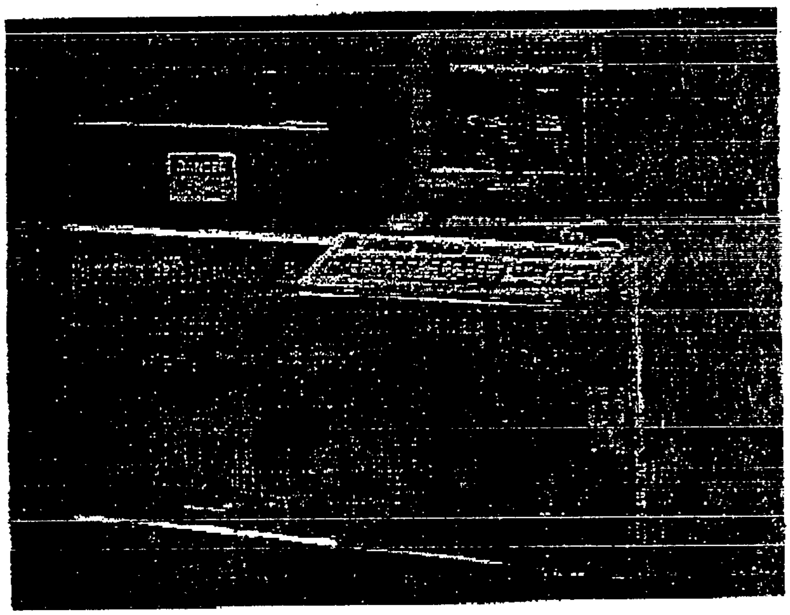

Figure 2. ROST Equipment

Technology Transition

Armstrong Laboratory and Loral Corporation signed a Cooperative Research and Development Agreement (CRDA) in 1993 to commercialize the Air Force-developed laser spectrometer system. A consortium consisting of the CRDA partners (USAF/Loral), Dakota Technologies Inc., and North Dakota State University submitted a proposal to the Advanced

Research Projects Agency (ARPA), Technology Reinvestment Project (TRP). In December 1993, ARPA selected the proposal to receive a two-year $1,600,000 grant, industry provide in-kind contributions and matching funds.

The ROST commercialization program has automated the collection and mapping of data, made equipment components smaller and more rugged, and developed user-friendly interfaces to allow easy use by environmental technicians. This instrument is also adaptable for monitoring well applications. ROST has potential for process control and even medical diagnostics.

Use of the ROST system should result in substantial savings in costs associated with characterization, monitoring, and remediation of hazardous waste sites. Loral is now offering site characterization services using the ROST system.

As a result of this technology transfer, the U.S. DOD will benefit from application of technology and knowledge gained; the private sector will receive a highly transferable and profitable technology; and all will benefit from a cleaner environment.

RAPID OPTICAL SCREENING TOOL

Description

ROST employs laser-induced fluorescence spectroscopy for in situ analysis of petroleum hydrocarbons (Figure 3). Ultraviolet light is required to excite the fluorescence of most of the aromatic compounds in petroleum hydrocarbons. Pulsed light in this wavelength region is obtained in ROST by frequency doubling the output of a dye laser pumped by a Nd:YAG laser. Either the 2nd or 3rd harmonic of the Nd:YAG can be used as the dye laser pump. The laser source and detection system (spectrometer) are located in a cone penetrometer truck. The pulsed laser light travels via fiber optic cable to and from an optical module located near the cone rod. There light is directed through a sapphire window onto the surface of soil pressing up against the window. Aromatic petroleum hydrocarbon molecules present will absorb the excitation light and emit fluorescence at longer wavelengths. The wavelength of light selected for excitation is in a range that is absorbed by aromatic petroleum hydrocarbons. A portion of the emitted fluorescence passes back through the window, is returned to the surface, and imaged through a monochromator. The wavelength-dispersed radiation is converted to an electrical signal by a photomultiplier tube and the electrical signal is analyzed by a digital oscilloscope and computer.

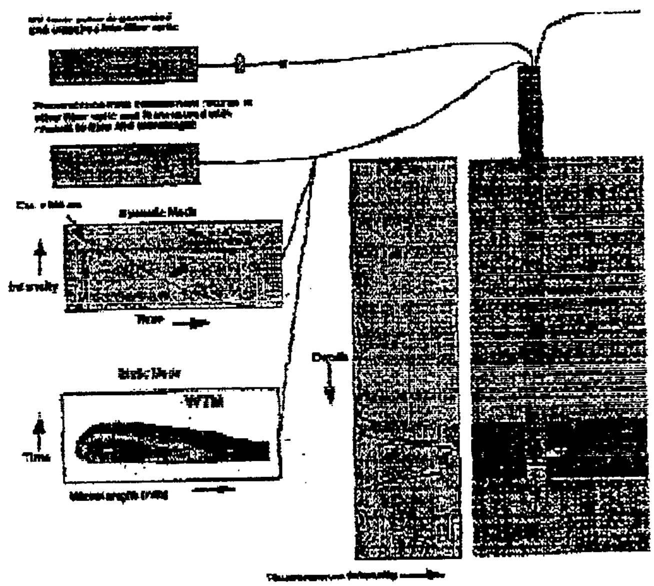

Figure 3. ROST Optical System Concept

The incoming data are continuously processed and displayed in FVD profile for the entire cone penetrometer push. The fluorescence signal from 50 successive laser shots (taking a total time of 1 second) is averaged for each data point acquired and displayed. Since the cone is pushed at 2 centimeters per second, the spatial resolution of the FVD data is 2 centimeters.

In addition to FVD profiles, ROST can differentiate petroleum fuel types. This is accomplished by acquiring WTMs during a short pause (approximately 1 minute) in the cone penetrometer push. A WTM is a three-dimensional graph of fluorescence wavelength, fluorescence lifetime (i.e., time scale over which the fluorescence signals are emitted), and fluorescence intensity. Petroleum products have a distinctive fluorescence signature which allows the field operator to identify the approximate nature of the contaminant. Emissions in the 260 to 300 nanometer (nm) range indicate single-ring aromatics like BTEX compounds. Emissions in the 300 to 350 nm range indicate two-ring aromatics such as naphthalene. Larger polycyclic aromatic hydrocarbons fluoresce at wavelengths longer than 350 nm. WTMs are especially useful for determining if multiple sources of contamination are present.

ROST can detect and characterize hydrocarbons such as gasoline, jet fuel, and diesel fuels (Figure 4).

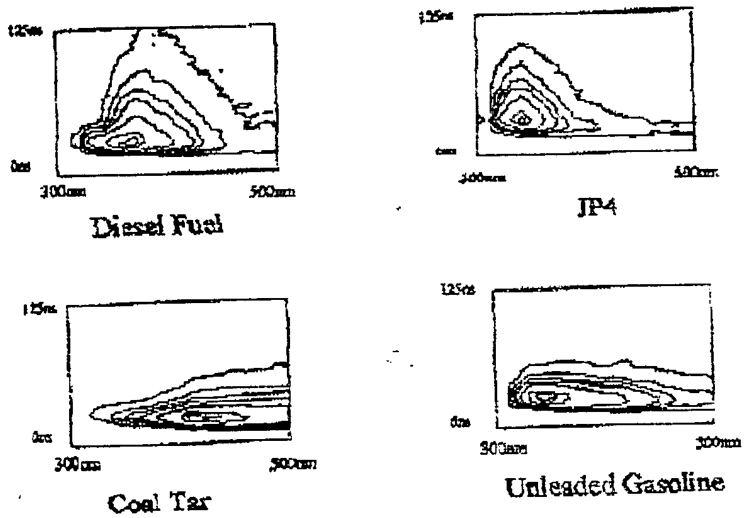

Figure 4. Fluorescence Emission Wavelength-Intensity-Lifetime Matrices (WTMs)

Benefits

ROST is extremely useful for soil and groundwater hydrocarbon contamination analysis when used with a cone penetrometer. ROST with variable wavelength (tunable), pulsed-laser source means that the excitation wavelength can be optimized for the contaminant of interest. Information regarding hydrocarbon type, depth, and distribution is available on-site at the conclusion of each push. In addition, geotechnical data are also collected. Typically, the vertical hydrocarbon profile (FVD) of a 30-foot push can be determined in less than 20 minutes. ROST, a self-contained, ruggedized system, can be permanently or temporarily installed on most new or existing cone penetrometer trucks.

RESULTS AND DISCUSSION

The ROST system has been demonstrated, field tested and integrated into site characterization plans at many commercial and government sites (Figure 5). ROST units have performed over 20,000 linear feet of field testing over the last 12 months.

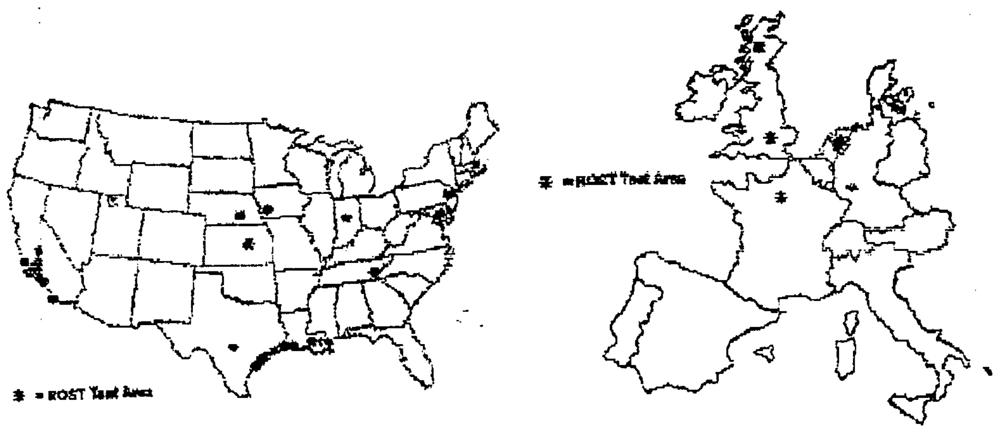

Figure 5. ROST Test Locations

These technologies are being further refined, demonstrated, and evaluated within numerous DOD, DOE, and EPA programs. The results discussed are from laboratory and field demonstrations by the Tri-Service and ROST consortium. Demonstrations were recently completed under the following: a)EPA Superfund Innovative Technology Evaluation (SITE) Program, b)Under an environmental Data Exchange Agreement (DEA) with the German Ministry of Defense, c)In the U.K. under the Building Research Establishment Agency program in London, Scotland, and Whales, d)With U.S. EPA/DOD/DOE Consortium for Site Characterization Technology at the National Hydrocarbon Test Site in California, and at e)Numerous other commercial and government sites.

The purpose of the EPA SITE Program demonstrations is to evaluate innovative technology and report the results. The German DEA provides for environmental technology transfer including demonstrations to help both countries deal effectively with environmental problems. In London the technology was used to investigate possible tank leakage at a retail petroleum distribution facility. An oil shale site which has been turned into a golf course was characterized in Scotland with a wide range of contaminants such as coal tar, lamp oil, and detergents. In Whales a BTEX contamination from a chemical manufacturing plant was characterized. The testing with the EPA/DOD/DOE Consortium is part of a larger effort to validate the LIF technology and establish a standard method for its use. The Tri-Services conducted a series of laboratory tests resulting in calibration curves with different fuels on various soil matrices. The calibration curve obtained in the laboratory for diesel fuel marine on a sand matrix indicates a detection limit less than 30 mg/kg (ppm). JP4 calibration curves on sand showed detection limits of 5 mg/kg.

A graphical representation of data from one push location illustrating vertical contaminant distribution, soil stratigraphy (based on tip resistance and sleeve friction) and Wavelength-Time Matrix (WTM) data collected by the cone penetrometer/ROST system in real-time is shown (Figure 6). Data Logs such as these are produced in the field, saving valuable time normally lost to delays waiting for analytical data when traditional methods (such as drilling/soil sampling) are used.

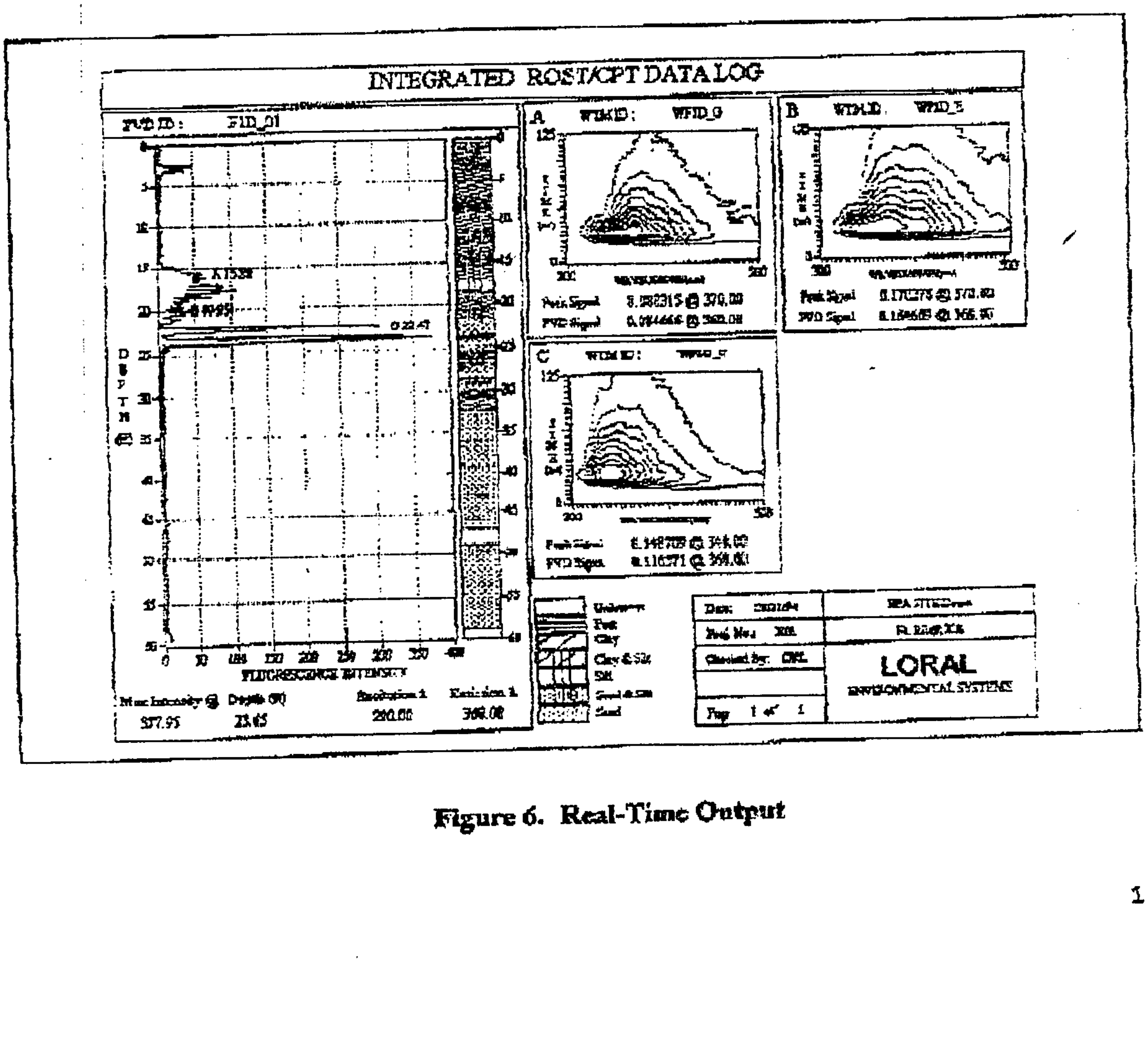

Figure 6. Real-Time Output

Prior to each push, an end to end test of the ROST instrument is performed using a standard reference check solution, which is contained in a cuvette cell that is pressed up against the sapphire window. This ensures the instrument is properly set up, operating correctly, and also provides a mechanism to normalize the resulting fluorescence data so data from multiple pushes or sites can be quantitatively compared. FVD profiles may be reported in units that relate to the fluorescence response of the reference check solution or using laboratory (or field) calibration curves FVD profiles may be reported in mg/kg equivalents. The vertical axis represents depth below ground surface. The horizontal displacement to the right is fluorescence intensity, which is directly related to petroleum hydrocarbon concentration. Data from multiple CPT/ROST push locations can be integrated using common contouring programs to gain a view of the overall distribution of petroleum hydrocarbons at the site (Figure 7).

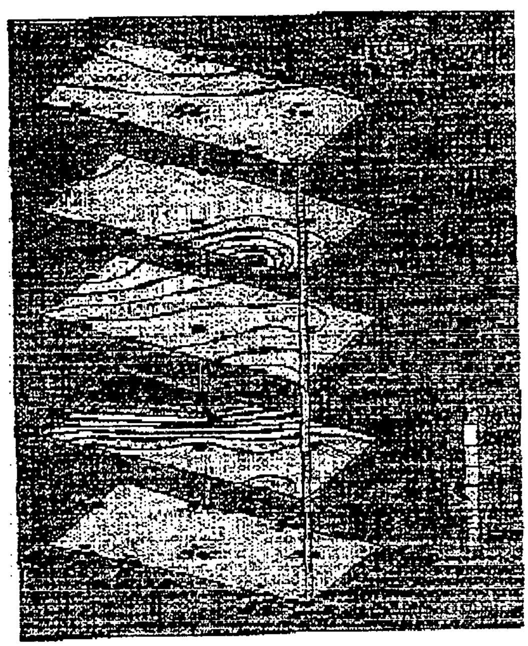

Figure 7. Hydrocarbon Plume Based on ROST Data

Analytical laboratory results collaborate the characterization of petroleum hydrocarbons by ROST. Areas having relatively high concentrations of petroleum hydrocarbons in soil samples correspond to areas where relatively high fluorescence intensities are observed. Furthermore, areas showing no fluorescence response are found to contain relatively low concentrations of petroleum hydrocarbons. Figure 8 compares fluorescence intensity to the results of laboratory analysis of field samples for total semi-volatile organic compounds by EPA Method 8310 showing the relative fluorescence intensity data is very similar to that of the laboratory results. An excellent correlation was obtained between ROST and results using total semivolatile organic compound analysis as well as total recoverable petroleum hydrocarbons by EPA Method 418.1 analysis. Data from in-situ testing indicates that at this site, material containing more than 1 ppm total semi-volatile organic compounds by Method 8310, is readily observed by ROST.

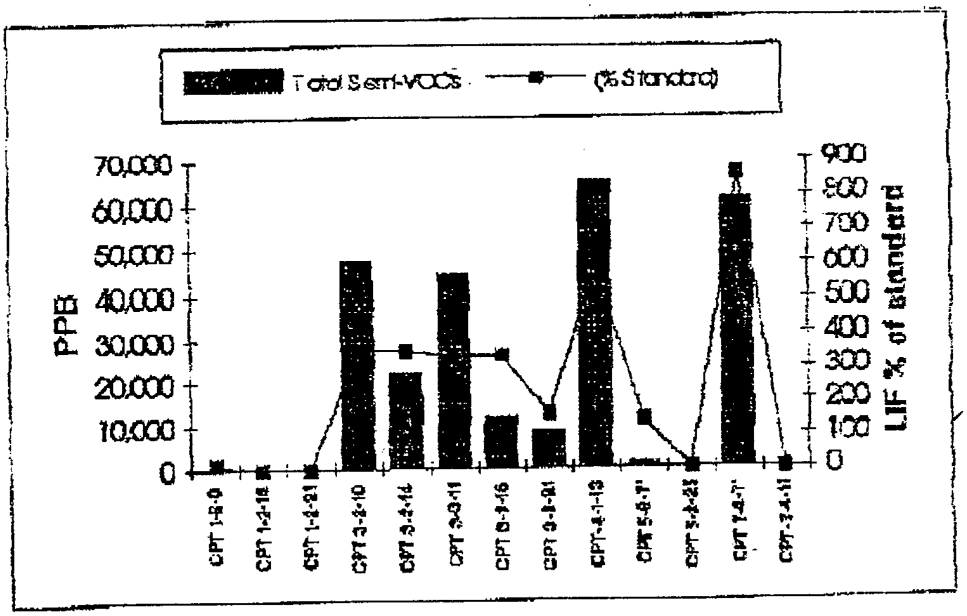

Figure 8. Fluorescence response versus field sample analytical results

Data accumulated verify that ROST can reliable map subsurface petroleum contamination in situ, in real-time, and in continuous vertical fashion

CONCLUSIONS

Screening for hazardous waste normally involves drilling of bore holes and monitoring wells. The process is slow, expensive, and results are often inconclusive. Remediation costs for U.S. government sites alone run as high as $500 billion. About 15 percent of that figure, or $75 billion, represents the price of screening and characterization. Laser induced fluorescence technology to detect aromatic hydrocarbons in situ is now a viable, field proven, commercially available technology. ROST and related technologies represent a landmark development in site characterization. Environmental investigators will be able to find, classify and map the distribution of many contaminants in days. Ongoing research will be developing techniques to detect and monitor contaminants such as chlorinated solvents, metals, and explosives which do not naturally fluoresce. Refining and demonstrating these technologies is at the heart of characterization, remediation and monitoring. These technologies may determine if remediation is needed, what remediation technology should be applied, whether the remediation is working, and when the cleanup effort is complete, all with the minimum of risk, time, labor, and cost.

Loral Corp. and it's partners are now making the ROST system available for hydrocarbon contaminated site characterization at both government and commercial sites in North America and Europe. ROST can lower the cost of testing from thousands of dollars per hole to just a few hundred dollars, the site characterization savings in addition to the value of improved site data will be of great benefit.

[1] ROST™ is a Loral registered trademark, hereafter referred to as ROST.