



Site Characterization and Analysis Penetrometer System (SCAPS) Downhole Nd:YAG Laser-Based Laser Induced Fluorescence Validation

Technology Demonstration Report

**Space and Naval Warfare Systems Center, San Diego
(SSC San Diego)
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1. Introduction

This technology demonstration report documents the field and laboratory methods used to verify a downhole 266 nm Neodymium: Yttrium Aluminum Garnet (Nd:YAG) laser-induced fluorescence (LIF) sensing technology and presents demonstration results. Space and Naval Warfare Systems Center, San Diego (SSC San Diego), formerly NCCOSC RDTE DIV, has prepared this report following the guidelines in the Environmental Security Technology Certification Program (ESTCP) Program Offices' document, "Final Report Guidelines for Funded Projects" dated 6 February, 1996. The technology demonstration report is divided into ten sections. Section 1. provides a broad overview of the purpose and background of the demonstration and a description

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of the technology demonstration process. Section 2. describes the downhole 266 nm Nd:YAG Site Characterization and Analysis Penetrometer System (SCAPS) LIF technology sensor. Section 3. provides a description of the demonstration sites. Section 4. presents the demonstration approach with sampling and analytical procedures. Section 5. assesses system technical performance. Section 6. provides cost related information. Section 7. discusses regulatory issues. Section 8. outlines the technology implementation. Section 9. reviews lessons learned as a result of this demonstration. Section 10. provides references to cited documents. Three appendices supplement this report: (1) Points of Contact (Appendix A), (2) Data Archiving and Demonstration Plan (Appendix B) and (3) A paper entitled, "In-Situ Monitoring of LNAPL Degradation using the SCAPS Optical Cone Penetrometer System" that was presented at the Fifth International Symposium on Field Analytical Methods for Hazardous Wastes and Toxic Chemicals in Las Vegas, NV, January 1997 (Knowles et al., 1997). Comprehensive data reports for North Island Fuel Farm site at Naval Air Station (NAS), San Diego, CA, and Naval Exchange (NEX) service station at the Hydrocarbon National Test Site at Naval Construction Battalion Center (NCBC), Port Hueneme, CA. are included by reference and contain the real-time printouts for the LIF sensors and the analytical laboratory results.

1.1 Background Information

At present, site characterization represents a significant portion of remediation efforts, accounting for about one-third or more of the total costs. Environmental site characterization traditionally depends on drilling, sampling and laboratory analysis. Delineation of subsurface contamination is most often based on trial-and-error placement of a significant number of monitoring wells and/or borings. Laboratory analysis of samples collected in the field is time consuming and costly. This traditional approach to site characterization hampers remediation efforts because of its uncertainty, time requirements and cost.

SCAPS was developed to address many of these deficiencies. SCAPS combines traditional cone penetrometer (CPT) technology with real-time chemical sensors to rapidly profile contaminants and geophysical properties in a cost effective manner. The Tri-Service SCAPS project has progressed to the point where eight SCAPS systems (four Army, three Navy, and 1 Department of Energy (DoE)) with the fiber-optic based LIF sensor for petroleum, oil, and lubricant (POL) contaminants are available for use at government sites. In addition, the Rapid Optical Screening Tool (ROSTTM) is currently offered as a commercial product by Fugro Geosciences, Inc. ROSTTM

was originally commercialized by Unisys Corporation via an LIF/CPT technology patent license and two government Cooperative Research and Development Agreements (CRADAs).

The ESTCP has an established program to accelerate acceptance and application of innovative monitoring and site characterization technologies that improve the way the nation manages its environmental problems. SSC San Diego demonstrated a downhole 266 nm Nd:YAG LIF sensing technology using the SCAPS platform to facilitate its acceptance and use for field screening of petroleum hydrocarbons in the subsurface.

Demonstrations were designed to evaluate this LIF sensor as a field screening method by comparing the downhole 266 nm Nd:YAG SCAPS LIF with the 337 nm nitrogen-based SCAPS LIF data and to data produced by conventional sampling and analytical methods. For the demonstrations, conventional sampling and analysis was accomplished by pushing a stab sampling penetrometer in very close proximity (within 8 inches) of the downhole Nd:YAG LIF push holes, collecting soil samples as close as possible to the push cavities, and analyzing discrete samples for petroleum hydrocarbons by DHS Method 8015-Modified and EPA Method 8021A-Modified. Data was collected during two separate demonstrations: (1) demonstration at the North Island Fuel Farm site at Naval Air Station (NAS), San Diego, CA, and (2) demonstration at the Naval Exchange (NEX) service station at the Hydrocarbon National Test Site at Naval Construction Battalion Center (NCBC), Port Hueneme, CA. The performance of the downhole Nd:YAG LIF technology during each demonstration was compared to conventional sampling and analytical methods used in site characterization.

This validation process has been used by SSC San Diego at more than 24 sites to provide a database for review by regulatory agencies in technology acceptance programs. The nitrogen laser-based SCAPS LIF recently completed validation/demonstration by several technology certification programs, including the following:

California Environmental Protection Agency (Cal-EPA) - Technology Certification Program (Cal EPA, 1996)

U.S. EPA, Department of Defense, and Department of Energy - Consortium for Site Characterization Technology (US EPA, 1997)

Western Governor's Association - Committee to Develop On-Site Innovative Technologies (Wesnousky et al., 1996)

Interstate Technology and Regulatory Cooperation Program (Wesnousky et al., 1996)

The demonstrations reported herein extend the validation database to include use of an additional laser source, the downhole 266 nm Nd:YAG laser, for use in a SCAPS LIF sensor.

The downhole Nd:YAG LIF technology demonstrated is a modification of the 337 nm nitrogen laser-based LIF sensor originally developed by the Navy's SSC San Diego and subsequently integrated into the cone penetrometer system through a Tri-Service collaborative effort. The miniature 266 nm downhole Nd:YAG laser was developed by the MIT Lincoln Laboratory (Zayhowski and Johnson, 1996). The laser source was adapted for use in the SCAPS system in a collaboration between the MIT Lincoln Laboratory and SSC San Diego. The downhole Nd:YAG laser source is intended to enhance the capabilities of the original nitrogen laser system by providing more effective excitation of single and double ring aromatic compounds using higher energy ultraviolet (UV) radiation. The fact that the miniature Nd:YAG laser source can be located in the probe near the window eliminates the need for an optical fiber to transmit low wavelength UV light ($\lambda < 290$ nm) from the surface truck and thereby provides a means of eliminating problems with high attenuation of low wavelength UV radiation in optical fibers.

The advantage of these SCAPS deployed technologies is that they provide better, faster, and cheaper information about the location of underground contamination and soil characteristics. Vertical spatial resolution of approximately 4 cm is over an order of magnitude improved over existing practices. Real-time data permits in the field sampling plan modifications for better delineation and immediate results rather than weeks to months delay awaiting laboratory results. A cost benefit analysis conducted by the DoE (Los Alamos) and documented in the FY93 Tri-Service Environmental R&D Strategic Plan, indicates a cost savings of 25 to 35% can be realized with SCAPS technology in a site investigation. Recent regulatory acceptance will pave the way for more widespread use of this innovative approach to mapping underground contaminant plumes at both DoD and private sites. This will help clean up sites more quickly and effectively, with potential savings of millions of dollars.

1.2 Official DoD Requirement Statement

The downhole 266 nm Nd:YAG LIF/CPT technology falls under the ESTCP focus area 1. Cleanup, subarea b. Site Characterization.

1.3 Objectives of the Demonstration

The purpose of the downhole 266 nm Nd:YAG LIF SCAPS technology demonstration was to generate field data appropriate for verifying the performance of the technology, and thereby facilitate the technology acceptance and use by the regulator and user communities for field screening of petroleum hydrocarbons in subsurface soils. To obtain the data required to verify the performance of the downhole 266 nm Nd:YAG SCAPS LIF for field screening of petroleum hydrocarbons in the subsurface, both primary and secondary demonstration objectives were identified.

The primary objectives of this demonstration were to evaluate the in situ downhole Nd:YAG LIF technology in the following areas: (1) its performance compared to conventional sampling and analytical methods, as well as to the 337 nm nitrogen-based LIF method; (2) the logistical and economic resources necessary to operate the technology; (3) data quality; and (4) the range of usefulness in which the technology can be operated. Secondary objectives for this demonstration were to evaluate the downhole Nd:YAG LIF technology for its reliability, ruggedness, and ease of operation.

1.4 Regulatory Issues

Regulatory acceptance of the nitrogen laser-based LIF SCAPS has contributed to the acceptance of this innovative approach to delineating underground contaminant plumes at both DoD and private sites. This technology has already been used to help clean up sites more quickly and effectively. Use of the nitrogen laser system has already resulted in significant cost savings.

The Lawrence Livermore National Laboratory report, "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)" (October 1995), derived as a result of an historical case analysis performed for the California State Water Resources Control Board, has generated interest in Risk-based corrective action (RBCA). The RBCA framework requires measurement of individual chemicals of concern with potential long term monitoring. The changing regulatory framework poses both a challenge and an opportunity for LIF/CPT technology application.

Incorporation of the 266 nm downhole Nd:YAG LIF into the original 337 nm nitrogen LIF system allows for (1) improved detection capabilities for lighter weight fuel products (namely fuels whose aromatic constituents are limited primarily to single and double ring compounds and (2) improved capability for detecting and monitoring the composition of light end aromatic components of fuel products that are the major constituents of concern for estimating the fate and transport of toxic compounds with respect to remediation strategies that are based on RBCA.

1.5 Previous Testing of the Technology

The Tri-Service SCAPS LIF technology has been validated at more than 24 sites since 1993. The Army/Navy/DOE operational SCAPS LIF systems have been deployed at many additional sites. More than 600 pushes covering over 12,000 vertical feet, verified by 101 borings or stab sampling pushes with more than 800 analytical samples have been accomplished with the SSC San Diego EDM-1 SCAPS system. Detailed descriptions of the operations conducted at some of these sites are available from SSC San Diego. Requests should be directed to Dr. S. H. Lieberman at the address listed in Appendix A, Points of Contact. The Nd:YAG system has been tested in the laboratory and at several sites prior to this demonstration/validation.

2. Technology Description

2.1 Description

The SCAPS CPT is the platform for a planned family of new rapid field screening technologies for surficial and subsurface contaminants. LIF sensors rely on impinging ultraviolet (UV) light to excite molecular electrons to excited/higher energy states. As the electrons return to lower energy ground states, the transition produces UV and visible fluorescence photons of longer wavelength than the UV excitation. The penetrometer deployed 266 nm downhole Nd:YAG LIF technology sensor demonstrated was originally developed through a collaboration between SSC San Diego and MIT Lincoln Laboratory through the SERDP supported Tri-Service (Navy, Army, and Air Force) SCAPS Program. The miniature 266 nm downhole Nd:YAG laser was developed by the MIT Lincoln Laboratory. The downhole Nd:YAG LIF system uses a miniature 266 nm laser coupled via an optical fiber with an optical detector to make fluorescence measurements. The measurement is made through a sapphire window on a probe that is pushed into the ground with a

truck-mounted cone penetrometer. Figure 1 shows a schematic of the 266 nm downhole Nd:YAG LIF system.

Data acquisition is automated under software control using a host computer. The computer controls the sensor system, stores fluorescent emission spectra and strain gauge data, and generates the real-time depth plots shown in Figure 2. From the spectral emission curve at each depth, the SCAPS software extracts the maximum intensity and associated peak wavelength for real-time depth display. The Raw Fluorescence and Wavelength at Peak strips of Figure 2 contain this data. SCAPS standard electrical cone penetrometer instrumentation consists of strain gauges measuring tip resistance and sleeve friction in accordance with ASTM Standard D3441. An empirical relationship between tip resistance and sleeve friction provides a soil type classification relating to grain size (Robertson and Campanella, 1989). This data is contained in the real-time display strips as Cone Pressure, Sleeve Friction, and Soil Classification. As the probe is forced into the ground, the real-time display presents a ten-foot interval on a scrolling basis.

2.1.1 The Cone Penetrometer Platform. Cone penetrometer test (CPT) and standard penetration test (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 SCAPS uses a truck-mounted CPT platform to advance its chemical and geotechnical sensing probe. The CPT platform provides a 20-ton static reaction force associated with the weight of the truck. The forward portion of the truck-mounted laboratory is the push room. It contains the rods, hydraulic rams, and associated system controllers. Underneath the SCAPS CPT push room is the steam cleaning manifold for the rod and probe decontamination system. The rear portion of the truck-mounted laboratory is the isolatable data collection room in which components of the LIF system and onboard computers are located. The combination of reaction mass and hydraulics can advance a 1-meter (m) long by 3.57-cm diameter threaded-end rod into the ground at a rate of 1 meter per minute (m/min) in accordance with ASTM Standard D3441. The rods, various sensing probes, or sampling tools can be advanced to depths in excess of 50 meters in naturally occurring soils. As the rods are withdrawn, grout can be injected

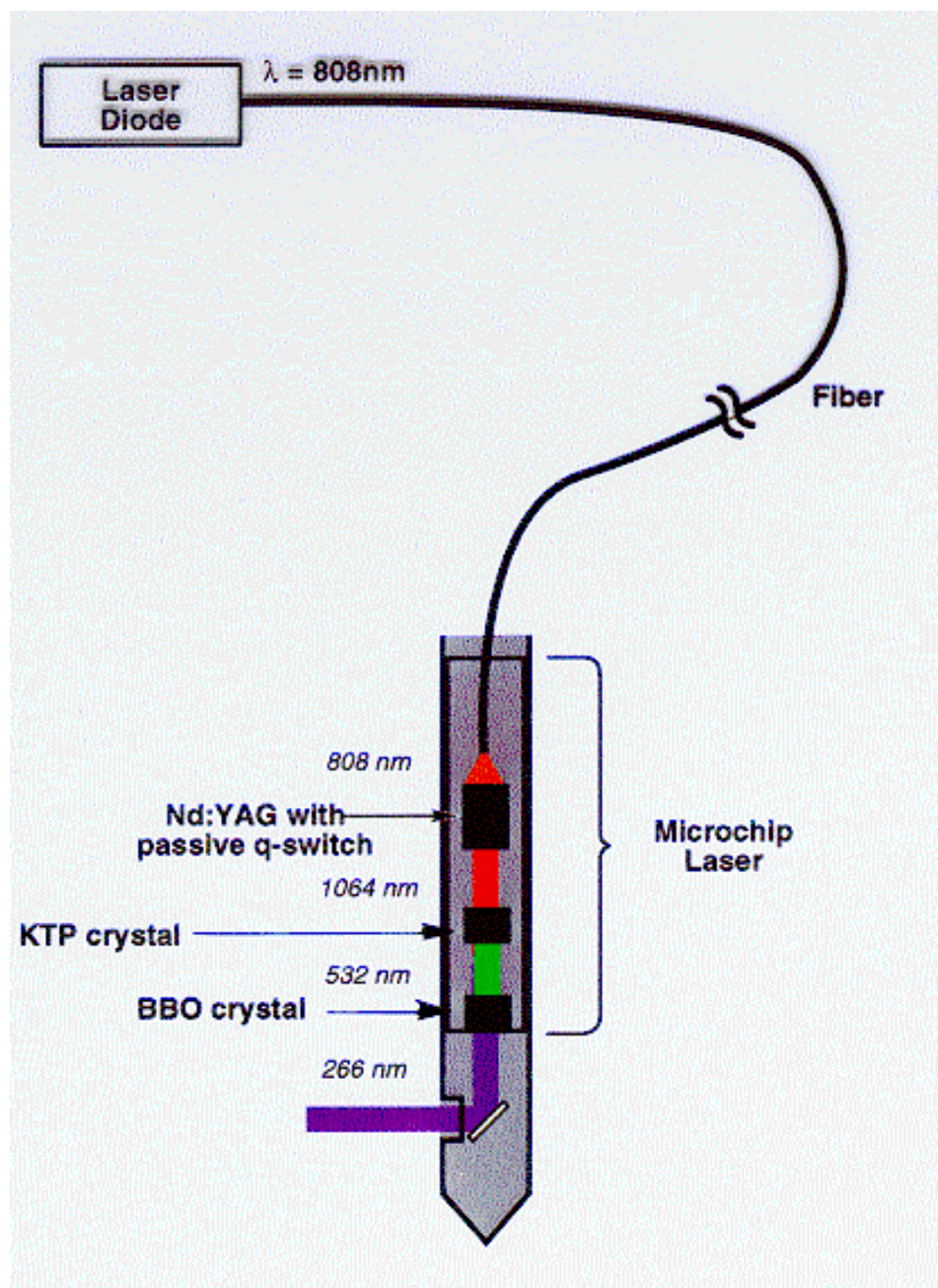


Figure 1. Schematic of Nd:YAG Laser System for Petroleum Hydrocarbons.

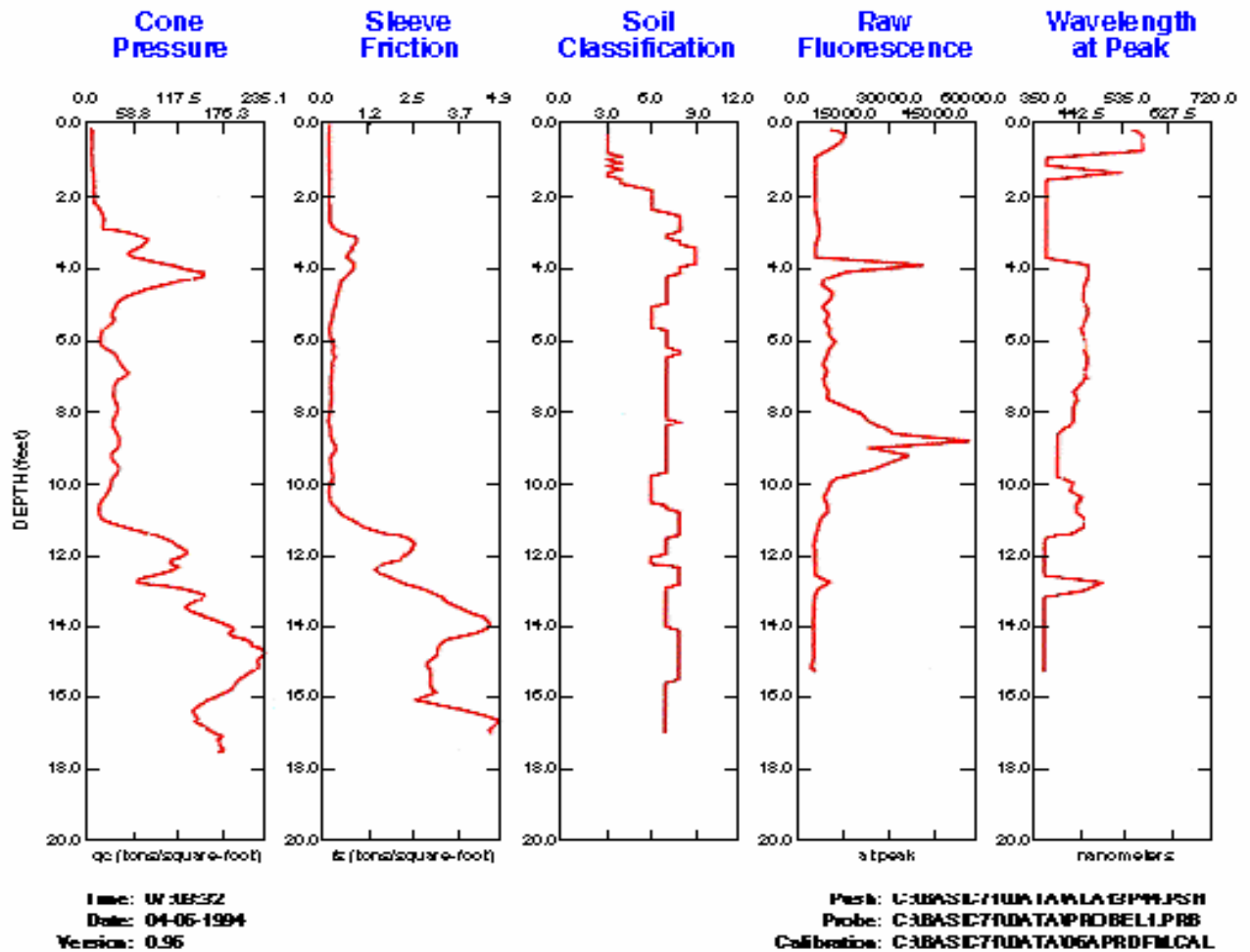


Figure 2. Real-Time Data Display of Fluorescence and Strain Gauge Data

through 6.35 mm diameter tubing within the interior of the SCAPS LIF umbilical, hydraulically sealing the push hole.

In addition to chemical sensors, groundwater, soil, and soil gas sampling tools can be used with the CPT. Groundwater sampling tools can vary from a slotted well-point design to a retractable well screen. Soil sampling is accomplished with core-type samplers. Soil gas sampling is typically accomplished by allowing subsurface vapors to equilibrate in teflon tubing within the rods. The soil gas is then either collected for delivery to an off-site laboratory or analyzed by an on-board gas

chromatograph. These tools were not the subject of this demonstration. Existing CPT systems do not allow in situ sampling tools and subsurface sensors to be used concurrently.

2.1.2 Cone Penetrometer LIF Probes. The lead probe rod can be fitted with various types of sampling tools and sensors. The CPT LIF systems use a steel probe containing the LIF sapphire optical window and cone and sleeve strain gauges. The excitation and emission optical fibers are isolated from the soil system by a 6.35 millimeter (mm) diameter sapphire window located 60 cm from the probe tip, mounted flush with the outside of the probe. The SCAPS LIF fibers are 365 micron (μm) in diameter and up to 100 m in length.

2.1.3 Downhole Nd:YAG Laser Source. The downhole Nd:YAG SCAPS LIF fiber optic-based system uses 266 nanometer (nm) ultraviolet (UV) light from a frequency quadrupled Nd:YAG (Neodymium:Yttrium Aluminum Garnet) laser. The novel Nd:YAG laser is located in the SCAPS probe to avoid the poor transmission properties of the optical fiber at 266 nm. The laser is excited using 808 nm light from a laser diode located in the SCAPS truck at the surface. The Nd:YAG laser was designed at MIT Lincoln Laboratory, and includes a small crystal of Nd:YAG bonded to a passive q-switch of Cr:YAG (Chromium:Yttrium Aluminum Garnet), with dielectric mirrors directly deposited on the crystals. The q-switched Nd:YAG laser operates at roughly 7 kilohertz (kHz) with pulselengths on the order of 100 picoseconds (psec) due to the short cavity of the laser. The 1064 nm pulses from the Nd:YAG laser are frequency doubled using a KTP (Potassium Titanyl Phosphate) crystal to 532 nm, and then frequency doubled again to 266 nm using a BBO (Beta-barium Borate) crystal. Because of the short pulselength and small beamwaist of the Nd:YAG laser, efficiency quadrupling of the laser radiation is accomplished with a single pass through both crystals. The final output at 266 nm is 3-5 milliWatts (mW) average power in approximately 7 kHz pulses. The 266 nm microchip laser used during this test is permanently bonded into an optical module designed at Lincoln Labs to deliver the 266 nm radiation to the sapphire window and collect the resulting fluorescence. This module was designed to fit into the SSC San Diego cone penetrometer probe with minor modifications to the probe. Note that this module is different from the standard SCAPS probe configuration where the excitation fiber is adjacent to the sapphire window with no other focusing optics.

2.1.4 Detection System. The SCAPS LIF system typically uses a pulsed laser fiber optic-based sensor in conjunction with the nitrogen laser system. As the pulse from the laser is launched into the excitation fiber, a photodiode is triggered which generates a synchronization

pulse that is fed into a pulse delay generator. The pulse from this apparatus is used to gate on a photodiode array (PDA) detector. Fluorescence stimulated in the in situ soil "sample" by the laser is collected by the emission fiber and returned to a spectrograph, where it is dispersed spectrally on the PDA. This arrangement allows for the rapid acquisition of temporal spectral data. Readout of a fluorescence emission spectrum, performed by an EG&G PARC Model 1460 optical multichannel analyzer (OMA), requires approximately 16 milliseconds (ms). For a laser firing at a rate of 20 Hz, an entire fluorescence emission spectrum measurement, composed of a 20 laser shot average, can be collected in approximately 1 second.

When the detection system is used with the 266 nm Nd:YAG laser, the high repetition rate of the laser exceeds the capabilities of the OMA detector. In this case, the detector is operated in the continuous wave (CW) mode without triggering from the Nd:YAG laser. The OMA is set up to collect ten 100 ms acquisition cycles of the OMA detector, approximating the operating characteristics of the nitrogen system. This will yield roughly the same depth resolution as that seen with the nitrogen laser system. Other than this change, the detection hardware is identical to that used with the nitrogen laser system, and the data display is unchanged.

Under normal operating conditions, fluorescence emission spectra are collected once per second as the penetrometer probe is pushed into the ground at a rate of approximately 1 m/min. This yields a measurement with a vertical spatial resolution of approximately 0.2 feet. A host computer equipped with custom software controls the fiber optic fluorometer sensor system and stores fluorescence emission spectra and conventional CPT sleeve friction and tip resistance data. The host computer is also used to generate real-time depth plots of fluorescent intensity at the spectral peak, wavelength of spectral peak, sleeve friction and tip resistance, and soil type characteristics as interpreted from the strain gauge data. The fluorescent intensity in the spectral window is plotted as a function of depth in real time as the probe is pushed into the soil. The entire fluorescent emission spectrum is stored on a fixed hard disk to facilitate post-processing of the data.

2.1.5 Dynamic Range. The linear dynamic range of the downhole Nd:YAG 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 non-linearity occurs at lower concentrations than in clay rich soils,

possibly due to self absorption (Apitz et al. 1992a) or saturation. The linear dynamic range of the downhole Nd:YAG 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.

2.1.6 Noise, Background, and Sensitivity. Three quantities are needed to determine the fluorescence threshold and the detection limit: noise, background, and sensitivity. These quantities are determined using the calibration samples prepared immediately prior to the site visit using soil from the site and standard analytical techniques.

The fluorescence intensity for each calibration sample was measured in triplicate daily at the start of operations. The three measurements were averaged to provide a single measured intensity for each concentration. The data was regressed to establish a slope and intercept. The intercept was given by the intensity of the unspiked calibration standard (0 ppm). The slope was found from the least squares fit using this intercept:

intercept: $b = y_0 = \text{intensity measured on 0 ppm calibration sample}$

$$\text{slope : } m = \frac{\sum (y_i - y_0) x_i}{\sum x_i^2}$$

The variance in the regression is given by:

$$V = (n - 1)^{-1} \sum (m x_i + b - y_i)^2$$

where V is the biased estimator of the residual mean square of the fit and the data, and the standard deviation σ of the fit is:

$$\sigma = \sqrt{V}$$

For the calibration soils, x is given by the concentration (C) of the target fuel, while y is the measured fluorescence intensity (I) of the sample. The sensitivity and background are defined as follows:

$$\text{sensitivity} = \text{slope of fitted data} = m$$

$$\text{background} = \text{intercept of fitted data} = b$$

The noise is defined as:

$$\text{noise} = \text{standard deviation of the fit} = \sigma$$

The noise is defined as 1.00 times the standard deviation in order to establish a conservative fluorescence threshold. The fluorescence threshold is given as the sum of the background and the noise values. Using the standard assumption of a normal "student's t" distribution statistics, and the number of points used in these fits (typically 4-5 points), this corresponds to an 80% confidence limit. This was chosen because the sensor is used as a field screening tool, and it was considered important to reduce the possibility for false negatives.

This procedure was carried out using only the lower concentration calibration standards. For example, using diesel fuel marine (DFM) as the target fuel, the standards consisted of samples with concentrations of 0 mg/kg, 500 mg/kg, 1000 mg/kg, 1500 mg/kg and 2000 mg/kg. Experiments have shown that for the full range of calibration standards (up to 100,000 mg/kg), the calibration data is not well fit by a linear regression. By restricting the data set to the low concentration samples, the data was well fit using the linear regression and this approach gives much more confidence in the sensitivity near the detection threshold.

2.1.7 Calculated Fluorescence Threshold and Detection Threshold. The quantities needed to calculate the downhole Nd:YAG SCAPS LIF fluorescence threshold and the detection threshold are now known. These are determined from:

$$\begin{aligned} \text{fluorescence threshold} &= \text{background} + \text{noise} \\ \text{FT} &= b + \sigma \end{aligned}$$

$$\begin{aligned} \text{detection threshold} &= \text{noise} / \text{sensitivity} \\ \text{DT} &= \sigma / m \end{aligned}$$

The fluorescence threshold is the quantitative limit that the fluorescence intensity must exceed in order to qualify as a "detect." If the fluorescence intensity is less than the fluorescence threshold, the sensor indicates "non-detect."

The detection threshold is the amount of contaminant (based on the target fuel used to prepare the spiked calibration samples) that corresponds to the fluorescence threshold. This is the practical detection level in mg/kg as determined from the calibration standards for a given site, and is found by taking the fluorescence threshold intensity and working back to the concentration needed to produce this intensity. Based on the results calculated for the sites up to this time using the nitrogen laser-based SCAPS LIF, the detection threshold will vary somewhat from site to site, but is approximately 100 to 300 mg/kg.

2.2 Strengths, Advantages, and Weaknesses

2.2.1 Technology Applications. The downhole Nd:YAG SCAPS LIF system was developed in response to the need for real-time in situ measurements of subsurface contamination at hazardous waste sites and to extend the capability provided by the previously demonstrated nitrogen laser-based SCAPS LIF system. The LIF systems perform rapid field screening to determine either the presence or absence of petroleum hydrocarbon contamination within the subsurface of the site. The site can be further characterized with limited numbers of carefully placed stab samplings, 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.

2.2.2 Advantages of the Technology. The LIF sensors are in situ field screening techniques 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. In addition, the SCAPS CPT platform allows for the characterization of contaminated sites with minimal exposure of site personnel and the community to toxic contaminants, and minimizes the volume of investigation derived waste (IDW) generated during typical site characterization activities. 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.

2.2.3 Limits of the Technology. This section discusses the limits of the downhole Nd:YAG SCAPS LIF technology as it is currently understood.

2.2.3.1 Truck-Mounted Cone Penetrometer Access Limits. The SCAPS CPT support platform is a 20-ton Freightliner 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. It is conceivable that some sites, or certain areas of sites, might not be accessible to a vehicle the size of the SCAPS CPT truck. The access limits for the SCAPS CPT vehicle are similar to those for conventional drill rigs and heavy excavation equipment.

2.2.3.2 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 before undertaking activities at a site.

2.2.3.3 Response to Different Petroleum Hydrocarbons. The relative response of the downhole Nd:YAG SCAPS LIF sensor depends on the specific product being measured. The instrument's sensitivity to different hydrocarbon compounds can vary by as much as two orders of magnitude (Lieberman et al. 1992; Davey 1994a; Apitz et al. 1992a, Apitz et al. 1992b). These variations in sensitivity are primarily a reflection of the variations in the polycyclic aromatic hydrocarbon (PAH) distribution found within petroleum hydrocarbon products. Other contributing factors such as optical density, self absorption, and quenching are less important. As mentioned previously, the downhole Nd:YAG SCAPS LIF sensor responds to the aromatic constituents in petroleum hydrocarbon products (i.e., single ring aromatics (e.g., benzene, toluene, ethyl benzene and xylenes (BTEXs)) and multiple ring aromatics (e.g., PAHs)) that fluoresce when excited at 266 nm. Aliphatic species do not contribute to the downhole Nd:YAG SCAPS LIF signal.

Precisely identifying the source of the fluorescence signal in complicated mixtures of aromatic molecules as petroleum products may not be possible at this time. In addition to the complex nature of the original fuel product, the fluorescence properties of a hydrocarbon contaminant in soil 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, volatilization and solubilization. In terms of degradation and transport, the BTEXs and lighter PAHs tend to volatilize, solubilize and biodegrade first, leaving the heavier PAHs as time progresses. There is also evidence that the BTEX and lighter PAHs are more easily transported through the soil, so that as time progresses there will be a chromatographic effect due to the soil column that acts to separate the light and heavy compounds.

In both fresh and aged spills, the 266 nm excitation laser is expected to yield improved detection of light weight aromatic components. BTEX compounds are not excited by the excimer (308 nm) and nitrogen (337 nm) lasers. Naphthalene is only weakly excited by the excimer laser. Therefore, the 266 nm laser source should improve detection of the more soluble (e.g., more mobile) aromatics.

2.2.3.4 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 fraction of analyte that is optically accessible at the window of the probe contributes to the fluorescence signal. Of the four influencing factors mentioned above, the dominant variable appears to be soil surface area (Apitz et al. 1992a). LIF sensitivity to petroleum hydrocarbons on soil has been shown to be inversely proportional to the available surface area of the soil substrate (Apitz et al. 1992b). 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 (Apitz et al. 1992b). 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 clayey soils (Apitz et al. 1992a). 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 effect of soil grain size has 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.

2.2.3.5 Spectral Interferences. The downhole Nd:YAG SCAPS LIF sensor is sensitive to any material that fluoresces when excited with ultraviolet light. 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 non-hydrocarbon 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. De-icing agents, antifreeze additives, and many detergent products are all known to fluoresce strongly. The potential presence of fluorescence emission from non-target (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 non-hydrocarbon fluorescence can lead to false positives for the presence of hydrocarbons. Non-hydrocarbon 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 report of findings. Because the SCAPS LIF sensor collects full spectral information, however, experience has shown that it is almost always possible to discriminate between hydrocarbon and non-hydrocarbon fluorescence by analyzing the spectral features associated with the data.

The downhole Nd:YAG SCAPS LIF sensor system uses a multichannel detection scheme to capture a complete fluorescence emission spectrum at each point along the push. An advantage of this approach is that spectral features are obtained that can be used to associate the signal with a specific petroleum class, mineral substance, or other material. The spectral patterns collected in situ provide the means to distinguish hydrocarbon fluorescence from potential interferents. The SCAPS LIF's ability to recognize non-hydrocarbon fluorescence has been tested in several

laboratory experiments. In one study (Andrews and Lieberman 1994), the spectra of eight fluorescent minerals and five fluorescent chemicals were obtained with the LIF sensor. These spectra were compared with the LIF spectra obtained from multiple samples of jet fuel, gasoline, diesel fuel, and lube oil. In all cases, both computer algorithm and human analysts could easily recognize the hydrocarbon spectra as being different from the non-hydrocarbon spectra. The specific substances used in the experiment were chosen because they fluoresced in the same spectral region as the fuel products. Many other fluorescent chemicals and minerals fluoresce in a spectral region far removed from the hydrocarbon spectra. The materials used included:

Calcium Carbonate	Resinous coal	Tide surfactant
Norbergite	Aragonite	Prestone antifreeze
Fluorite	Fossil Algae	Simple Green detergent
Scapolite	Turritella agate	Quinine sulfate

In addition, the organic component of some soils contains humus. This naturally occurring residue of plant decay often contains some small amount of fluorescent PAHs. Laboratory tests (Davey et al. 1994b) have demonstrated that humics do not interfere with SCAPS LIF detection of hydrocarbon on soil. This is because humic fluorescence is minimal at concentrations found in even the most organic-rich soils.

2.3 Factors Influencing Cost and Performance

As with any analytical instrument the cost for a site investigation is dependent upon the number of samples analyzed. For the LIF/CPT method this represents the number of data points collected. The number of data points collected is a function of the number of pushes and the depth per push. As previously detailed, depth resolution of data points is 3 to 6 cm. Thus the major factor influencing cost at a site is the size of the site. For the SCAPS system, cost is quoted on a per day basis assuming a specified production rate, and includes all facets of operation: field crew labor; permits, plans and data reporting; transit time to and from site, and the SCAPS LIF/CPT truck.

A number of site and system factors affect performance. Penetrometer limitations prevent use in hilly terrain and in some soils, such as conglomerate with cobbles and boulders or cemented material. The contaminant product type and degree of weathering as well as matrix effects impact system sensitivity. If present, non- POL fluorescent materials can interfere with system performance providing false positive results or reduced sensitivity. System factors impacting

performance include system alignment and fiber length. Coupling efficiency due to alignment and attenuation over the fiber length influence the amount of emission energy delivered to the detector.

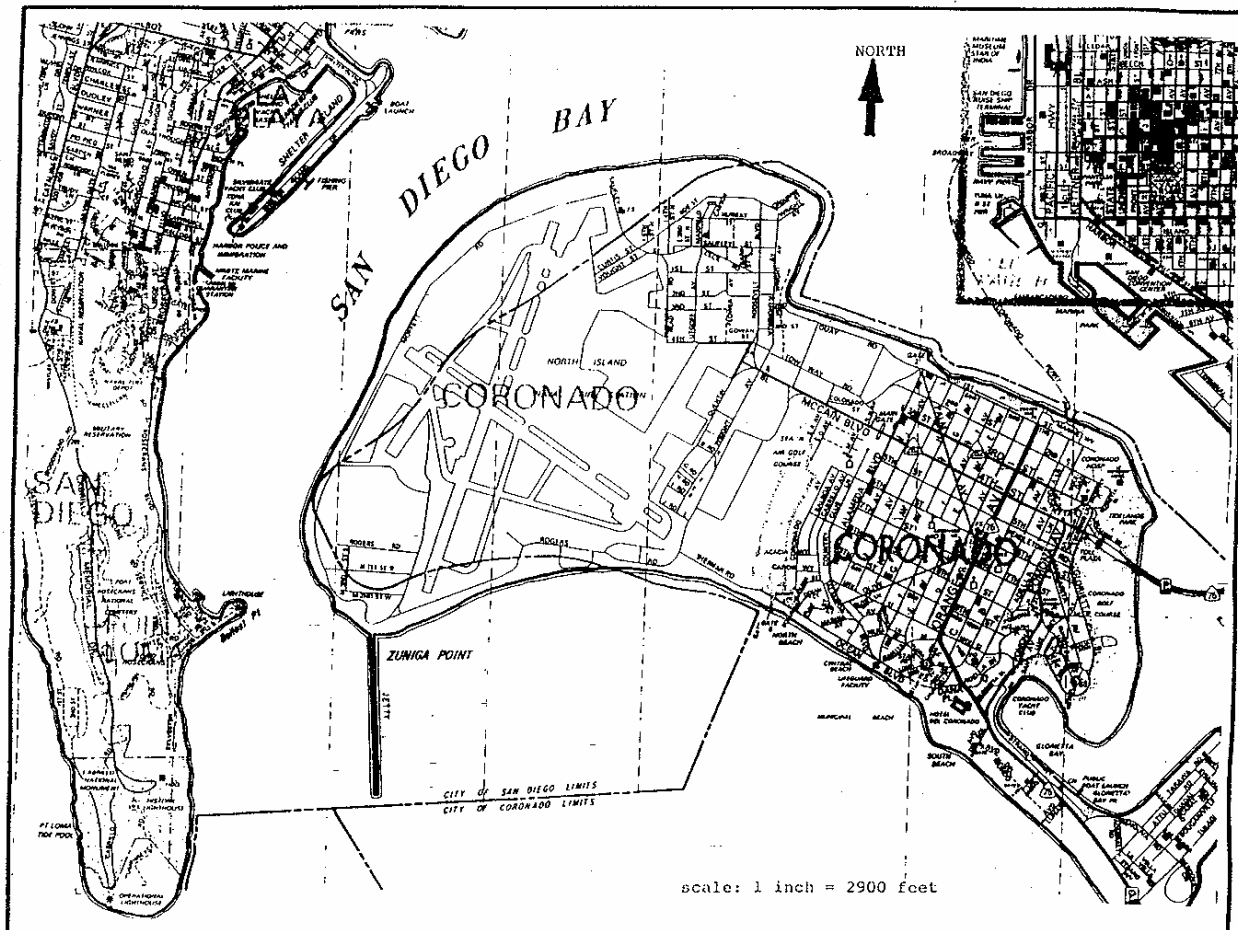
3. Site/Facility Description

3.1 Background

The objective of the downhole Nd:YAG SCAPS LIF technology's demonstration was to generate field data appropriate for verifying the performance of the technology, and thereby facilitate the technology's acceptance and use by the regulator and user communities for field screening of petroleum hydrocarbons in the subsurface. The two sites selected under this project were the North Island Fuel Farm site at Naval Air Station (NAS), San Diego, CA, and at the Naval Exchange (NEX) service station at the Hydrocarbon National Test Site at Naval Construction Battalion Center (NCBC), Port Hueneme, CA.

3.2 Site/Facility Characteristics

3.2.1 North Island Fuel Farm Site at Naval Air Station San Diego. NAS San Diego is located on the northern portion of Coronado Island, a peninsula extending into the San Diego Bay, in San Diego County, California. The general location of North Island is depicted in Figure 3. The



portions of the base, which includes the North Island Fuel Farm, are underlain by artificial fill soils derived from the dredging of San Diego Bay. The eastern portion of the base is underlain by artificial fill which was deposited during the filling of the Spanish Bight. The Southern shoreline of the base is underlain by beach deposits.

The elevation of the base ranges from sea level at the periphery of the majority of the base to approximately 38 feet above mean sea level (msl) in the central portion of the base. At the North Island Fuel Farm groundwater exists at a depth of approximately 15 feet below ground surface and is reported by Southwest Division to be subject to minor fluctuations in elevation as a result of tidal forces.

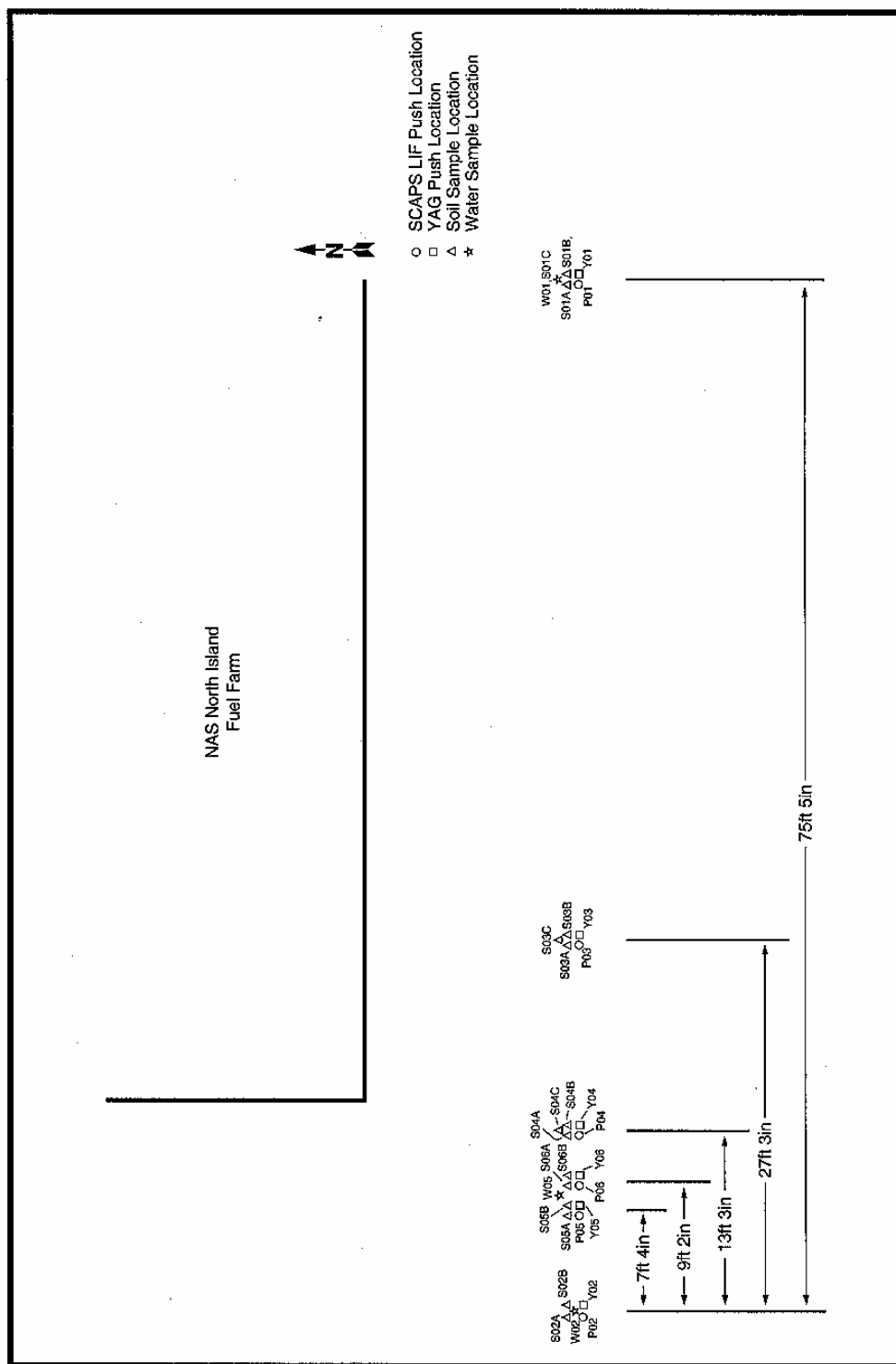


Figure 4. NAS San Diego, CA Site Map.

The North Island Fuel Farm at NAS San Diego stores fuel in concrete and steel underground storage tanks (USTs) and in steel above ground storage tanks. Numerous underground utilities are present at the North Island Fuel Farm, including product distribution, electrical, water, telephone and sewer lines. Previous investigations have indicated that petroleum hydrocarbons, including JP-5 and diesel fuel marine (DFM), are present in the vadose zone and as light non-aqueous phase liquid (LNAPL) or free product. The site map is shown in Figure 4.

3.2.2 Naval Exchange (NEX) Service Station at NCBC Port Hueneme. NCBC Port Hueneme is located in Ventura County, California, about 45 miles northwest of Los Angeles County. Established in 1942 to meet World War II military requirements, NCBC covers 1,647 acres of coastal land situated 5 miles northwest of the Santa Monica Mountains in Southern California. The approximate location of NCBC Port Hueneme is shown in Figure 5. NCBC Port Hueneme is an active naval facility where remedial investigation/feasibility studies under the Navy's Installation Restoration Program (IRP) are currently in progress. NCBC Port Hueneme has been identified as the Hydrocarbon National Test Site of the Strategic Environmental Research and Development Program, and the NEX Service Station as one specific innovative remedial demonstration area. The NEX Service Station is located at the southeast corner of Dodson Street and 23rd Avenue. The map for this site including LIF and soil CPT push locations is depicted in Figure 6.

NCBC Port Hueneme lies in the western portion of the Ventura Basin within the Transverse Ranges geomorphic province. Rocks of the Transverse Ranges have been deformed by regional strike-slip and thrust faulting, resulting in highlands and basins, and folding that trends east to west. The Ventura Basin is the most prominent of the basins. The Oxnard Plain represents the present topographic surface of deposition with the Ventura Basin. NCBC is on the western margin of the Oxnard Plain. The topography at NCBC is generally flat, sloping gently from about 5 and 10 feet above msl in the western and southern portions of the installation, respectively. The average surface elevation across the installation is about 10 feet msl.

NCBC is underlain by about 300 feet of unconsolidated clay, silt, sand, and gravel of Holocene age that overlie clay, shale, and sandstone of Pleistocene and older ages. The understanding of near-surface geology in the vicinity of NCBC is based on information derived from soil borings drilled during previous investigations at the installation. The geology within 30 feet of the

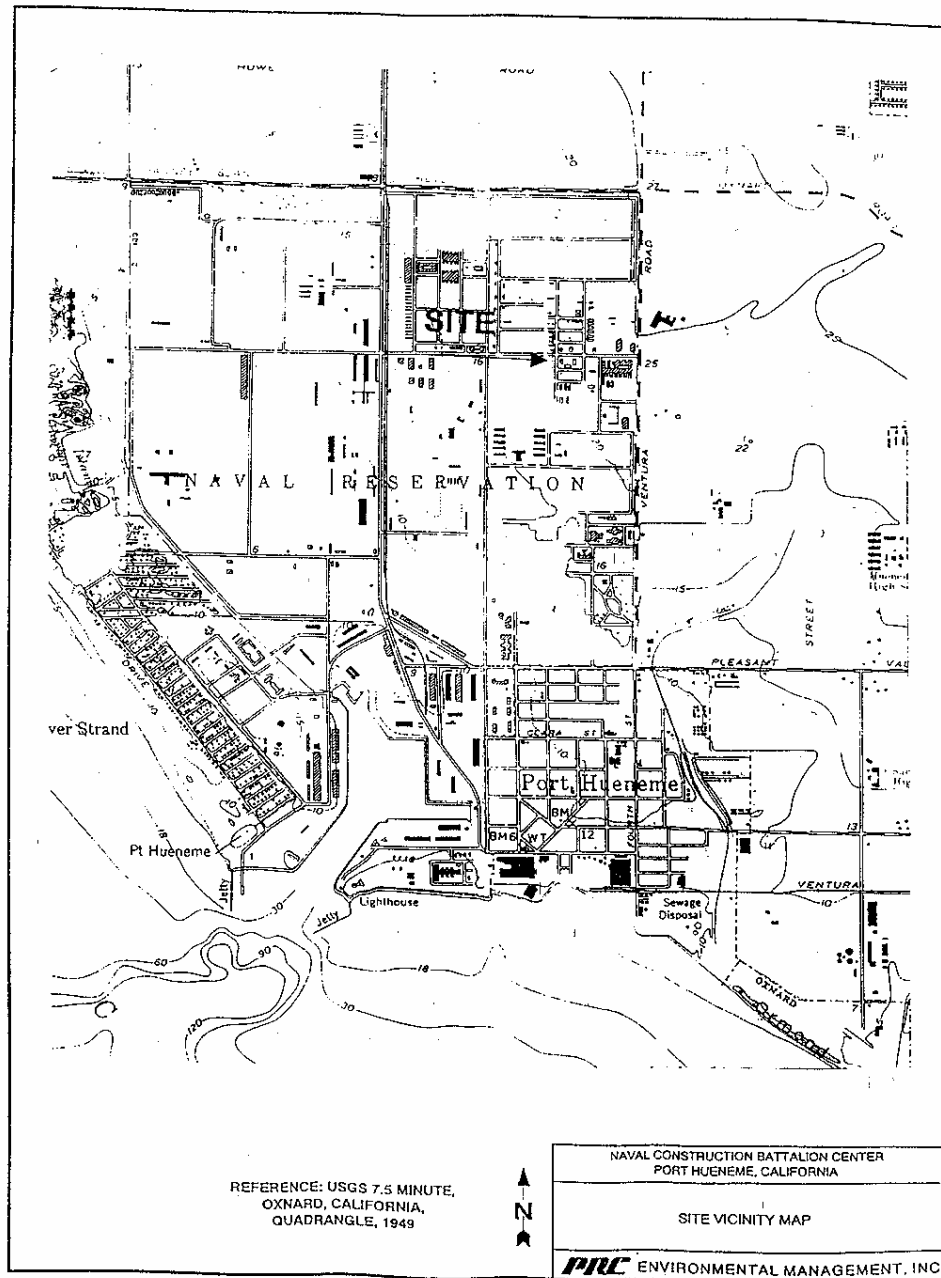
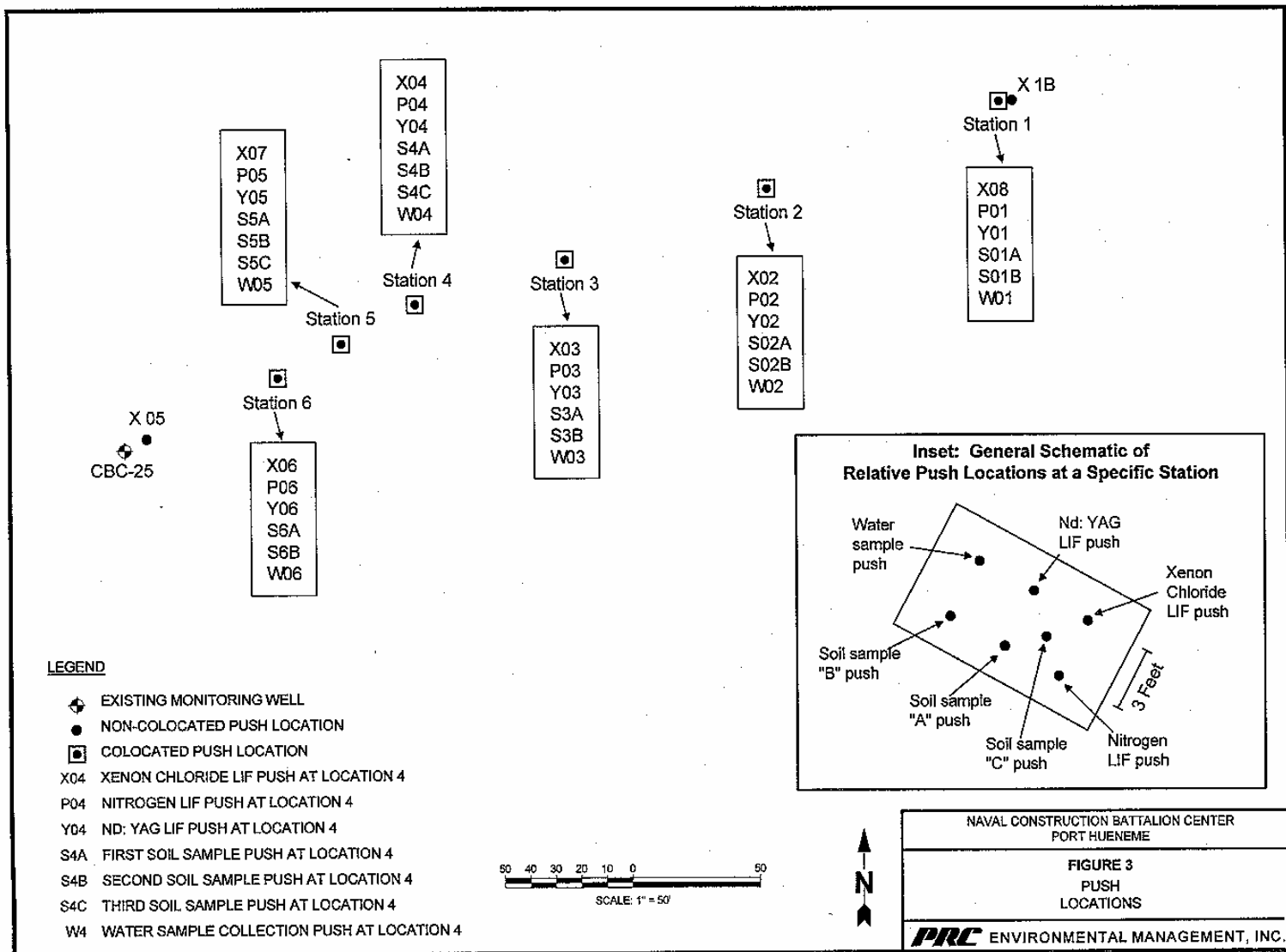


Figure 5. NCBC Port Hueneme, CA Location Map

Figure 6. NEX Service Station at NCBC Port Hueneeme, CA Site Map.



surface consists of consolidated sands, silts, and clays with minor amounts of gravel and fill material. The unconsolidated deposits are typically represented by three units: an upper fine-grained, silty sand unit, encountered from the ground surface to a maximum depth of 5 feet; an intermediate fine- to coarse-grained sand unit; and an underlying sandy to silty clay unit. Groundwater beneath NCBC is encountered at about sea level.

The NCBC Port Hueneme NEX Service Station contains two active gasoline USTs. Previous investigations of the site have recorded elevated concentrations of total petroleum hydrocarbons and BTEXs in soil and groundwater samples from the gasoline hydrocarbon plume at the site. Previous remedial strategies for the site have included the installation and operation of a groundwater pump-and-treat system and a soil vapor extraction system. Although neither system is currently active, both are scheduled to be retrofitted to aid in a proposed bioventing air sparging remediation system.

4. Demonstration Approach

4.1 Performance Objectives

The method provides semi-quantitative data on the in situ distribution of POL products from the fluorescence response induced in the monocyclic (e.g., benzene, toluene, ethyl benzene, and xylenes) and polycyclic aromatic hydrocarbon compounds that are components of POL products. Specific claims for the downhole Nd:YAG SCAPS LIF sensor are:

1. Near continuous measurements generated by the sensor provide detailed mapping of the distribution of subsurface petroleum contamination. At standard push rates of 1 meter/minute, fluorescence data is typically collected at intervals of at a minimum every 0.2 feet.
2. The distribution of contamination provided by the LIF push data shows good qualitative agreement with the pattern of contamination derived from analytical measurements (DHS Method 8015-Modified and EPA Method 8021A-Modified) of semicontinuous soil samples and agrees well with the corresponding nitrogen LIF data.

3. Direct comparisons of sensor data with samples collected using a CPT stab soil sampler by pushing in very close proximity to the push hole, using the "detect/non-detect" criteria, show good agreement with a conventional laboratory method (DHS Method 8015-Modified). Historically, agreement between the nitrogen laser-based LIF sensor and the analytic soil measurements has exceeded 80 percent, and the correlation for this demonstration is similarly expected to exceed 80 percent, a commonly accepted criteria for successful field screening of subsurface contaminants.
4. The downhole Nd:YAG SCAPS LIF sensor uses a detector system comprised of a spectrograph coupled to a linear photodiode array detector to collect the spectral signature of the induced fluorescence emission response. The entire fluorescence spectrum is collected and stored throughout the push.
5. Qualitative use of spectral data provides a means of distinguishing different classes of hydrocarbon products, and can also be used to minimize potential false positives from non-POL fluorophores. Different contaminants often have a different BTEX and PAH distribution, resulting in a distinctive fluorescence spectrum for each class of contaminants. When dissimilar spectra are encountered during a site characterization, this can be indicative of more than one contaminant. Differences in spectral signatures can also be used to discriminate non-hydrocarbon fluorophores present in the soil.
6. Data from the downhole Nd:YAG LIF sensor is available in real time as the sensor is advanced into the ground. This allows real time decisions on how deep to sample the site.
7. The location of future pushes can also be decided in real time at the site using the information available from all previous pushes. This can greatly speed location of the edge of the contamination plume.
8. The downhole Nd:YAG LIF method can detect the presence of hydrocarbons in the bulk soil matrix throughout the vadose, capillary fringe and saturated zones.
9. Measurements can be made to depths up to 150 feet, when the downhole Nd:YAG LIF sensor is used in conjunction with an industry-standard 20 ton penetrometer push vehicle.

10. Geotechnical sensors (cone pressure, sleeve friction) are integrated with the downhole Nd:YAG LIF sensor to provide simultaneous continuous geotechnical and stratigraphic information to aide in interpreting contaminant distributions.
11. The in situ nature of the downhole Nd:YAG LIF sensor minimizes possibilities for contaminating or altering soil samples that are inherent with traditional collection, transport and analysis procedures.
12. The downhole Nd:YAG LIF sensor provides more accurate measurement of the depth of the contaminant, especially for sites where the contaminant is found in the saturated zone (which is often where BTEX is found), because the downhole Nd:YAG LIF sensor does not suffer from the sampling difficulties encountered by other common methods such as soil boring/split spoon sampling and stab sampling. During typical operations, the uncertainty in depth with the SCAPS LIF sensor is approximately 7.5 cm.
13. The LIF sensor produces minimal IDW. A typical 6 meter push with the SCAPS LIF sensor produces approximately 40 liters of water IDW (used to clean the push rods). A typical 6 meter boring produces 210-285 liters of soil IDW as well as 40 liters of water used to clean the augers. Furthermore, the penetrometer rods are steam cleaned directly upon removal from the ground, reducing potential contamination hazards to site personnel.

4.2 Physical Setup and Operation

The SCAPS truck mounted CPT platform is a stand-alone, roll-on, roll-off unit requiring no outside utilities during operation. No special structures, either temporary or permanent are required for operation. All power is supplied from a generator operated off the truck diesel motor and is regulated through an uninterruptable power supply with a bank of batteries. An external electrical power input is also available. An hydraulic system, integrated into the truck, provides the force to insert the probe into the ground and also powers the grout pump. Water, from onboard tanks, is consumed in the steam cleaning system and during grouting. A local source of water is required for refilling the onboard tanks. Another consumable is grout. These items may be acquired locally or carried along in the SCAPS support vehicles. Steam cleaning rinsate water is collected in DOT rated 208 liters (55 gallon) drums and handled as potentially hazardous waste. Operations yield approximately half a drum of rinsate waste a day. Wastewater disposal is

coordinated with the responsible party for the site and handled locally after results of sampling are obtained.

4.3 Sampling Procedures

To assess the comparability of the data acquired by the downhole Nd:YAG LIF technology to data generated by established, conventional analytical methods, as well as nitrogen LIF data, downhole Nd:YAG SCAPS in situ fluorescence data were compared to analysis results of sampled soil. A series of pushes and comparison borings were advanced. Sets of co-located pushes (one downhole Nd:YAG SCAPS LIF push, one nitrogen SCAPS LIF push, and one CPT stab sampling push) were performed both within and outside of the plume area. Soil samples were obtained using the CPT stab-sampling probe and were included as a push in each set of pushes.

During the demonstration sampling, the SCAPS CPT pushed the downhole Nd:YAG SCAPS LIF probe and acquired the corresponding data. After the probe was pushed to the desired depth, the probe was retracted. The SCAPS CPT rig then moved approximately 20 cm away from the push and a second push using the nitrogen SCAPS LIF system was advanced. Following the nitrogen SCAPS LIF push, the SCAPS CPT was positioned approximately at the center of the 20-cm (8-inch) wide area between the two holes and a third push using the CPT stab sampling probe using 6.6-inch long, 1.5-inch diameter, hollow stainless steel tubes was advanced. The sampler was pushed using the SCAPS CPT, in accordance with the ASTM D3441, the standard for CPT.

The Mostap 35PS sampler is an approximately 34-inch long, 2-inch diameter steel penetrometer tip, which includes a 21-inch long sample barrel containing three 6.6-inch long stainless steel soil sampling tubes.

Soil samples were collected at depths of interest determined from review of the fluorescence profile data. Only tubes containing sample soils that appeared relatively undisturbed were used. Samples for confirmatory analysis were collected from the lower and middle (deeper) 6.6-inch soil tubes in the 21-inch sampler. The sample was teflon-sealed, capped, taped, labeled, logged, and placed into a chilled ice chest. Each confirmatory sample was analyzed by DHS Method 8015-Modified (TPH) and EPA Method 8021A-Modified. After chemical analysis was completed at Ceimic laboratory (San Diego, CA) the soil samples were returned to SSC San Diego for further analysis by LIF techniques.

Samples for geotechnical analysis were sealed and shipped to the Law/Crandall laboratory (San Diego, CA) in the stainless steel tubes retrieved from the split spoon sampler. Those samples chosen for geotechnical analysis were generally the uppermost (shallowest) tube of the three from the split spoon sampler, but only when the tube appeared full as a result of complete sample recovery by the split spoon sampler.

4.4 Analytical Procedures

DHS Method 8015-Modified for TPH and EPA Method 8021A-Modified for BTEX and methyl tertbutyl ether (MTBE) were selected as the confirmatory analytical methods for the downhole Nd:YAG LIF technology. The TPH method was chosen because of its widespread and generally accepted use in delineating the extent of petroleum hydrocarbon contamination. The TPH method is currently used as an indicator of petroleum contamination. The TPH method determines aromatic hydrocarbons in the C6 to C40 range. It is the most comparable analytical method corresponding to the objective of demonstrating rapid field screening using the downhole Nd:YAG LIF. The EPA Method 8021A-Modified was chosen because of its widespread and generally accepted use in determining the presence of BTEX and MTBE in petroleum hydrocarbon contamination. It is important to note that these analytical methods do not measure exactly the same constituents that are targeted by the downhole Nd:YAG LIF POL sensor but were selected because they represent the technology that is currently being used on a day-to-day basis to make decisions about the distribution of subsurface POL contamination.

Method 8015 modified (TPH) utilizes a gas chromatograph coupled with a flame ionization detector (GC/FID) to separate the components of the contaminant by molecular weight. The hydrocarbon extract is mixed with a surrogate internal standard (SIS) for quality control, and a quantitative internal standard (QIS) for quantification. The chromatogram produced by this analysis covers the carbon range from C7 through C36 and can help to identify the product type ("fingerprint") (Douglas et al, 1992) using the n-alkane pattern distribution, pristane and phytane ratios, and the width of the unresolved complex mixture.

The EPA 8021A-Modified method employs a purge and trap technique in which an inert gas is bubbled through either the contaminant extract of the soil or the contaminated water sample. Then the volatiles obtained by purging and trapping are passed through a gas chromatograph with a photoionization detector and an electrolytic conductivity detector in series to measure the contaminant according to the retention time of the constituents, ionization potential differences of

the constituents and differential conductivity differences of the constituents. The measurement of this volatilized sample is compared to similar measurements of standard solutions containing BTEXs and MTBE, as well as soil samples spiked with BTEX and MTBE standards, in order to quantify the contaminants.

It is recognized that Methods 8015 and 8021A are subject to systematic biases related to the composition of the POL contamination and therefore it is anticipated that there will be some deviations between results from the sensor and the different methods.

One of the main difficulties in comparing the methods results from uncertainty in establishing the depth from which the soil sample was obtained. Due to the sharp vertical boundaries of the contamination plume, an error of 6 inches in the sample depth can change from strongly impacted (greater than 10,000 ppm) to clean (less than 100 ppm). For this reason, after chemical analysis was completed at Ceimic laboratory (San Diego, CA), the soil samples were returned to SSC San Diego and further analyzed by LIF techniques using the 266nm Nd:YAG laser, the nitrogen laser and the excimer laser.

5. Performance Assessment

5.1 Performance Data

Data reports have been completed for North Island Fuel Farm at NAS San Diego, California and NEX Service Station at NCBC Port Hueneme, California. The reports compile all raw data, laboratory results, and notes and observations from field operations and laboratory analyses. Copies of these reports can be obtained from Dr. S. Lieberman at the address listed in Appendix A.

5.1.1 North Island Fuel Farm at NAS San Diego, California. Three sets of co-located investigations; SCAPS downhole Nd:YAG LIF push, SCAPS nitrogen LIF push, and the Mostap 35PS stab sampler CPT push, were advanced during validation operations at NAS San Diego North Island Fuel Farm on November 12-15, 1996. Thirty-seven discrete soil samples were collected and analyzed by traditional methods as part of the validation effort. SCAPS soil classification and field observations of stab sampler collected soils coincided as sands. The

locations of these pushes are shown in Figure 4. The nitrogen LIF pushes are designated by P0#, the downhole Nd:YAG pushes by Y0#, and soil samples by S0#. A photograph of the site with the push locations marked with cones is shown in Figure 7. The plume boundary was delineated to within less than 2 feet (the location is marked by the tall two cones that mark the position of pushes 5 and 6). The leaking underground tank is located behind the fence shown in the photograph.



Figure 7. Photograph of NAS North Island site with push locations marked with cones. Push 2 is closest to the camera. The plume boundary was localized between the two pushes marked with tall cones.

In general, comparisons of the nitrogen and downhole Nd:YAG LIF data illustrated in Figures 8 and 9 correlate very well. The contaminant plume occurs between 12 and 14 feet below ground surface (bgs) and is greatest at push location 1 diminishing as the cross section moves away from push 1 to push 3, 4, and 6. Pushes 5 and 2 were found by both LIF sensors to be clean. The laboratory TPH results versus fluorescence show that laboratory results for TPH track patterns observed for in situ fluorescence data quite well. Figures 10 and 11 depict the in situ depth logs for the SCAPS LIF with TPH values portrayed as a bar graph opposite the LIF data at the appropriate depth. In a couple of instances the stab sampler was pushed again in close proximity to its first push and soil samples at the same depths were obtained and are shown in open and closed bars at the same depths. From this data reproducibility can be assessed.

Due to some variability in the data and to verify sample depth, all of the soil samples were reevaluated at SSC San Diego as single point tests using both the nitrogen and 266nm Nd:YAG lasers. This data is illustrated as bars opposite the TPH data in Figures 12 and 13. Unlike previous SCAPS LIF validation efforts, the soil samples were not homogenized prior to evaluation for TPH (because of concern about loss of volatiles). As a result, soil sample used for TPH and the single point tests were collected at depths that were slightly offset from the in situ data. This is not as important in clean and heavily impacted regions of the plume. However this unavoidable artifact of the sample collection procedure may affect correlations in regions of strong gradients (e.g., near the upper and lower surfaces of the plume as well as the leading edge of the plume). And these are the regions of the plume that are of most interest in evaluating the 266 nm downhole Nd:YAG laser source. Even so, as can be seen in Figures 12 and 13, contaminant distributions as indicated by laboratory data and fluorescence data track reasonably well. The only discrepancies occur at the plume edges where the presence of the contaminant changes rapidly with slight changes in depth. Push P02, which exhibited background fluorescence response, showed TPH values of less than 25 ppm while P01 exhibited elevated fluorescence and TPH concentrations as high as 130,000 ppm. TPH chromatograms confirmed a JP-5 contaminant and were quantified as such.

Additionally, the soil samples were evaluated for BTEX using EPA Method 8021A-Modified and for volatile organic compounds using a gas chromatogram/mass spectrometer method, EPA Method 8260. These data are illustrated in Figures 14a-15b. These results correspond to the previous findings indicative of a plume between 12 and 14 feet bgs most heavily impacted at push 1 and diminishing to the west.

Similar to the nitrogen laser-based SCAPS LIF systems, the 266nm Nd:YAG LIF sensor collected spectral emission data at every depth that measurements were made. The spectral data obtained during the downhole 266 nm Nd:YAG pushes was evaluated to determine if the anticipated increase in detection capability for light weight aromatic compounds, over the previously demonstrated nitrogen laser-based SCAPS LIF system, was realized. As previously discussed, the 266 nm excitation laser is expected to provide improved detection capability for the light weight, more mobile, more easily degraded single ring aromatic compounds (i.e., BTEX compounds).

Figures 16-19 show the spectra resulting from Pushes Y01, Y03, Y04 and Y06, respectively. The data are normalized at 425 nm in order to compare spectral shape at the lower emission wavelengths. These results are discussed in greater detail in the paper included in Appendix C entitled "In-situ Monitoring of LNAPL Degradation using the SCAPS Optical Cone Penetrometer System." It was published in the Proceedings of the Fifth International Symposium on Field Analytical Methods for Hazardous Wastes and Toxic Chemicals (Knowles et al., 1997).

The spectral data shows that the short wavelength emission observed at 350 nm in Pushes 1 and 3 is greatly reduced in Push 4, and absent in Push 6 as one move away from the source zone towards the edge of the plume. These observed spectral shifts are consistent with the idea that there is a loss of more volatile, more easily degraded, lighter weight aromatic compounds moving away from the source zone. This loss of light weight aromatics as the plume moves away from the source is substantiated by the 8021A and 8260 data shown previously in Figures 14a-15b.

5.1.2 NEX Service Station at NCBC Port Hueneme, California. Validation field operations and technology demonstration at NCBC Port Hueneme NEX Service Station were carried out 17-21 March, 1997. This site is an active petroleum dispensing facility and has had documented releases of gasoline into the subsurface. A vicinity map was shown in Figure 5. Six SCAPS nitrogen laser LIF pushes, six downhole Nd:YAG LIF pushes, and fourteen SCAPS CPT stab sample push holes were completed. Additionally, at the Port Hueneme Service Station site, eight SCAPS xenon chloride LIF pushes were completed. A total of twenty three soil samples were collected; one each from holes S2B, S3B, S4A, S4B, S4C, S5A, S5B, and S5C, two from stab sample holes S1B, S3A, S6A and S6B, three from stab sample hole S1A and four samples from

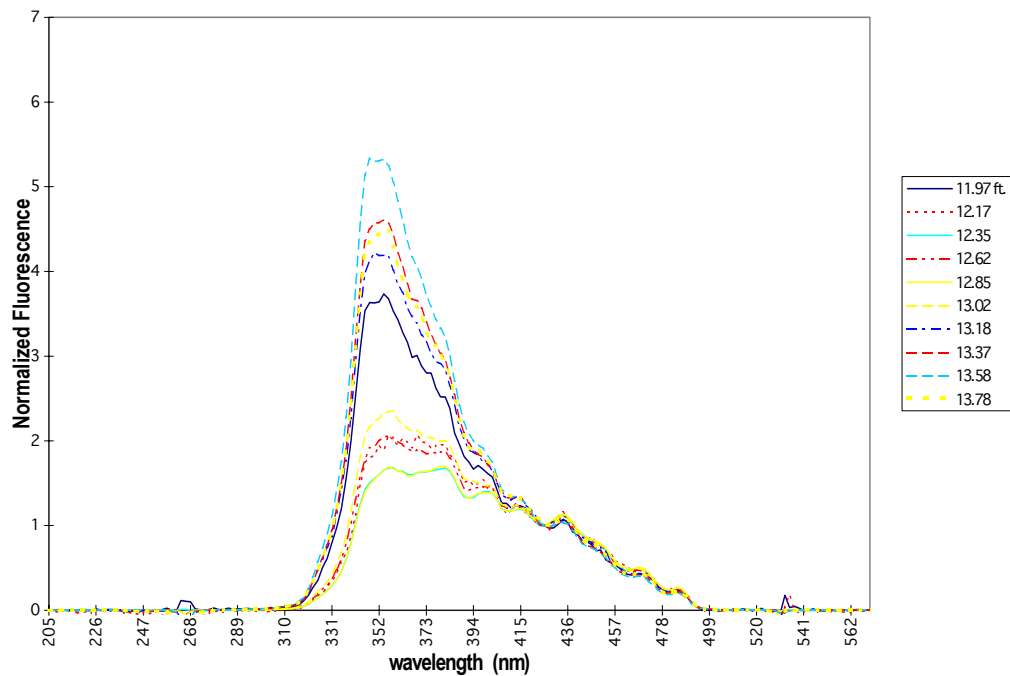


Figure 16. Normalized Spectra from North Island Fuel Farm Push Y01

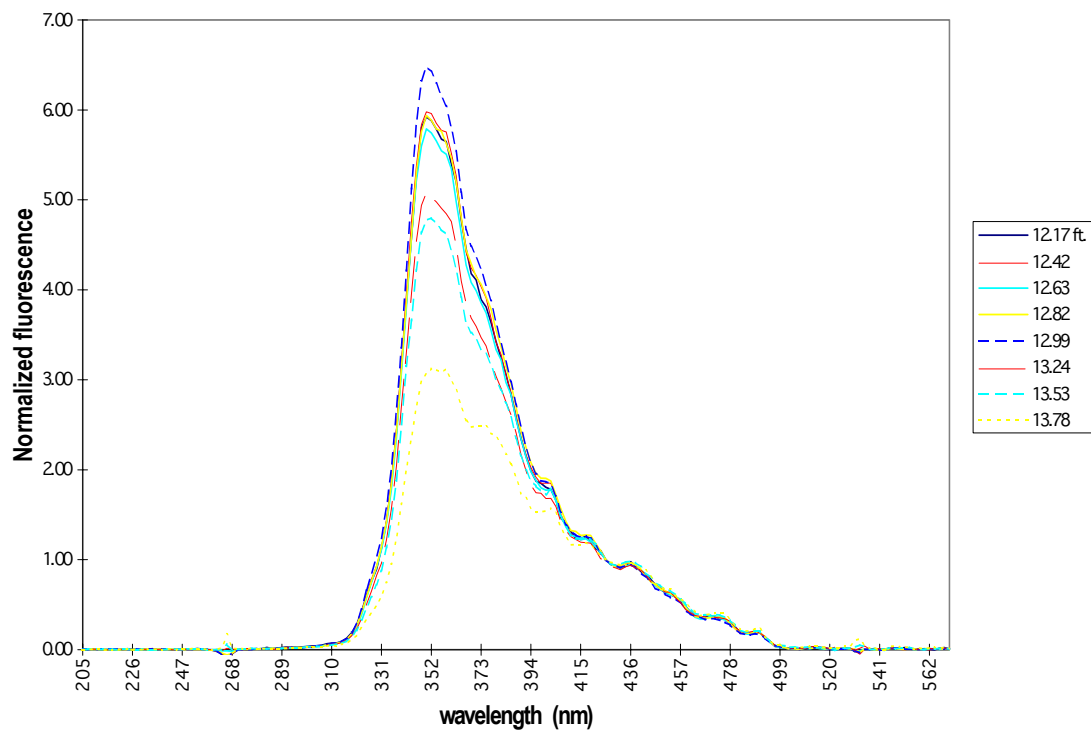


Figure 17. Normalized Spectra from North Island Fuel Farm Push Y03

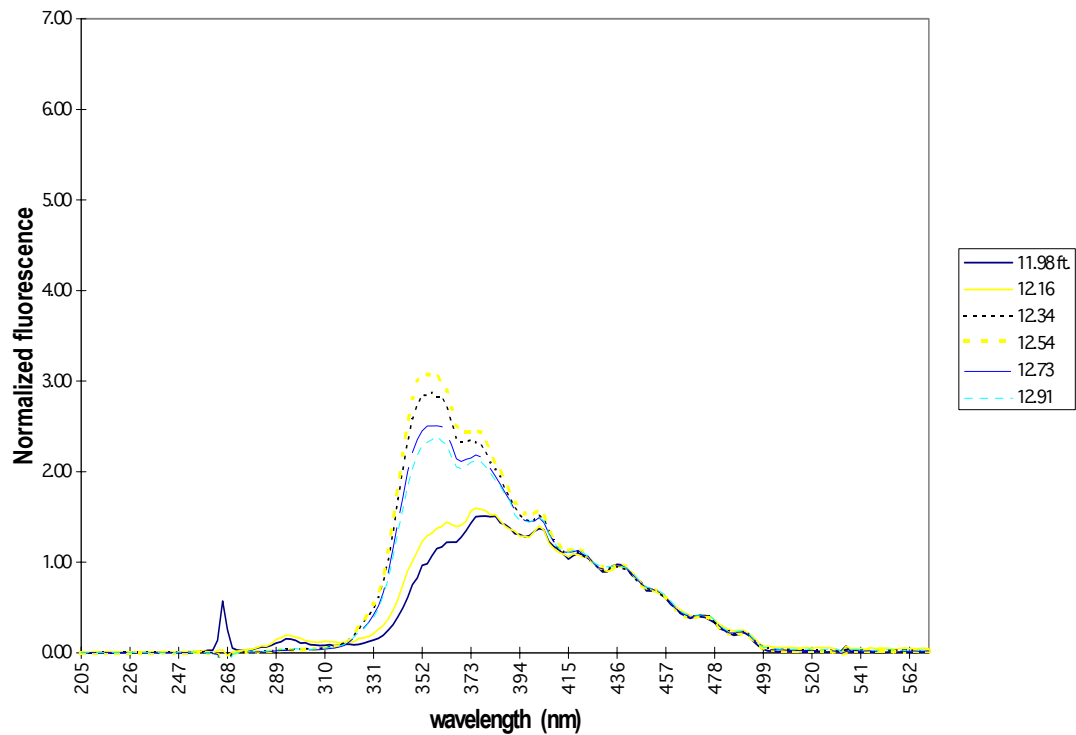


Figure 18. Normalized Spectra from North Island Fuel Farm Push Y04

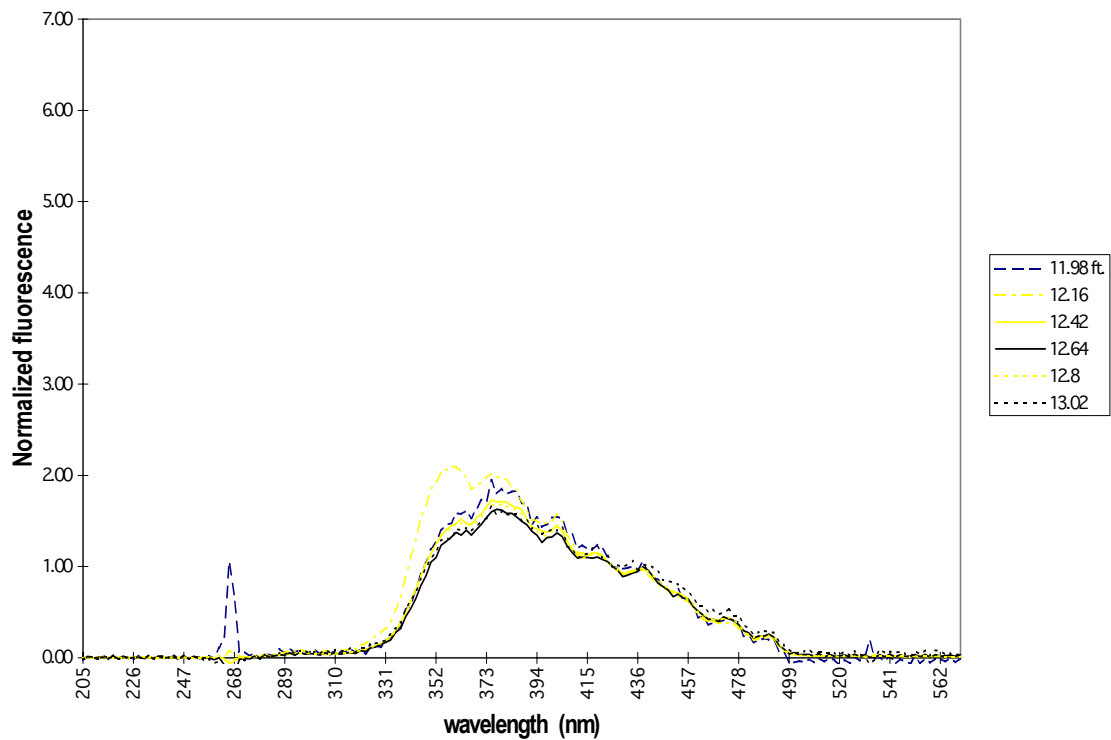


Figure 19. Normalized Spectra from North Island Fuel Farm Push Y06

hole S2A. Six investigative points consisted of a SCAPS nitrogen LIF push, a SCAPS xenon chloride LIF push, a SCAPS downhole Nd:YAG LIF push, and a SCAPS stab soil sample push. These push locations are illustrated in Figure 6. A photograph of the site with push locations marked with cones is shown in Figure 20.



Figure 20. Photograph of NEX Service Station site at NCBC Pt. Hueneme, California. Cones mark the position of push locations 1 through 5. Push 5 is closest to the camera, push 1 is closest to the truck. The source of the leak was the NEX Service Station which is located behind the truck in the picture.

Some difficulties were encountered during this part of the demonstration. The SCAPS software had the distance from the probe tip to the sapphire window set so that it could not be altered. However, all three different LIF probe window locations were different from that in the software. The nitrogen and excimer LIF probes' actual window position was 0.5 feet further from the probe tip, while the downhole Nd:YAG LIF probe's actual window position was 0.2 feet closer to the probe tip. Thus, the recorded and actual probe depths are not the same. In addition, as described earlier, unlike previous SCAPS LIF validation efforts, the soil samples were not homogenized prior to chemical (TPH and BTEX) and laboratory LIF evaluation. Every soil sample tested in the laboratories came from slightly different depths. Again, this is most important at the upper and lower surfaces of the plume as well as the leading edges where the presence of the contaminant changes rapidly with slight changes in depth. These are the regions of greatest interest for evaluation of the downhole 226 nm Nd:YAG LIF sensor.

The in situ LIF fluorescence at depth plots are illustrated in Figures 21-23 for the nitrogen LIF, excimer LIF and downhole Nd:YAG LIF, respectively. In general, the data correlates well. The contaminant plume is found between 9 and 12 feet bgs. Fluorescence was greatest at push locations 1 and 3 and decreased to the southeast. This corresponds well with the TPH results which range from 11,000 ppm and 16,000 ppm for pushes 1 and 3, respectively, to less than 20 ppm for push 6. See Figure 24. In every case, for all LIF data as well as chemical data, push 2 which is between pushes 1 and 3 has low values. The analytical chromatograms are consistent with a gasoline/diesel contaminant product type, thus TPH is quantified as gasoline/diesel (C7-C30).

Additionally, the strain gauges in the downhole Nd:YAG LIF probe did not work properly and soil classification profiles could not be gathered during those pushes. This data was collected during the nitrogen and excimer LIF pushes. Soils consisted of clays, sands, and admixtures of clay and sand, which coincided generally with the SCAPS real-time profile classification.

In order to determine if there was spectral evidence of loss and/or degradation of light weight aromatic compounds, as was seen at the North Island test site, a ratio of the fluorescence emission at 353 nm and 425nm was plotted in Figure 25. The ratio of short to long wavelength emission decreases moving towards the plume boundaries. Again, this is consistent with the hypothesis that there is a loss of lightweight aromatics moving away from the source zone.

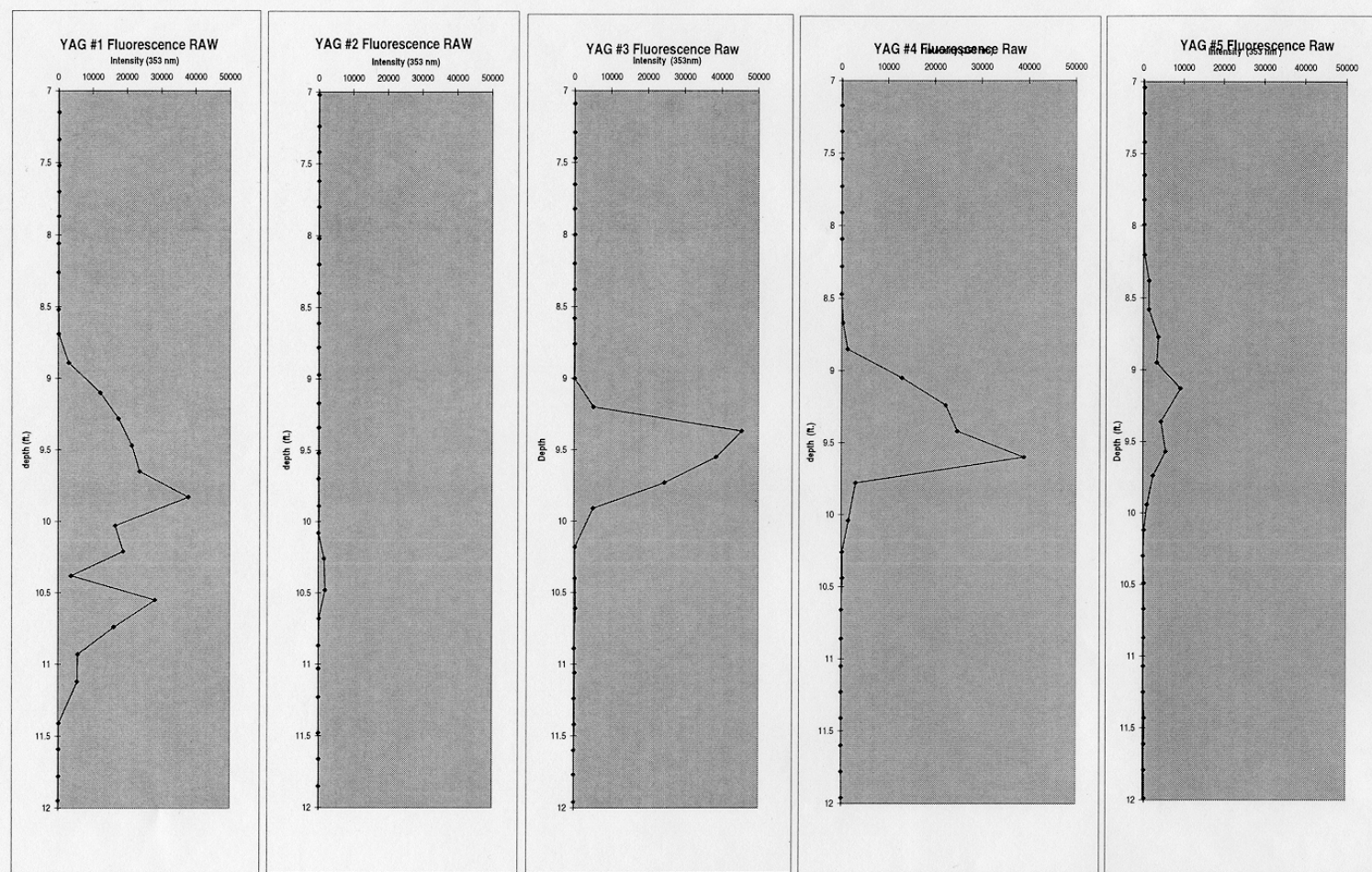


Figure 23. In Situ Downhole Nd:YAG LIF Data for Port Hueneme Service Station

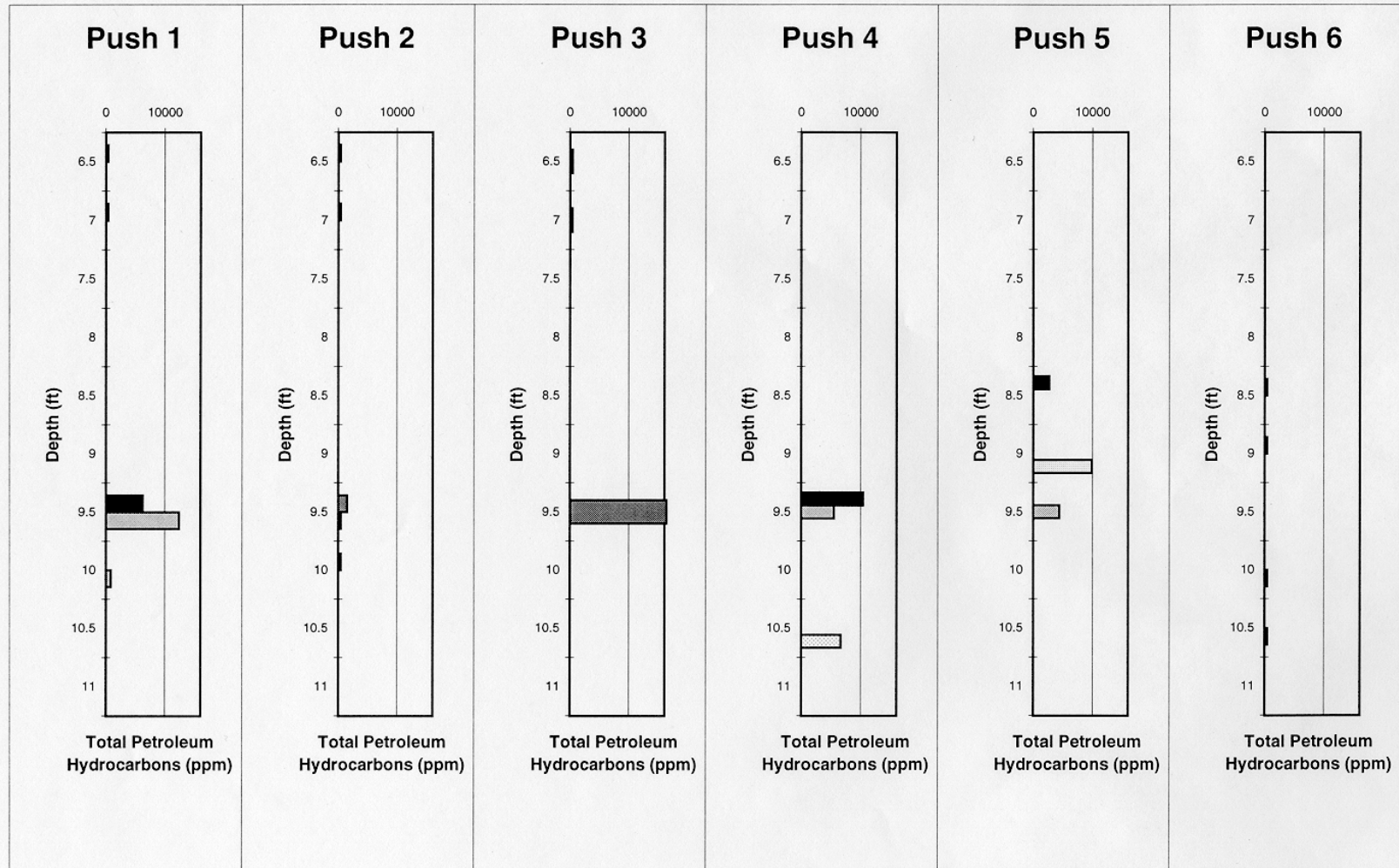


Figure 24. Total Petroleum Hydrocarbons for Port Hueneme Service Station

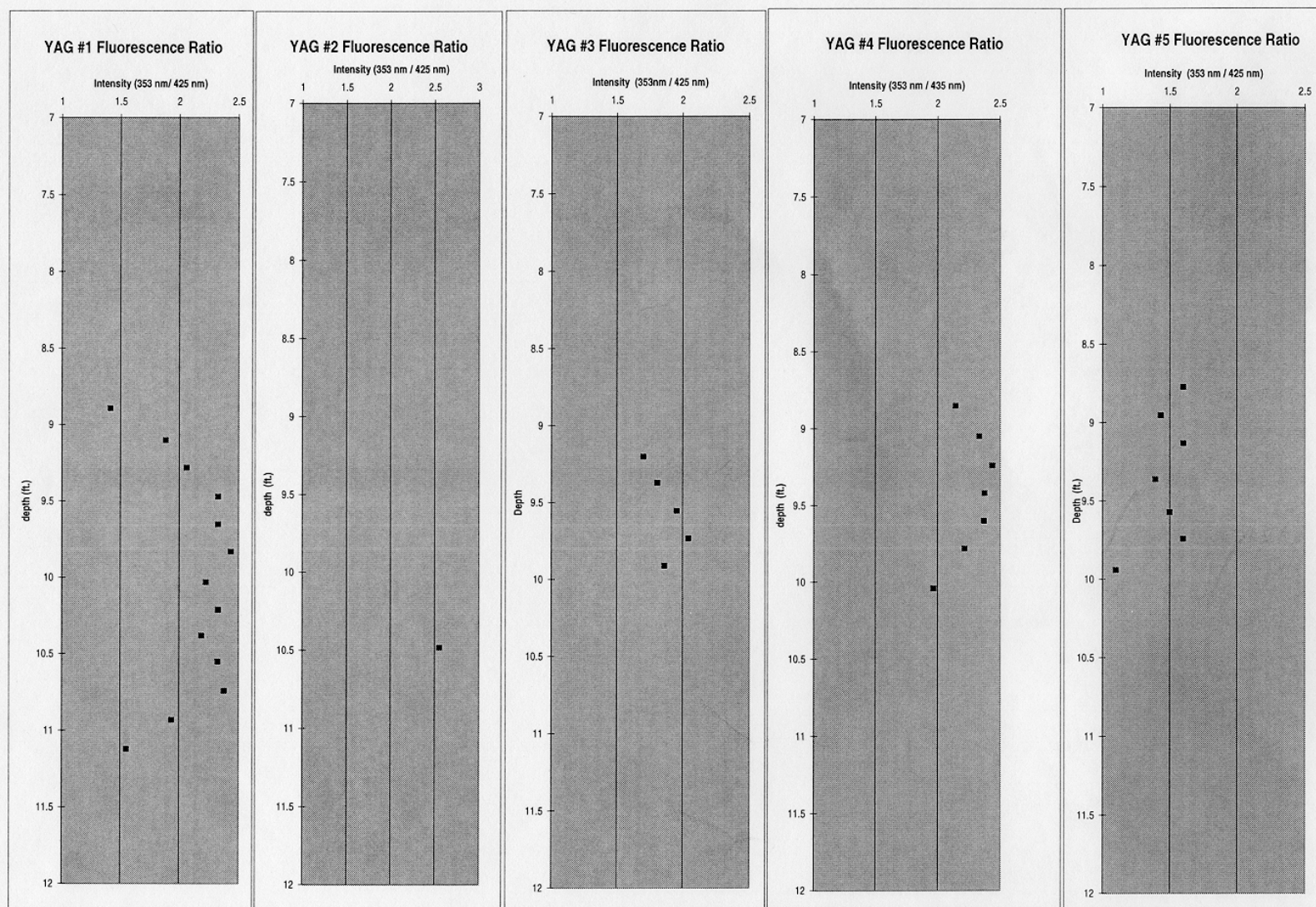


Figure 25. Ratio of Short to Long Wavelength Fluorescence for Port Hueneme Service Station (Nd:YAG data)

Additionally the individual spectra were evaluated. Figures 26-30 show the spectra from Pushes Y01, Y02, Y03, Y04 and Y05, respectively. The data are normalized at 425 nm in order to compare spectral shape at the lower emission wavelengths. Again, a reduction in the emission fluorescence at 350 nm is consistent with loss of lighter weight aromatics towards the edge of the plume possibly due to weathering, solubilization, differential transport or biodegradation. The 8021A data shown in Figure 31 confirms this result.

The overall patterns observed in contaminant distributions indicated by the different LIF systems are very similar. It is not possible determine whether differences in fluorescence profiles are due to small-scale variability in contaminant distribution or difference due to the detection capability of the different excitation systems. In general, laboratory results show the same general patterns observed in the LIF results; indicating maximum contaminant levels at approximately 10 feet and lowest levels at pushes 2 and 6.

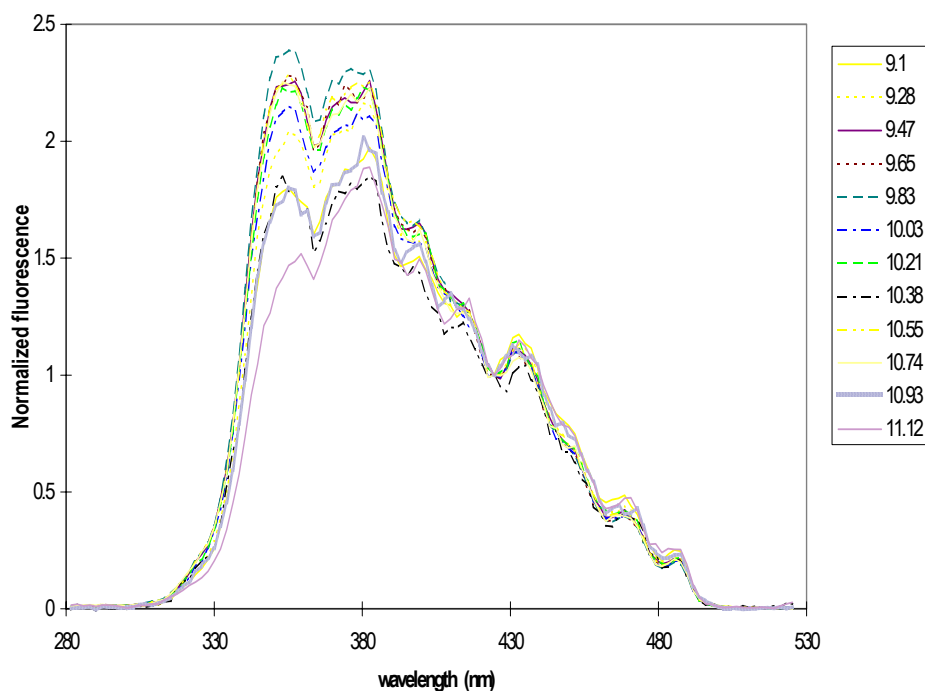


Figure 26. Normalized Spectra from Port Hueneme Service Station Push Y01

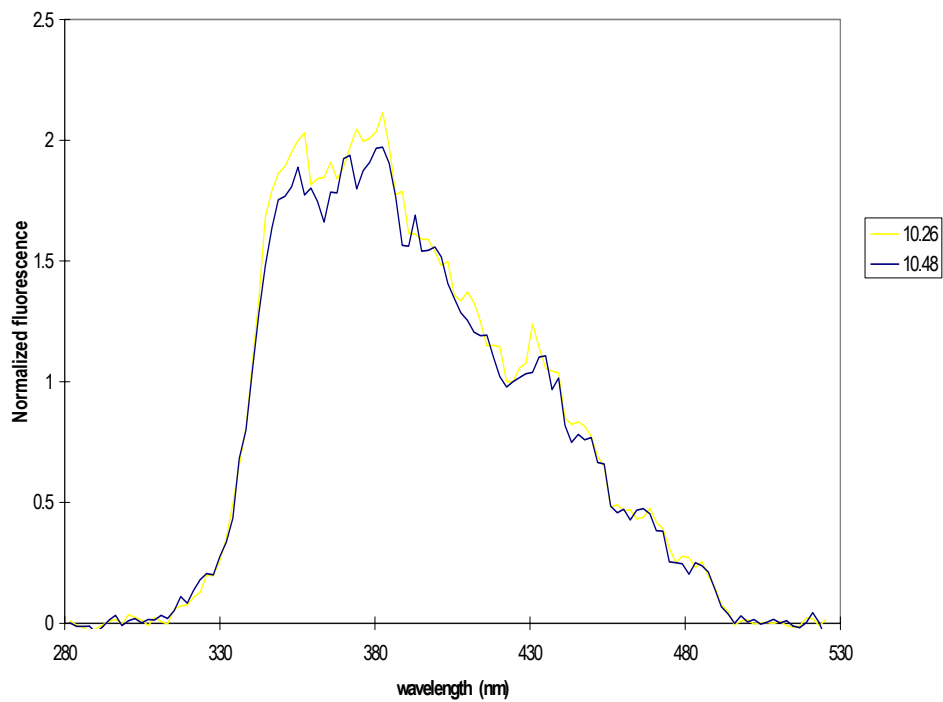


Figure 27. Normalized Spectra from Port Hueneme Service Station Push Y02

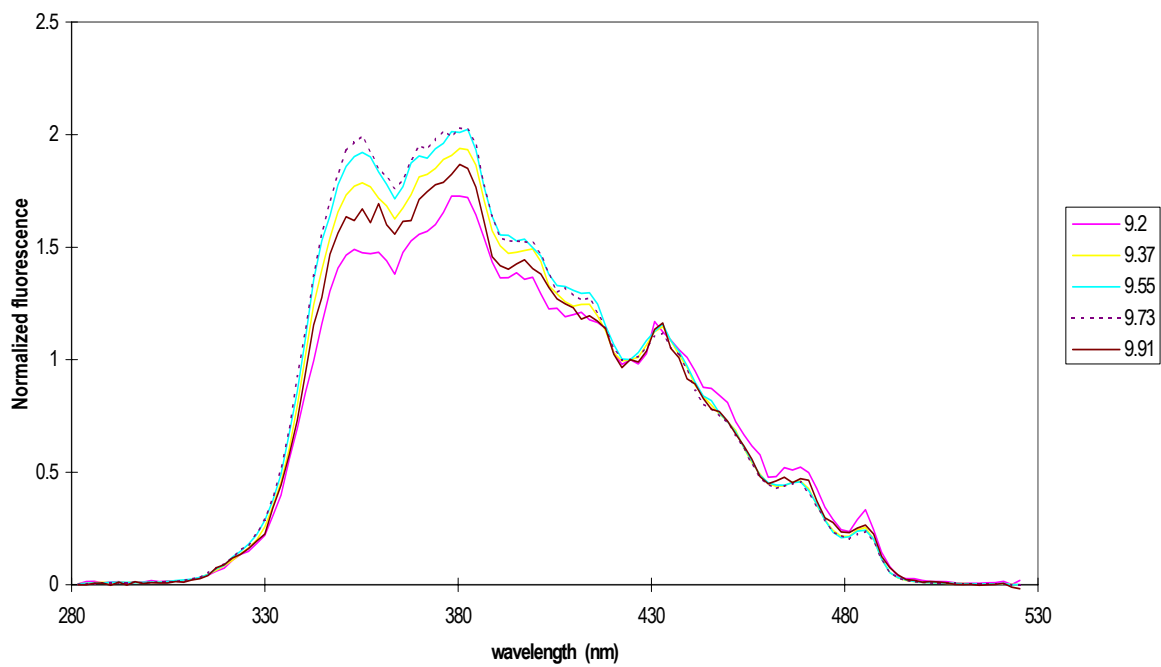


Figure 28. Normalized Spectra from Port Hueneme Service Station Push Y03

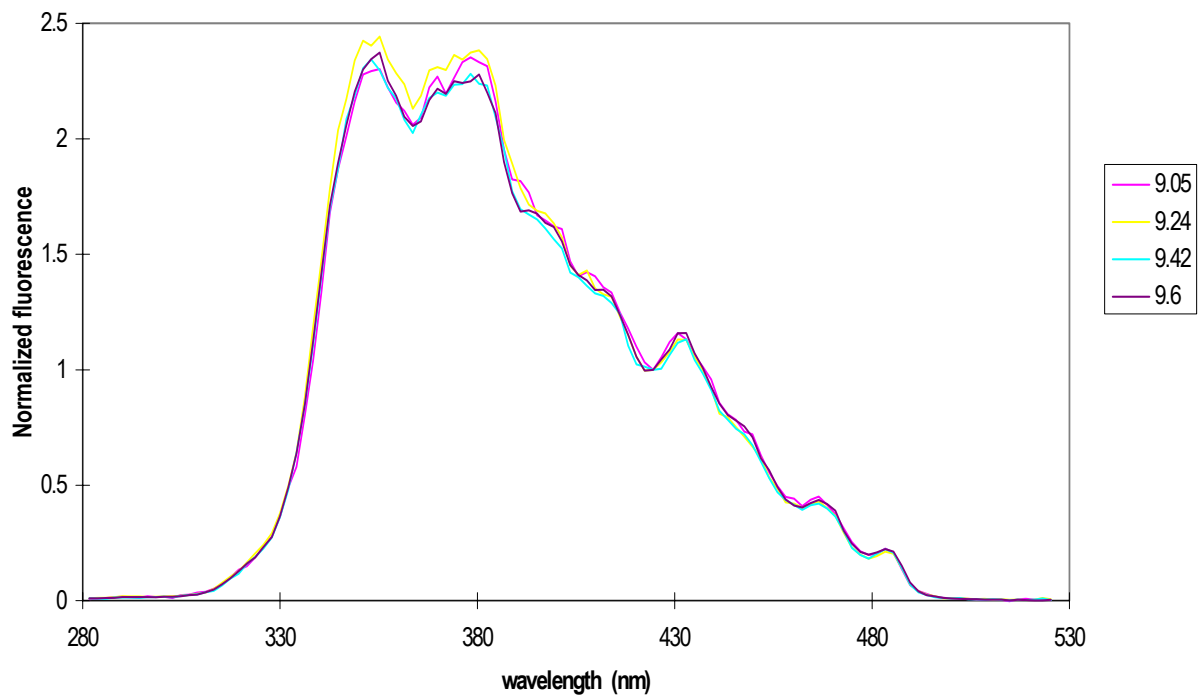


Figure 29. Normalized Spectra from Port Hueneme Service Station Push Y04

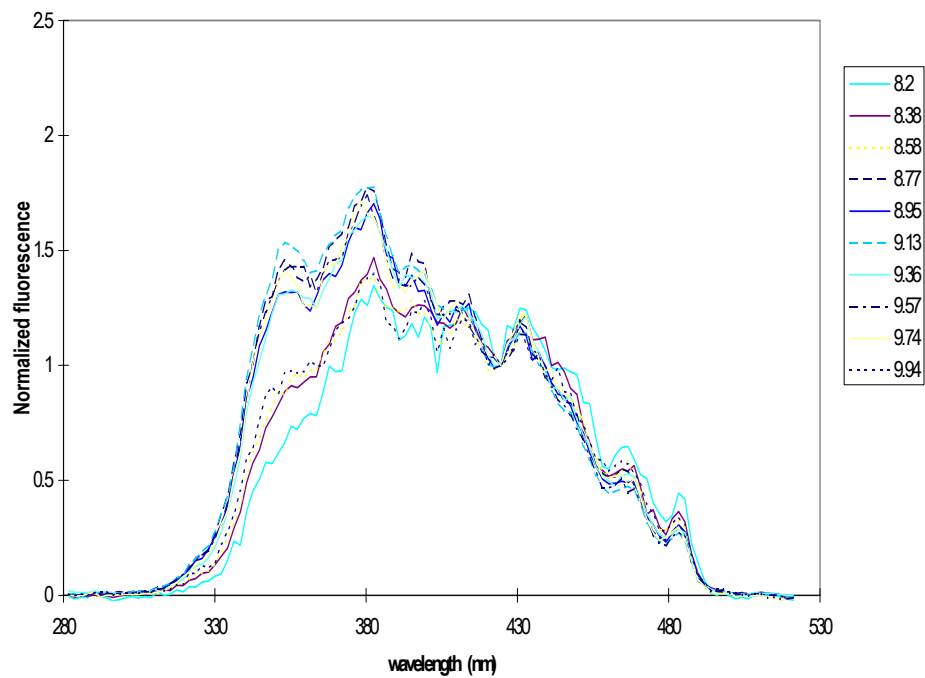


Figure 30. Normalized Spectra from Port Hueneme Service Station Push Y05

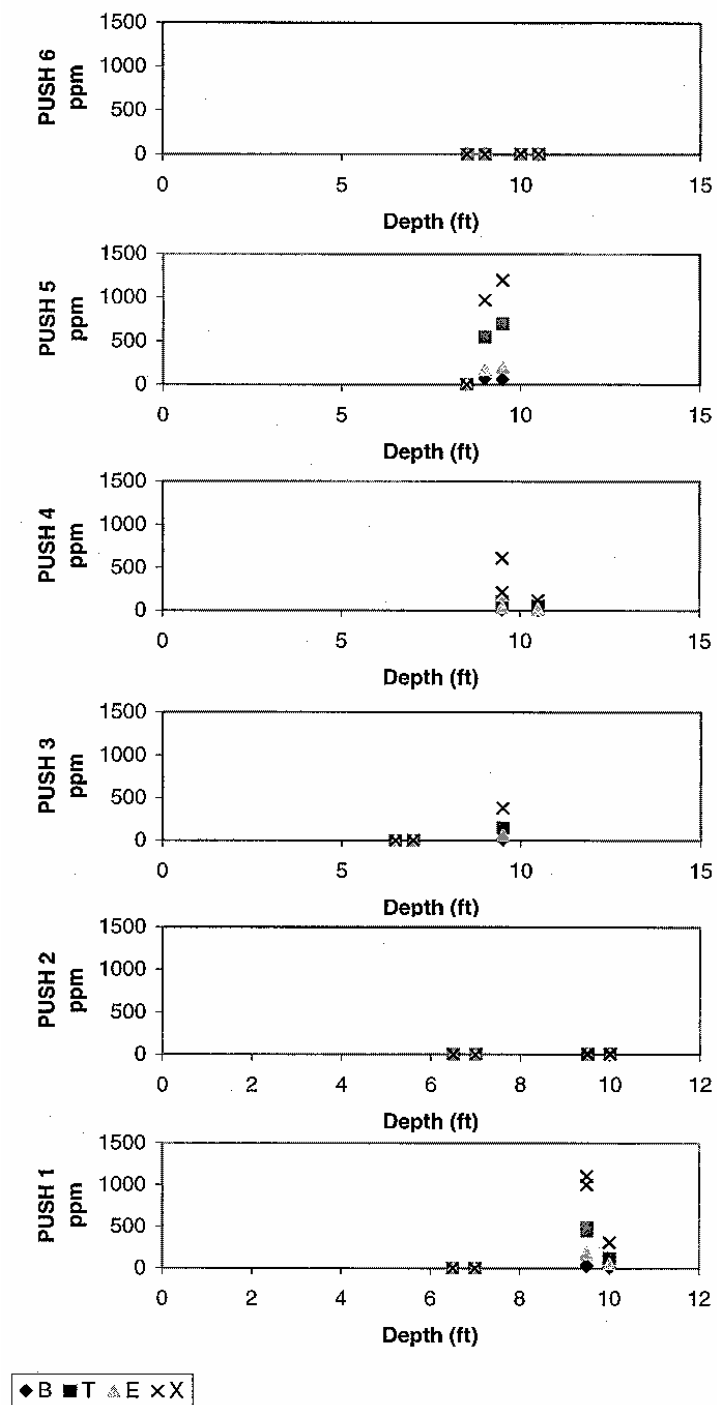


Figure 31. BTEX from 8021A for Port Hueneme NEX

One serious operational problem was encountered with the downhole Nd:YAG laser at both the North Island and Pt. Hueneme. That problem was the instability in the output of the Nd:YAG. It is thought that this instability was primarily the result of thermal variations experienced by the CPT probe. Some of the thermal variations are believed to be induced by frictional forces as the probe is pushed into the ground. Other thermal variations resulted from the steam cleaning procedure that is normally used to clean the CPT probe upon withdrawal from the push hole. However, even when the steam cleaning procedure was modified to minimize heating of the probe section containing the laser module, unacceptable high variability in laser output was still experienced. It is the conclusion from this effort that to optimize this laser system for this application a method needs to be implemented for better controlling the power output of the laser system. It should be noted that the laser system used in this demo was a prototype system, the technology has undergone improvements since this effort was launched. Also, the UV passively Q-switched microchip lasers have been licensed to Uniphase Lasers and Fiberoptics, and should be commercially available within approximately one year. It is likely that the commercialized product may be more stable and better able to accommodate variations in environmental conditions.

In addition to the capability of the downhole Nd:YAG LIF sensor to qualitatively delineate the contaminant distributions, it was also planned to evaluate the semi-quantitative performance of the sensor system using the same method previously used to evaluate the nitrogen LIF sensor. This method was based on comparisons of the nitrogen LIF "detect/non-detect" data at a specified site specific detection threshold with laboratory results for total petroleum hydrocarbons (TPH; EPA Method 8015-Modified). Typical confidence intervals for the "detect/non-detect" data generated during field screening of petroleum hydrocarbons have ranged from 80 to 95 percent. However, variability in the output energy of the laser caused by fluctuations in the temperature rendered the calibration data for the downhole Nd:YAG LIF sensor unreliable. Therefore, "detect/non-detect" data could not be generated for the downhole Nd:YAG LIF sensor.

5.2 Data Assessment

The primary objective of this demonstration was to verify the performance of the downhole 266nm LIF/CPT technology for extending the capability of the nitrogen laser-based LIF sensor for in situ field screening of petroleum hydrocarbons. Results from this demonstration showed that all three laser systems (SCAPS nitrogen laser, SCAPS xenon chloride laser, and SCAPS downhole 266nm Nd:YAG laser) yielded very similar patterns of subsurface contamination. Qualitatively, in situ

Nd:YAG LIF measurements compare favorably with laboratory measurements of validation soil samples.

Additionally, evaluation of spectral data demonstrated enhanced capability of the 266 nm Nd:YAG laser system to directly detect spectral differences in emission signatures at plume boundaries. This results primarily from the fact the 266 nm laser source is more effective for inducing fluorescence in the single ring aromatic (e.g., BTEX) compounds. These compounds are in general more mobile, and more easily lost due to volatilization and/or microbial degradation. Because the 308 nm excimer and 337 nm nitrogen laser source only excite heavier weight aromatic compounds they are not capable of detecting spectral differences that arise from loss of single ring aromatic compounds. The fluorescence measurements were also compared against actual distributions of the source material as indicated by laboratory analyses of validation soil samples for total petroleum hydrocarbons (TPH) (DHS Method 8015-Modified) and BTEX as documented by EPA Method 8021A-Modified which quantifies both BTEX and MTBE.

Two significant technical issues were identified as a result of this effort. One was the instability in laser power output discussed previously. The second was the design of the sampling scheme for verification of an in situ measurement by off-site analysis. Small-scale spatial heterogeneities make it very difficult to make rigorous comparisons of in situ data with measurements performed on discrete laboratory samples.

5.3 Technology Comparison

The LIF/CPT method provides real-time data as the probe is pushed into the ground enabling field modifications to the sampling plan. This capability provides a more timely and thorough investigation using LIF/CPT and avoids the drawn out iterative process typical of site characterization when using traditional sampling and off-site laboratory analysis.

The validation effort has produced comparison data to support the utility of LIF/CPT application. In general, comparisons of laboratory 8015 modified (TPH), 8021A modified and 8260 results versus fluorescence show that laboratory results track patterns observed for in situ fluorescence data quite well.

6. Cost Assessment

6.1 Cost Performance

Factors affecting the cost of LIF/CPT operations include labor, material, travel, permitting, utility location, location surveying, work plan and report preparation, and equipment mobilization. Additional cost may be incurred for coring if the ground surface is too hard for penetration (cement). SCAPS LIF/CPT cost has been quoted as \$4,000 per day plus per diem.

6.2 Cost Comparisons to Conventional and Other Technologies

This demonstration has focused on the effectiveness of the CPT/LIF technology to perform field screening at a POL impacted hazardous waste site. Table 1 presents a direct comparison between the costs using CPT/LIF versus conventional drilling, sampling, and laboratory analysis for field screening. For a site investigation with 10 holes to a depth 30 feet, the table shows the cost for SCAPS LIF/CPT is approximately one-third the cost of conventional sampling with a sampling ratio of 30 to 1 in favor of LIF/CPT. On a per sample basis, the conventional sampling is approximately 100 times more costly. For the LIF/CPT technique, regulators may require a minimum number of confirmatory samples which can be obtained using CPT sampling devices. This would increase the SCAPS LIF/CPT cost as presented in the table but only 3 or 4 samples would be required at less than \$1,000 additional cost.

A Los Alamos report, "Cost Effectiveness of the Site Characterization and Analysis Penetrometer System" focused on the effectiveness of the CPT/LIF technology to improve the placement and reduce the number of monitoring well. For a set of scenarios, cost was compared between site characterization (defined as drilling, coring, and installing monitoring wells) with and without using SCAPS LIF/CPT. They concluded, a cost savings of 30% to 50% over the use of conventional monitoring wells alone is possible assuming 50% of planned conventional wells can be avoided by the use of SCAPS.

In a more recent case study conducted at the Navy's Fleet Industrial Supply Center Manchester, the real cost of characterizing the same site using traditional and SCAPS methods. The 4-1/2 acre site was characterized by both methods. The SCAPS study costs \$110k, or 60% of the traditional study cost (\$188k). These values were total project costs, including plans, reports,

Table 1. Cost Comparison of SCAPS CPT/LIF and Conventional Sampling.

SCAPS LIF/CPT In Situ Measurement		Conventional drilling with hollow stem auger, split spoon sampling and off-site analysis	
10 pushes to 30 ft LIF and geotechnical data	Cost	10 borings to 30 ft 60 soil samples for TPH analysis	Cost
2 field days @ \$4,000 per day	8,000	Drilling @ \$50/ft for 300 ft	15,000
1 sample/2 inches for LIF = 1,800 total samples	Included in basic cost	TPH lab analysis @ \$80 per sample x 60 samples	4,800
1 sample/inch for geotechnical data	Included in basic cost	Geotechnical lab analysis @ \$100/sample x 5 samples	500
4 Waste drums @ \$40/drum	160	28 Waste drums @ \$40/drum	1,120
Decon water testing	1,000	Decon water testing	1,000
Waste soil testing	0	Waste soil testing	3,000
Waste soil not produced	0	Waste soil disposal 20 drums x \$100/drum	2,000
Decon water disposal 4 drums x \$100/drum	400	Decon water disposal 8 drums x \$100/drum	800
4 man crew included	0	Geologist @ \$60/hr x 40 hrs	2,400
4 man crew included	0	Technician @ \$40/hr x 40 hrs	1,600
TOTAL	9,560	TOTAL	32,220
per sample cost (1,800 samples)	\$5.31/sample	per sample cost (60 samples)	\$537/sample

and field work. A 40% cost avoidance is consistent with earlier projected cost avoidance figures (see above). Note also that SCAPS provided a more complete characterization because of the vertical and a real resolution of the data. The advantage of the high-resolution data is not quantified in this analysis. Finally, because SCAPS provides real-time data, the likelihood that iterative field sampling efforts will be required to completely characterize a site is greatly reduced. The time and cost savings associated with minimizing return site visits is not included in this estimate.

7. Regulatory Issues

7.1 Approach to Regulatory Compliance and Acceptance

The approach to regulatory acceptance envisioned for the Nd:YAG sensor system and other newly developed direct-push sensor systems would follow the path that emerged from the successful validation of the SCAPS nitrogen-based LIF sensor system.

This path to promote regulatory acceptance is based on assembling a comprehensive set of field measurements that directly compare the performance of the sensor system with traditional EPA methods for a variety of contaminants under different hydrogeological conditions. The cornerstone of obtaining as broad an acceptance as possible is linking these technical efforts with multi-state and national certification/verification programs such as the California EPA, Department of Toxic Substance Control's Technology Certification Program (Cal Cert) and US EPA's Consortium for Site Characterization Technology program. For the case of the SCAPS nitrogen laser LIF sensor system, these opportunities were subsequently linked to the Western Governors Association, Demonstrating Onsite Innovative Technologies (WGA/DOIT) project. Interest by the WGA/DOIT project subsequently led to the establishment of a SCAPS-LIF Interstate Technology and Regulatory Cooperation group (ITRC) Technology Specific Task Group (TSTG) with the goal to achieve acceptance by each of the seven TSTG member-states (UT, NB, NM, LA, NJ, ID, CA) and using Cal Cert as the protocol. For the SCAPS nitrogen laser LIF system these efforts resulted in the successful certification by the Cal Cert Program (Cal EPA, 1996), verification by the US EPA (US EPA, 1997) and endorsement of the Cal Cert certification by the WGA (Wesnousky et al., 1996).

Because the Nd:YAG laser system represented a less mature technology, funding was not requested (or provided), for pursuing the California certification or US EPA verification for the downhole Nd:YAG sensor system. Results from this evaluation suggest that several technical issues need to be resolved before this system can be successful in these forums.

8. Technology Implementation

8.1 DoD Need

50,000 leaking underground storage tanks. 2,000 sites. Site characterization represents a significant portion of remediation efforts accounting for about one-third or more of the total costs. DoD presently spends in excess of \$50M/year for well drilling and site characterization.

8.2 Transition

Fluorescence-based direct push sensors are currently being marketed in the United States and Europe by at least four different primary suppliers (Delft Geotechnics (The Netherlands), Fugro Geosciences Inc. (Houston, TX), Laser Labor Adlershof (Germany) and Vertek (South Royalton, VT). In addition, there are presently nine systems being operated by the US Government (4 Army, 3 Navy, 1 DoE, and 1 US EPA). The companies listed above, as well as the government owned systems, represent transition potentials for this technology. Implementation of a mature configuration of this technology is commercially very attractive because it makes use of a simple solid state device (compared to present laser sources) that provides a capability that meets or exceeds that of present commercial systems. It is anticipated that the commercial version of the microchip laser system currently under development by Uniphase Lasers and Fiberoptics will facilitate this transition.

9. Lessons Learned

Results from this effort demonstrated the capability of the downhole Nd:YAG laser system to provide good qualitative agreement with patterns of petroleum hydrocarbon contamination measured by conventional laboratory measurement. As with other direct push sensors, much greater spatial resolution is possible than with conventional sampling methods. In addition, the capability for inducing fluorescence in lighter weight aromatic compounds provided by the downhole Nd:YAG laser extends the capability of the LIF technology to monitor volatilization and/or degradation of light weight aromatic compounds.

The most significant lesson learned from this effort is that real-world operational environments reveal shortcomings of systems that may not be apparent from laboratory evaluations. More specifically, problems observed with variable laser output, which appear to be related to variations in temperature, are much more severe in the field than was encountered in the laboratory environment. This is because in the operational environment there can be variables such as frictional heating of the probe or ancillary procedures such as steam cleaning of the probe that may result in unanticipated variations in the operating conditions. The second observation is that is very difficult to eliminate questions of sample variability when attempting to compare in situ measurements with discrete samples collected for laboratory analysis. These sampling problems are even more problematic when concerns relative to sample volatility preclude homogenization of samples.

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Appendix A

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Appendix B

Data Archiving and Demonstration Plan

Field validation data collected as a part of this project is archived in the SSC San Diego SCAPS Project Office, San Diego, CA. Electronic copy of the field data is stored on 3.5" floppy disk in the data acquisition software custom binary format. Hardcopy plots, field notes, work plans, analytical laboratory results, and data reports are also maintained in the SSC San Diego SCAPS Project Office. Requests for copies of the data or reports should be made to Dr. Stephen Lieberman at the address listed in Appendix A, Points of Contact.