



# Project Summary

## Field Validation of a Penetrometer-Based Fiber-Optic Petroleum, Oil, and Lubricant (POL) Sensor

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**Comprehensive comparisons of in situ measurements from a cone penetrometer-deployed laser induced fluorescence (LIF) petroleum, oil, and lubricant (POL) sensor with traditional field screening methods were performed. Operational procedures were developed to facilitate comparison between methods and across multiple sites. Using a field screening detect/non-detect criterion, agreement between sensor measurements corresponding to the sampled interval and the laboratory analytical measurements on those samples was better than 85 percent. Comparison between measurements from the two accepted analytical techniques, on splits of the same sample, was only slightly better. We conclude that the LIF-POL sensor, deployed from a cone penetrometer, provides significant advantages for subsurface field screening of POL-contaminated sites. The LIF technique offers the advantages of rapid, in situ, real-time measurements, coupled with increased data density, not possible with traditional screening methods.**

***This Project Summary was developed by EPA's Environmental Sciences Division, National Exposure Research Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

### Introduction

The U.S. Environmental Protection Agency (EPA), Environmental Sciences Division-Las Vegas (ESD-LV) evaluated

field screening techniques to expedite site characterization and monitor corrective actions. In collaboration with the Naval Command, Control and Ocean Surveillance Center, RDT&E Division (NRaD), the effort described here was undertaken to evaluate the use of a cone penetrometer system equipped with a fiber optic-based laser-induced fluorescence (LIF) petroleum, oil, and lubricant (POL) sensor for real-time field screening of subsurface POL contamination.

The feasibility of using a truck-mounted cone penetrometer system to push chemical sensors into the ground to delineate subsurface contaminant plumes was first demonstrated through the Department of Defense (DOD) Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) program. The LIF cone penetrometer test (CPT) technology was developed through a collaborative effort of the Army, Navy, and Air Force under the Tri-Service SCAPS program. To satisfy the objective of this Inter-Agency Agreement (IAG), a comprehensive inter-comparison effort was established to directly compare sensor results with conventional sampling and laboratory analyses. This effort was proposed as a jointly funded collaborative effort between the U.S. EPA and the U.S. Navy and as such leverages funding provided by Naval Facilities Engineering Command. This IAG enabled confirmatory sampling work to be performed at two sites: Naval Air Station, Alameda, CA, and Guadalupe Oil Field, Guadalupe, CA. To date, confirmatory sampling has been performed at 16 sites in addition to the two above listed

sites, therefore summary results will be presented.

### System Description

The SCAPS system uses a truck-mounted CPT platform to advance its chemical and geotechnical sensing probe into subsurface soils. CPT has been widely used in the geotechnical industry for determining soil strength and soil type from measurements of tip resistance and sleeve friction via an instrumented 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-m long by 3.57-cm diameter threaded-end rod into the ground at a rate of 1 m/min in accordance with American Society of Testing and Materials (ASTM) Standard D3441, the standard for CPT. The rods, various sensing probes, or sampling tools can be advanced to depths in excess of 50 m in naturally occurring soils. As the rods are withdrawn, grout can be injected through ¼-in.-diameter tubing within the interior of the probe's umbilical cable, hydraulically sealing the push hole. The platform is fitted with a self-contained decontamination system that allows the rods and probe to be steam cleaned as they are withdrawn from the push hole, through the steam cleaning manifold, and back into the CPT push room. Subsurface investigation in this manner produces rinsate but no soil cuttings as investigation derived waste.

LIF sensors rely on impinging ultraviolet (UV) light to excite molecular electrons to higher energy states. As the electrons return to lower energy states, the transition produces UV fluorescence photons of longer wavelength than the UV excitation. The LIF POL sensor probe consists of a standard penetrometer probe modified with a ¼-in.-diameter flush-mounted sapphire window which is 24 in. behind the probe tip. Two 500-µm silica clad silica optical fibers, one for laser excitation and one for fluorescence emission, are included in the 300-ft umbilical cable and are internally mounted in the probe terminating at the sapphire window. Excitation light at 337 nm, gener-

ated from a pulsed nitrogen laser (0.8 ns pulse width, 1.4 mJ pulse energy), travels down the optical fiber and excites fluorescence from polycyclic aromatic hydrocarbons (PAHs) in the soil. The method detects PAHs in the bulk soil matrix throughout the vadose, capillary fringe, and saturated zones. The emission fiber collects the laser-induced fluorescence and returns it to the surface.

At the surface, the fiber is coupled to a spectrograph where the light is spectrally dispersed. The dispersed light then impinges on an intensified linear photo diode array detector (1024 pixels) which is gated on for 100 ns at the time of signal return. An optical trigger from the pulsed laser via a pulse delay generator is used to gate the detector. The laser-induced fluorescence signal is emitted over a broad range of wavelengths longer than the excitation wavelength. Approximately 16 msec is required to read the fluorescent signal from a single laser shot. The maximum spectral resolution is approximately 0.5 nm. The detector is set to measure the wavelength range from 350 to 720 nm. In practice, the system usually integrates the emission from 20 laser shots with detector pixels grouped by four. Since the laser repetition rate is 10 Hz, the total time to collect a fluorescence emission spectrum is two seconds. This represents approximately a 2.5- depth resolution. The spectral resolution for pixels grouped by four is approximately two nm. An optical multichannel analyzer accumulates the detector readings and reports the sum as a single measurement to the data acquisition computer.

Data acquisition is automated under software control using a 486 host computer. The computer sets and controls the sensor system, stores fluorescent emission spectra and strain gauge data, and generates the real-time depth plots. From the spectral curve at each depth, the SCAPS software extracts the maximum intensity and associated peak wavelength for real-time depth display. 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. 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 10-ft interval on a scrolling basis.

LIF is a nonspecific field screening technique which detects PAH compounds with

at least two aromatic rings but is most effective for three and more aromatic rings. To date, LIF measurements over optical fibers have not been used extensively for detection of the single ring aromatic compounds, BTEX (benzene, toluene, ethylbenzene, and xylenes). The general trend is the fewer the number of rings the shorter the excitation wavelength required. Greater attenuation of this shorter wavelength UV radiation in optical fibers is a technological barrier for transmitting the excitation pulse over long fiber lengths.

Table 1 presents detection limits for common fuel products found as soil contaminants. Measurements were made in the laboratory on spiked soils over a 50-m fiber and are reported at the 95 percent confidence level. Detection limits vary with fuel type depending on constituent compound abundance. Detection limits also vary with soil type due to particle size and mineralogy. Most importantly, these limits fall well within the range of utility considering regulatory action limits.

**Table 1.** Detection Limits for the LIF POL Sensor

Soil Type	Fuel Type		
	Unleaded Gasoline	Diesel Fuel #2	Diesel Fuel Marine (DFM)
Soil A Sand	17 ppm	329 ppm	14 ppm
Soil B China Lake	36 ppm	25 ppm	4 ppm
Soil C Columbus	121 ppm	83 ppm	5 ppm

### Sampling Procedure

SCAPS site operations typically consist of two phases: site investigation and validation. In the investigation phase, pushes were performed to delineate the plume boundaries. During the validation phase, areas of interest were selected from the first phase and then revisited. At the selected locations, a validation push was performed followed immediately by collection of confirmatory soil samples.

During validation, the SCAPS CPT pushed the LIF POL sensor probe into the ground and acquired fluorescence and geotechnical data. After the probe was pushed to the total depth anticipated or was blocked from further penetration, the probe was retracted. The CPT rig moved away from the location and a hollow stem auger (HSA) drill rig was positioned approximately 20 cm (8 in.) from the push hole. The HSA rig drilled a hole such that

the advancing auger flights destroyed the push hole while allowing for the collection of split spoon soil samples within approximately 7.5 cm (3 in.) (horizontally) of the push cavity. This offset between the push hole and the auger boring permitted sampling far enough apart so that the soil samples were not affected by possible cross contamination due to sloughing down the penetrometer hole, yet near enough to minimize variability due to small scale spatial heterogeneities of the soil and the contaminant distribution. This sampling strategy ensured that samples were representative of the region sampled by the LIF POL sensor. Each borehole was logged by a geologist. Soil samples were collected with a split spoon sampler lined with 15-cm (6-in.) long stainless steel tubes. The sampler was driven in advance of the lead auger using a 63.5-kg (140-lb) slide hammer falling over a 75-cm (30-in.) distance, in accordance with ASTM 1586, the Standard Penetration Test.

A California modified split spoon sampler was used for sample collection. The split spoon sampler was a 75-cm (30-in.) long, 7.5-cm (3-in.) diameter steel tool. The sampler consisted of a 10-cm (4-in.) long (reduced to 5 cm (2 in.) when fully threaded) cutting head or shoe section, followed by either a 45-cm (18-in.) or 60-cm (24-in.) long sample barrel containing three or four 15-cm (6-in.) long stainless steel soil sampling tubes, and ending in a waste soils catch barrel section.

Soil samples were collected at depth intervals to confirm the LIF POL sensor depth profile in both background and elevated fluorescence intervals. The sampler was overdrilled approximately 15 cm (6 in.) prior to retrieval to reduce the amount of sloughed soils typically found in the bottom of the borehole. Only tubes containing sample soils that appeared relatively undisturbed were used. Samples for confirmatory analysis were collected from the lower and middle (deeper) 15-cm (6-in.) soil tubes in the 45-cm (18-in.) sampler. The sample was Teflon-sealed, capped, taped, labeled, logged, and placed into a chilled ice chest. Each confirmatory sample was analyzed by EPA Method 418.1 Total Recoverable Petroleum Hydrocarbon (TRPH), a water analysis method modified for soil, and EPA Method 8015-Modified Total Petroleum Hydrocarbon (TPH). Samples for geotechnical analysis (soil moisture, grain size, and density) were sealed and shipped 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 if the tube appeared full as a result of complete sample recovery by the split spoon sampler. In each boring, these sampling procedures were usually repeated four to eight times to gather samples for traditional laboratory analytical measurements. From three to eight validation borings were performed at a site.

### **Analytical Methods**

EPA method 418.1 (TRPH by infrared absorption) and EPA method 8015-Modified (TPH by GC/FID) represent two of the most frequently used methods employed for delineating nonvolatile POL contamination. It is important to note that these analytical methods do not measure exactly the same constituents that are targeted by the 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. This data is then compared with the in situ fluorescence data gathered with the sensor.

### **Data Analysis**

LIF POL sensor data is evaluated on a detect/non-detect basis to determine percentage agreement between sensor data above or below a fluorescence threshold and both TRPH and TPH results above or below a sensor detection threshold. SCAPS independently provides detect/non-detect data relative to a specific detection limit derived for a specific fuel product on a site-specific soil matrix. The detection limit is determined for the site by generating a concentration calibration response curve for a set of calibration standards (spiked site-specific soil samples) prepared by standard addition.

### **Results and Discussion**

For an in situ field screening measurement technique, such as LIF, determining the accuracy of the technique presents a particular challenge. This is because it is not a simple matter to confidently assign a "true" value to a subsurface contaminant distribution. With conventional laboratory-based measurements, the accuracy of the method is a function of both the sampling errors and errors associated with the measurement method. To evaluate the accuracy of a laboratory method, the conventional approach is to compare the results obtained from analysis of a spiked sample of known concentration. It should be recognized, however, that this approach does not address the issue of

whether the result is an accurate representation of the true value of the contaminant in the ground. In other words, errors related to sampling are not addressed. Because there is no independent measure of the subsurface value of contaminant concentration, it will be necessary to evaluate the accuracy of the in situ measurement by comparing in situ results with results from conventional methods that may not provide a true value of the subsurface contaminant distribution because of errors associated with the sampling process.

It should be noted that the three methods for quantifying hydrocarbon contamination discussed in this document (namely the analytic EPA Methods 418.1 and 8015-Modified, and the LIF method) all measure and quantify the amount of contaminant using a different physical property of the contaminant. The EPA Method 418.1 measures the infrared absorption of the extract from the soil sample. The EPA Method 8015-Modified passes the extract from the soil sample through a gas chromatograph and uses a flame ionization detector to measure the contaminant according to the retention time of the constituents. The LIF method measures the fluorescence (under laser excitation) from the PAHs present in the contaminant.

The two EPA Method measurement techniques require comparison to a similar measurement of a target fuel in order to quantify the contaminant. Note that it is not possible to ensure that the target fuel is identical in composition to the contaminant extract. The EPA Method 418.1 uses a single standard hydrocarbon mixture for quantification, while EPA Method 8015-Modified quantifies using a target fuel that produces a similar chromatogram. The LIF method does not use an extract from the soil sample, but measures the contaminant in situ as it is presented to the window of the probe. For this reason, the LIF POL sensor is more sensitive to matrix effects. Because of this matrix sensitivity, the LIF POL sensor does not employ a target fuel for quantification but only to set a detection threshold for the site.

Another difference between in situ and conventional laboratory-based measurements is that laboratory measurements usually employ extraction or matrix simplification procedures, whereas in situ measurements offer limited opportunities for controlling matrix effects. For the LIF POL sensors, studies have shown that variability in sensor response results from changes in the sample matrix and from variations in fluorescence response re-

lated to fuel product type, age, and origin of the hydrocarbon contaminant. Since it is not possible to account for all sources of variability that affect sensor response at this time, the sensor is intended to operate as a field screening method. It will provide only qualitative data on the distribution of petroleum hydrocarbon contamination.

The approach for evaluating accuracy presented here depends on the direct comparison of in situ sensor data with the analysis of discrete samples collected as close as possible to the soil sample measured by the in situ sensor. Although it is believed that this approach provides the best opportunity for evaluating the accuracy of the in situ measurement, it should be noted that it will not be possible to account for all variability associated with the uncertainty in depth from which the discrete samples are collected. It is possible that the depth of the discrete sample may be in error by up to 15 cm (6 in.) in the vadose zone. Due to sloughing and flowing sand conditions in the water saturated zone, depth measurement uncertainty during discrete sampling may be greater. In stratified soils, sharp vertical boundaries of the contamination plume may exist. This sampling error could therefore lead to poor comparisons between in situ data and laboratory data. For example, due to an error of 15 cm (6 in.) in the sample depth, contaminant concentration can change from strongly impacted (greater than 10,000 ppm) to not impacted (less than 100 ppm). For this reason, the depth of the sample must be known for the comparability of the samples to be firmly demonstrated. In addition, because there will be several inches of horizontal offset between the push location and the location of the split-spoon sampler, there may also be some small-scale horizontal variability that will not be accounted for. Both the vertical uncertainty and the small-scale horizontal variability will not be a factor when comparing the two laboratory methods because splits of a homogenized sample will be measured.

### Summary Results for Sixteen Sites

To date, validation efforts at 16 sites have been completed. These sites presented varied hydrogeological conditions including: (1) arid with deep groundwater and (2) coastal with tidally-influenced shallow groundwater. These sites also presented various contaminant source products including old refinery waste, heat-

ing oil, diesel fuel marine, and JP-5 jet fuel.

Based on the results calculated for the sites to date, the LIF POL sensor detection threshold varies somewhat from site to site, but it is approximately 100 to 300 mg/kg as TRPH by EPA Method 418.1. Scatter plots of the LIF POL sensor data versus TPH and TRPH show a trend of increased fluorescence with increased TPH or TRPH. Table 2 contains the cumulative contingency analysis results on a percentage basis showing better than 85 percent agreement between sensor and analytical measurements. As expected, comparison between analytical methods is slightly better since these measurements were made on splits of the same sample.

**Table 2.** Sixteen Site Cumulative Contingency Analysis Results Summary (n=552)

Comparison	% Correct	% False Positive	% False Negative
LIF vs. TRPH	87	5	7
LIF vs. TPH	86	7	7
TPH vs. TRPH	95	2	3

### Naval Air Station, Alameda Results

SCAPS field operations were undertaken at Naval Air Station (NAS), Alameda, CA, Site 13 - Former Oil Refinery, from the 17th of March through the 6th of April 1994. Validation operations were performed from the 4th through the 6th of April 1994. A total of 37 pushes were performed during phase one SCAPS investigation. After review of phase one data, eight validation pushes were performed each directly followed by a hollow stem auger boring and sample collection. Forty-five samples were collected from the eight validation borings.

The calculated fluorescence threshold was 10,620 relative fluorescent counts, with a corresponding detection threshold of 137 ppm. Contingency analysis was performed on the data. The percentage of false negatives was 7 percent versus TRPH and 4 percent versus TPH. The percentage comparability or percentage correct versus TRPH was 91 percent and versus TPH was 87 percent. These results are very favorable considering the comparison between laboratory analytical methods with 11 percent false negative and 87 percent comparability. Table 3 summarizes these contingency results.

**Table 3.** NAS, Alameda Contingency Analysis Results Summary (n=45)

Comparison	% Correct	% False Positive	% False Negative
LIF vs. TRPH	91	2	7
LIF vs. TPH	87	9	4
TPH vs. TRPH	87	2	11

### Guadalupe Oil Field Results

The SCAPS was employed at the Guadalupe Oil Field in San Luis Obispo County, CA, for subsurface investigation of diluent contaminated soils on the 23rd of August through the 2nd of September 1994. Validation pushes with overborings and sampling were performed on the 7th through the 8th of September 1994. A total of thirty-two SCAPS push holes were advanced during phase one investigation. After review of phase one data, an additional four validation holes were pushed, subsequently overbored, and a total of 23 soil samples collected. Soil samples were sent to an analytical laboratory for analysis by EPA Methods 418.1 (TRPH by IR) and 8015-Modified (TPH by GC/FID).

The calculated fluorescence threshold was 350 relative fluorescent counts, with a corresponding detection threshold of 77 ppm. Contingency analysis was performed on the data. There were no false negatives versus TRPH and 6 percent versus TPH. The percentage comparability or percentage correct versus both TRPH and versus TPH was 88 percent. These results are very favorable considering 88 percent comparability between the two laboratory analytical methods. Table 4 summarizes these contingency results.

**Table 4.** Guadalupe Oil Field Contingency Analysis Results Summary

Comparison	% Correct	% False Positive	% False Negative
LIF vs. TRPH	88	12	0
LIF vs. TPH	88	6	6
TPH vs. TRPH	88	12	0

### Conclusions and Recommendations

The SCAPS technology was developed to provide rapid, in situ, real-time field screening of the physical and chemical characteristics of subsurface soil at hazardous waste sites. The current configu-

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ration is designed to quickly, and cost effectively distinguish hydrocarbon-contaminated areas from unimpacted areas. Although the LIF POL sensor induces only the PAH portion of the petroleum hydrocarbons to fluoresce, petroleum hydrocarbons are the general target analytes. This capability allows further investigation and remediation decisions to be made more efficiently, on site, and reduces the number of samples that need to be submitted to the laboratory for costly confirmatory analyses. A site can then be further characterized with reduced numbers of borings or wells placed on a plume specific sampling pattern rather than a grid. Remediation efforts can be directed on an expedited basis as a result of the immediate availability of the LIF POL sensor and soil matrix data. Further, the SCAPS CPT platform: (1) allows for the

characterization of contaminated sites with minimal exposure of site personnel and the community to toxic contaminants, and (2) minimizes the volume of investigation derived waste (IDW) generated during typical site characterization activities.

As a result of field experience and efforts undertaken to validate the SCAPS LIF POL sensor, the following items are recommended.

- Further development should be pursued to refine the LIF measurement technique for expanded use in additional applications such as monitoring in situ remediation.
- Continue research efforts to develop better quantitative aspects in defining the dominant chemical source of the fluorescence. Improve contaminant discrimination by

spectral signature using neural network pattern recognition techniques and developing a database of fluorescent signatures.

- Develop methods to compensate for matrix effects using additional sensors and algorithms accounting for grain size distribution and volumetric moisture content.

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*The complete report, entitled "Field Validation of a Penetrometer-Based Fiber-Optic Petroleum, Oil, and Lubricant (POL) Sensor," (Order No. PB98-100472; Cost: \$21.50, subject to change) will be available only from*

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