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6. AUTHOR(S)
William C. McGinnis, Michele Davey, Karina D. Wu, and Stephen H. Lieberman

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Computer Sciences Corporation (CSC)

San Diego State University Foundation

Naval Command, Control, and Ocean Surveillance Center
RDT&E Division (NRaD), Code 521
San Diego, CA 92152

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Data from a new field screening technique using a fiber optic laser induced fluorescence (LIF) petroleum, oil, and lubricant (POL) chemical sensor deployed from a truck mounted cone penetrometer is presented. The system provides real-time, in situ measurement of petroleum hydrocarbon contamination and soil type to a maximum depth of 150 feet with a vertical spacing of two inches. Each depth measurement records the fluorescent spectrum from 350 to 720 nm. Spectral signatures can be used to track a single or multiple contaminants across a site. Real-time measurement permits on site interpretation and "plume chasing." Field data from SCAPS (Navy) field operations is presented to show how the system ca be used for rapid three-dimensional delineation of a POL contaminant plume.

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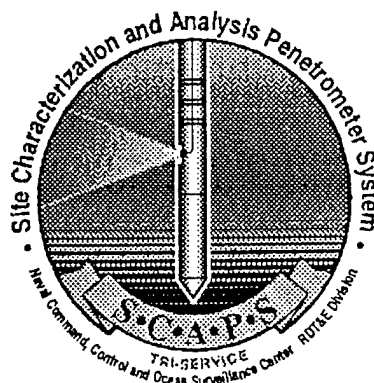| 17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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William C. McGinnis, Michele Davey,
Computer Sciences Corporation (CSC)

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Stephen. H. Lieberman,
Naval Command, Control, and Ocean Surveillance Center, Research
Development Test and Evaluation Division (NRaD), Code 521, San Diego
CA 92152

SERDP
Strategic Environmental Research
and Development Program
A Partnership to Improve the
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2. INTRODUCTION

In recent years, DOD efforts in environmental site characterization, remediation, and monitoring have drastically increased. Federal environmental exemptions have been rescinded and in this era of environmental awareness, requirements for environmental cleanup are becoming more stringent. Additionally, the base realignment and closure (BRAC) process requires land facilities be cleaned prior to closure. Traditional site characterization technologies are inadequate due to poor spatial resolution of data, length of time required for analysis and decision making, and cost. The need for site characterization, remediation, and monitoring services and technologies is both immediate and long term. Thus investment in alternative and developing technologies and expedited transitioning to the field promises to provide better data quality and substantial long term cost savings.

To address the site characterization and monitoring needs, the Naval Command, Control and Ocean Surveillance Center, RDT&E Division (NRaD) in collaboration with the Army and the Air Force under the Site Characterization and Analysis Penetrometer System (SCAPS) Program has developed a fiber optic laser induced fluorescence (LIF) chemical sensor system for real-time detection of petroleum, oil, and lubricant (POL) hydrocarbons. The chemical sensor has been integrated with a truck mounted cone penetrometer system for in situ subsurface contaminant screening. The SCAPS provides a capability for real-time chemical and geotechnical measurements permitting in the field decisions, i.e. sampling plan modifications, thus providing a unique on site "plume chasing" capability.

Laser induced fluorescence spectroscopy techniques via a cone penetrometer have matured to where several systems are in the field performing site investigations. The Navy's SCAPS truck has now been in the field for over a year ad has completed subsurface field screening investigations for POL contaminants

at eight sites. Capabilities and limitations have been reported for laboratory and demonstration systems. This paper reports capabilities and limitations "where the rubber meets the road," meaning capabilities and limitations gleaned from initial field site investigations performed with the Navy's SCAPS truck.

3. SYSTEM DESCRIPTION

Laser induced fluorescence (LIF) sensors rely on impinging ultraviolet (UV) light to excite molecular electrons to higher energy states. As the electrons return to lower energy, the transition produces fluorescence photons of longer wavelength than the UV excitation. A schematic of the LIF system deployed in the cone penetrometer is shown in Figure 1. Details of the system have previously been described.[2] Relevant features are reviewed here.

The 20 ton mass of the truck is used as reaction mass for a hydraulic ram which forces an instrumented probe into the ground at a rate of three feet per minute to a maximum depth of 150 feet. For SCAPS, a standard penetrometer probe is modified with a ¼ inch diameter sapphire window flush mounted 24 inches behind the probe tip. Two 365 micron silica clad silica optical fibers, one for laser excitation and one for fluorescence emission, are included in the 300 foot umbilical cable and are internally mounted in the probe terminating at the sapphire window. Excitation light at 337 nm, generated from a pulsed nitrogen laser (0.8 ns pulse width, 1.4 mJ pulse energy), travels down the optical fiber and excites fluorescence from three and more aromatic ring polycyclic aromatic hydrocarbons (PAHs) in the soil.[3] 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 which is gated on for 100 nanoseconds at the time of signal return. An optical trigger from the pulsed laser is used to gate the detector. The laser-induced fluorescence signal is emitted over a broad range of wavelengths longer than the excitation light. The fluorescent signal from a single laser shot is read in 16 msec with a maximum spectral resolution of ~0.5 nm. The detector is set to quantify 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 20 hertz, the total analysis time to collect a fluorescence emission spectrum is 1 second. This represents approximately a 2 inch depth resolution. The spectral resolution for pixels grouped by 4 is ~2 nm. An optical multichannel analyzer accumulates the detector readings and reports the sum as a single measurement to the data acquisition computer. Figure 2 presents a representative spectral curve from a push at a site in Alameda.

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 shown in Figure 3. From the spectral 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 3 contain this data. SCAPS standard electrical cone penetrometer instrumentation consists of strain gauges measuring tip resistance and sleeve friction in accordance with American Society of Testing and Materials (ASTM) Standard D3441. An empirical relationship between tip resistance and sleeve friction provides a soil type classification relating to grain size. 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. Data acquisition time for the 20' push displayed in Figure 3 was on the order of 12 minutes. Including grouting and relocating, push start to push start was less than one hour. Focusing on the data, the fine scale depth resolution is readily apparent. Also, within the Raw Fluorescence profile

intensity increases and decreases with penetration depth, supporting the argument that the measurement is reversible, i.e. the probe window is self cleansing.

Figure 4, Hydrocarbon Guidelines, is a broad brush presentation of relevant hydrocarbon information. Along the top are two scales. The first depicts the number of carbon atoms per molecule. For example, C_6 represents benzene, hexane, or cyclohexane. The second scale is an associated boiling range for molecules of that size. The first section presents a list of common hydrocarbons found as subsurface contaminants. The lines span the carbon range for constituent compounds. The diamond shapes for gasoline, diesel, and kerosene represent a relative abundance for constituents with that carbon range. For example, gasoline spans the carbon range from C_5 to C_{13} with C_9 compounds of greatest abundance.

The center section of Figure 4 presents EPA accepted analytical techniques. The numbers are EPA method numbers. The horizontal lines represent the ranges of compounds detected. As the figure shows, target compounds vary significantly with method. Additionally, methods vary from analyte specific to nonspecific. The last section portrays where the SCAPS LIF technique fits in. The SCAPS technique adds a real-time in-situ method to the available suite of measurement tools.

SCAPS is a nonspecific field screening technique which most effectively detects polycyclic aromatic hydrocarbon (PAH) compounds with three and more aromatic rings. An alternative SCAPS configuration uses 290 nm excitation which extends the range of target compounds to two and more aromatic ring compounds. To date, LIF measurements over optical fibers have not been used effectively for detection of BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds. High attenuation of short 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 over a 50 meter fiber and are reported at the 95% confidence level. Detection limits vary with fuel type depending on constituent compound abundance. Limits also vary with soil type, in a complex manner. Most importantly, these limits fall well within the range of utility considering regulatory action limits.

4. CAPABILITIES AND LIMITATIONS

The capabilities and limitations presented in this paper are gleaned from over a years experience at eight POL sites. Data from field operations will be presented and discussed to highlight the following capabilities: contaminant discrimination by spectral signature, reproducible/high resolution measurements, and in-the-field plume delineation.

Table 1. Detection Limits for the LIF POL Sensor

Soil Type		Fuel Type	
	Unleaded	Diesel #2	Diesel Fuel, Marine
Sand	17 ppm	329 ppm	14 ppm
China Lake	36 ppm	25 ppm	4 ppm
Columbus	121 ppm	83 ppm	5 ppm

Limitations are a result of both the LIF physical process as well as a result of hardware/ technology constraints. As discussed with Figure 4, Hydrocarbon Guidelines, the technique is not compound specific. 337 nm UV excitation effectively targets PAH compounds with three and more rings. Thus we do not directly detect the BTEX compounds which are of concern due to their higher mobility.

Optical fiber attenuation provides a hardware constraint. Fiber attenuation increases with fiber length, which limits the total length of cable and therefore the depth of penetration. Attenuation also increases significantly with shorter wavelength. Hence, light in the excitation region for BTEX compounds transmits very poorly.

This technique measures contaminant on and between soil particles. The measurement is a bulk measurement of surface concentration independent of phase. Target compounds in the soil water, soil gas, soil mineral, and non-aqueous (free product) phases all contribute to the fluorescent signal. Thus mobile and immobile fractions are not distinguished.

The method is inherently quantitative, however, considerations due to measurements on soil and in the field relegate it to semi-quantitative. A major factor is that quantification is contaminant dependent. Sensor sensitivity changes with different contaminants. The product used for calibration may not accurately represent what is in the ground. Additionally, what is in the ground can be changing with depth. In another paper presented at this meeting, the use of artificial neural networks for processing spectral and soil classification data to apply more appropriate calibration factors is discussed (Andrews and Lieberman, 1994).

Contaminant Discrimination by Spectral Signature

The SCAPS system performed work at an old oil refinery site in Alameda, CA. The contaminant of interest was weathered oil refinery spoils, a heavy tar-like product. Figure 3 displays the real-time data display for push P44 at this site. This push was located in the general area of interest from the refinery site as well as down gradient from a recently operated gasoline filling station. Push P44 shows two impacted depth intervals, a shallow one at about four feet and a deeper one over the eight to ten feet range. A change in peak wavelength between these two depth intervals can be seen on the Wavelength at Peak profile. This observation suggests we have two distinct contaminants in the ground. Figure 5 plots various spectra from the SCAPS data at these depth intervals. Notice the three consistently shaped spectra for the eight to ten feet interval and the distinctly different spectrum at four feet. Again suggesting two contaminant products.

Confirmatory sampling was performed for this push using traditional techniques, a hollow stem auger with a split spoon sampler and analytical laboratory analysis. EPA Method 8015 Chromatograms from an analytical laboratory for a sample from each depth interval are displayed in Figures 6 and 7. Figure 6 represents a heavier weight product which we see repeatedly from contaminated samples across the site, the old refinery spoils. Figure 7 on the other hand is a much lighter product resembling gasoline. This is consistent with the interpretation as gasoline light non-aqueous phase liquid (LNAPL) contamination on the groundwater down gradient from a filling station.

Push Reproducibility

There is an unresolved question as to how reproducible is the SCAPS measurement. If one were to measure the same hole twice, how closely would the profiles agree? We address this question with nearby pushes located within three feet of one another.

At the Alameda site, a total of forty-five pushes were performed. Eight of these pushes, validation pushes, were located within three feet of a previous push and were overdrilled and sampled. Referring to push P44 again, Figure 8 shows P30 overlaid with P44 and plotted on the same graph. These nearby pushes demonstrate the qualitative reproducibility of SCAPS data.

Comparing the other nearby pushes at this site and at other sites, in many cases the agreement is better than in Figure 8 but never much worse. Fluorescent features appear at very nearly the same depths with approximately the same magnitudes. Agreement is not exact but the general patterns match. Given soil variability on this scale, the suggestion is that SCAPS data is reproducible.

Figure 9 presents data in cross section from three nearby pushes performed at Guadalupe Oil Field Site, P24, P33, and P34. End to end distance was less than ten feet. Push P24 was performed first followed later by validation pushes P33 and P34. The stippled areas under B33 and B34 represent hollow stem auger borings which were collocated with the pushes. Confirmatory sample intervals are portrayed by solid rectangles in the boring. EPA methods 418.1, TRPH, and 8015, TPH, analytical measurements performed on the samples are posted next to the sampled interval. Non-detect analytical measurements from samples in boring B34 confirm the low level fluorescence signal in push P34 as clean. Considering the similar profile with P34 suggests that push P24 is likewise a clean hole.

Push P33 displays a distinctly different fluorescent profile. Analytical measurements again confirm the fluorescence signal. Low levels of fluorescence have low or non-detect analytics and high levels of fluorescence have correspondingly high analytical measurements. Within the nine to eleven feet depth range concentrations were measured up to 62,000 ppm for TRPH and 54,000 ppm TPH. When removed from the ground, this sample was dripping with contaminant. For some samples, the EPA method concentrations varied by over an order of magnitude. The juxtaposition of these profiles suggests that contaminant distribution can vary sharply over a short distance, in this case three feet, and that differences between fluorescent profiles reflect changes in the contaminant distribution, vertically and horizontally. The conclusion is that SCAPS provides reproducible measurements in an homogeneous environment and also accurately delineates plume boundaries when the contaminant distribution changes.

Plume Delineation

Since fluorescence is a relative measure of contaminant concentration, fluorescent intensity can be interpolated between pushes to give a continuous plume model. Figure 10 depicts the 3D contaminant plume model from the Alameda site. A total of forty-five SCAPS pushes were interpolated. The vertical lines represent the push locations. The plume is constrained on all sides by clean holes. On one side however, the plume is not well delineated due to sparse data. This area was physically inaccessible for SCAPS investigation. An interactive viewer allows manipulation of this model. The view can be zoomed, rotated, or sliced. A 3D view of the plume cut out to a hot spot is shown in Figure 11.

The contaminant model sliced along an East-West transect is shown in Figure 12. The figure shows fine scale microstructure, a result of the high depth resolution. The raw fluorescence and analytical data along this same cross section is displayed in Figure 13. Note that the TRPH and TPH measurements in general confirm the fluorescence observations. When there is low level fluorescence, analytics are low and when fluorescence is high, analytics are high. Also, note that in some instances the two EPA accepted analytical techniques differ by over an order of magnitude. The analytical data can also be interpolated. The 3D model is not of great value since samples were only collected along this transect. However, Figures 14 and 15 present the TPH and TRPH interpolated images sliced along this transect. For these images, the fine scale microstructure is lacking. Comparison of these transects reveals that agreement

between LIF measurements and analytical measurements is as good as the agreement between the two EPA accepted analytical measurements.

5. CONCLUSIONS

With over a years operational experience at eight sites, the overall impression is that the SCAPS technology provides a very effective tool for subsurface field screening and site characterization. The technology is presently licensed to industry and being commercialized under a Technology Reinvestment Program grant and Cooperative Research and Development Agreements with DOD agencies. Regulatory acceptance and certification at federal, state, and local levels is actively being pursued.

SCAPS provides spectral data which can effectively be used to discriminate contaminant products in the subsurface downhole and across the site. In an homogeneous environment, nearby SCAPS measurements (<3' apart) frequently show reproducible depth patterns. Considering soil variability on this scale, fluorescent features appear at the same depth with the same magnitude. However, field data has shown contaminant distribution can vary sharply over a small scale. Thus different fluorescence versus depth profile patterns reflect contaminant distribution differences. Fine scale vertical resolution with subjective horizontal placement provides data density to effectively delineate plume boundaries both vertically and horizontally. The ability to detect plume boundaries and real time results enables a unique on site "plume chasing" capability.

Finally, advances in enabling technologies (e.g. fiber optics and lasers) will continue to improve this evolving technology as it hits the marketplace.

6. ACKNOWLEDGMENTS

7. REFERENCES

1. S. H. Lieberman, G. A. Theriault, S. S. Cooper, P. G. Malone, R. S. Olson, and P. W. Lurk, "Rapid Subsurface in situ Screening of Petroleum Hydrocarbon Contamination Using Laser Induced Fluorescence Over Optical Fibers," in Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Second International Symposium, pp. 57-63, 1991.

2. S. H. Lieberman, S. A. Apitz, P. G. Malone, and S. S. Cooper, "Real-Time in situ Measurements of Fuels in Soil: Comparison of Fluorescence and Soil Gas Measurements," Proceedings??, 1993?

3. S. E. Apitz, G. A. Theriault, and S. H. Lieberman, "Optimization of the Optical Characteristics of a Fiber-Optic Guided Laser Fluorescence Technique for the *in situ* Evaluation of Fuels in Soils," in Environmental Process and Treatment Technologies, (T. vo-Dinh, Ed.) pp. 241-254, 1992.
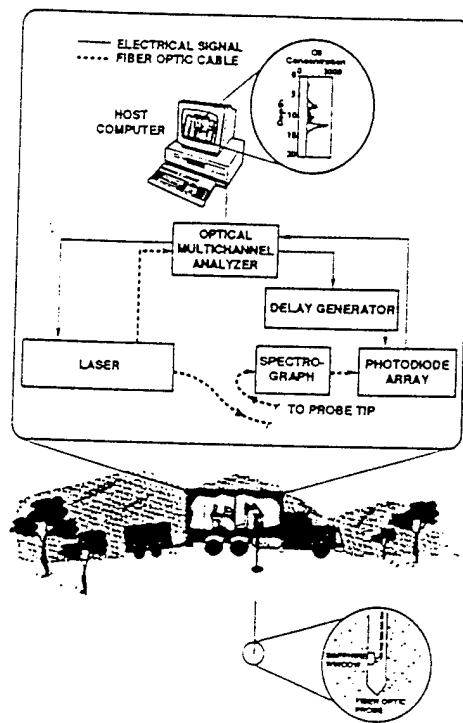
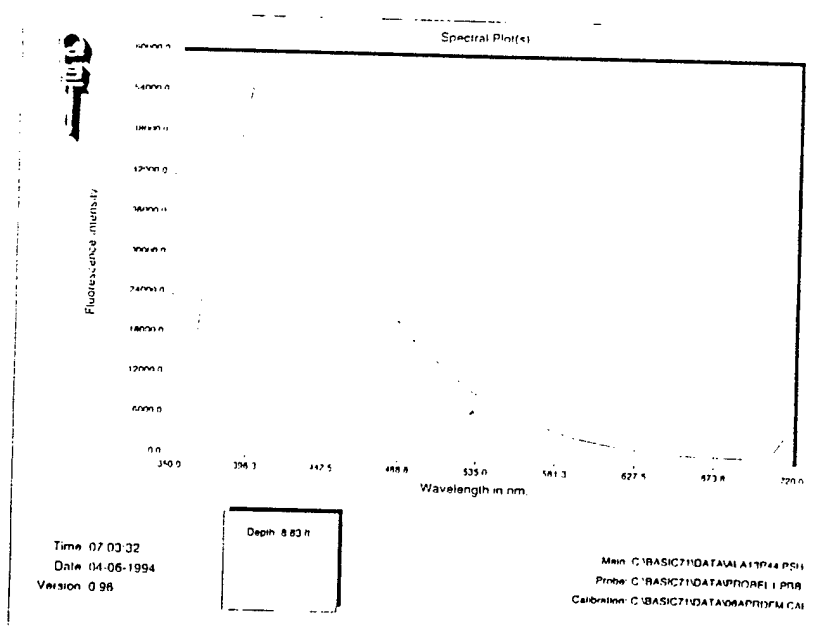Figure 1. Schematic of fiber optic sensor system for petroleum hydrocarbons.

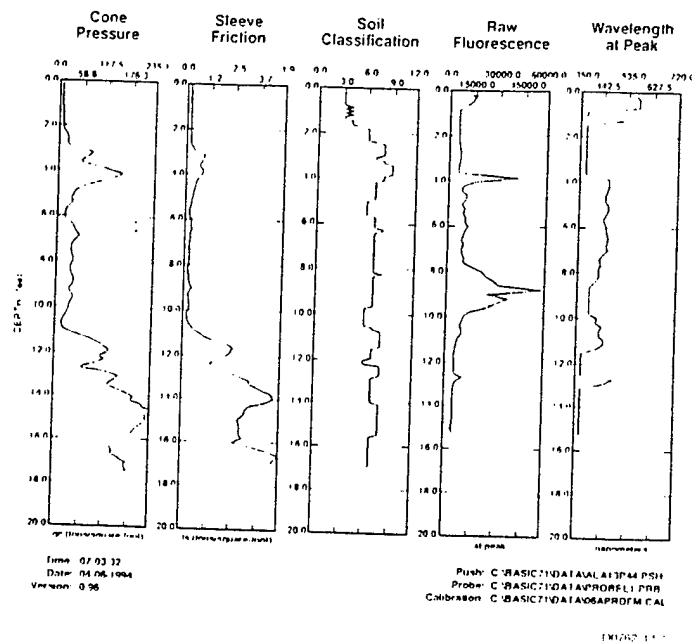Figure 2. Spectral Curve from 8.83' depth for push P44 at an Alameda site.

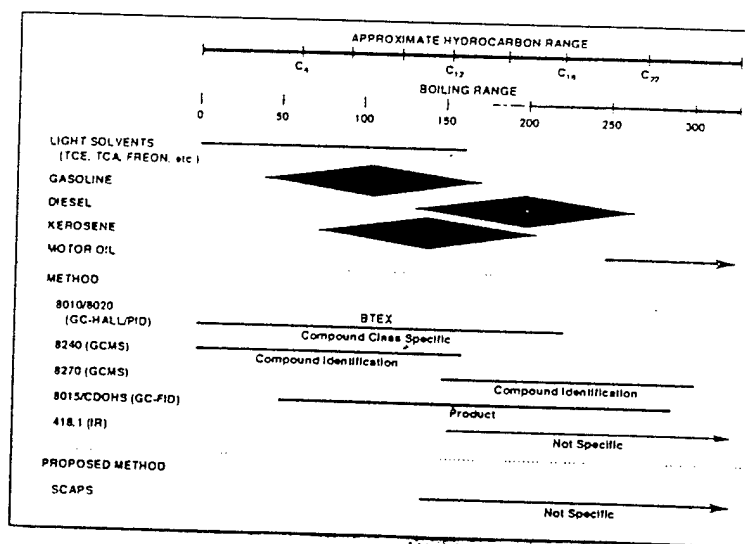Figure 3. Real-time data display for push P44 at an Alameda site.

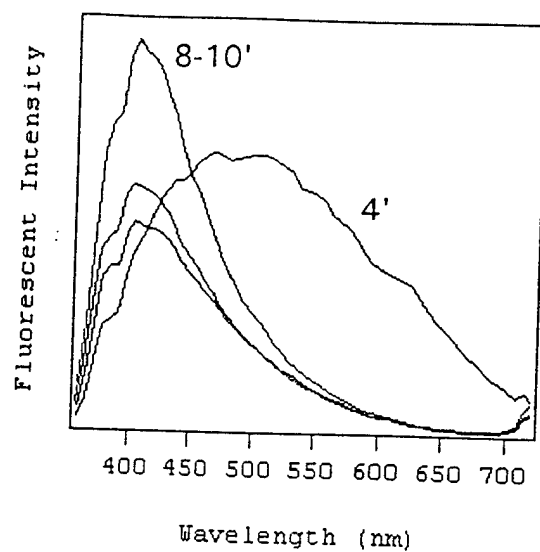Figure 4. Hydrocarbon Guidelines Chart.
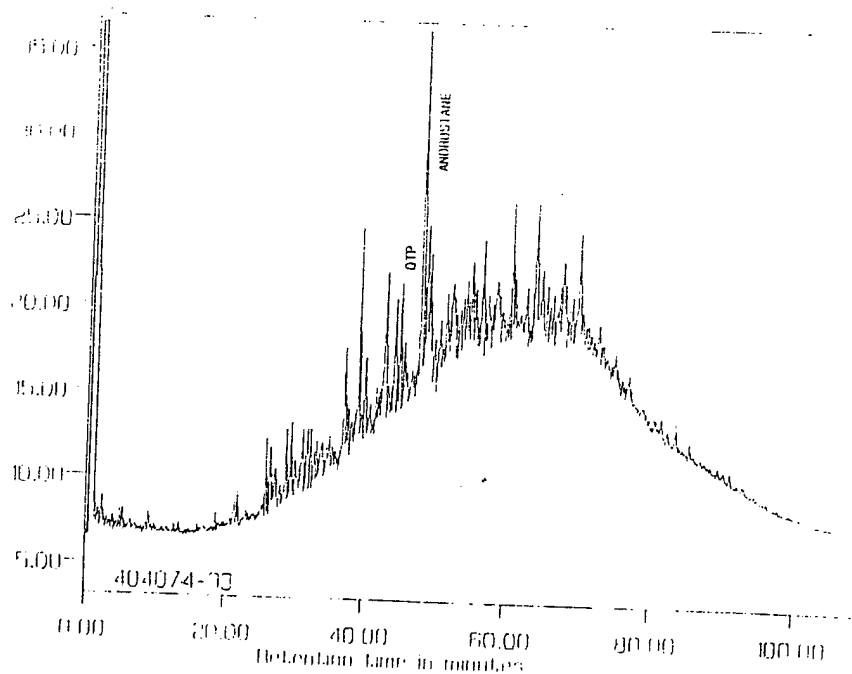
Figure 5. Spectra at Various Depths from Alameda Push P44.
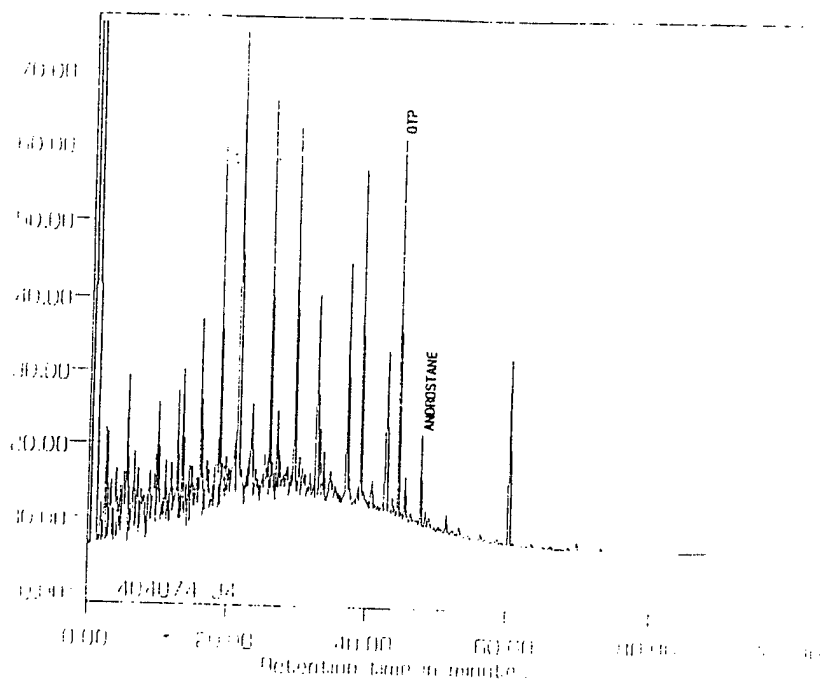

Figure 6. EPA Method 8015 Chromatogram for Push P44, 4'

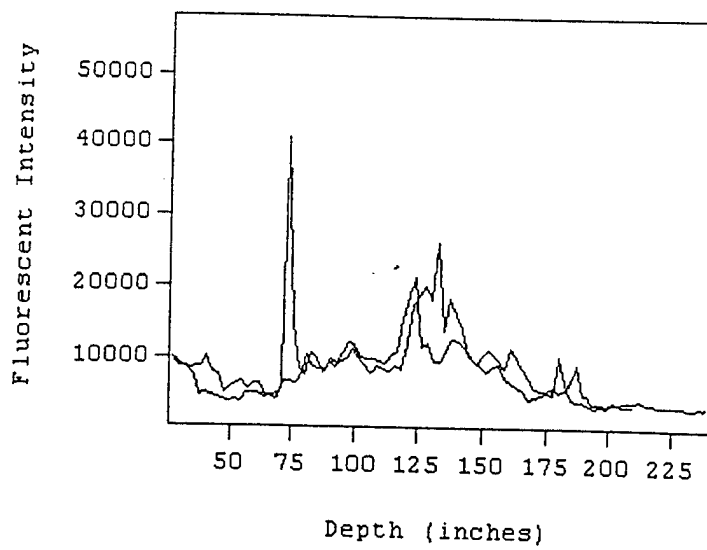Figure 7. EPA Method 8015 Chromatogram for Push P44, 9'
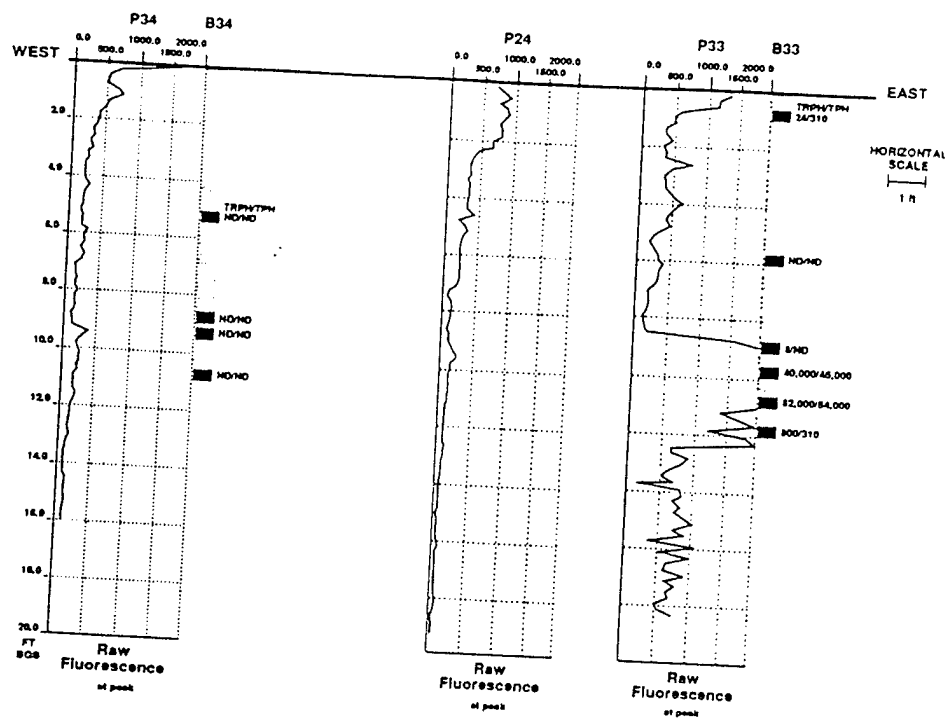

Figure 8. Overlay of Nearby Alameda Pushes P30 and P44.

Figure 9. Guadalupe Oil Field Data Profile.
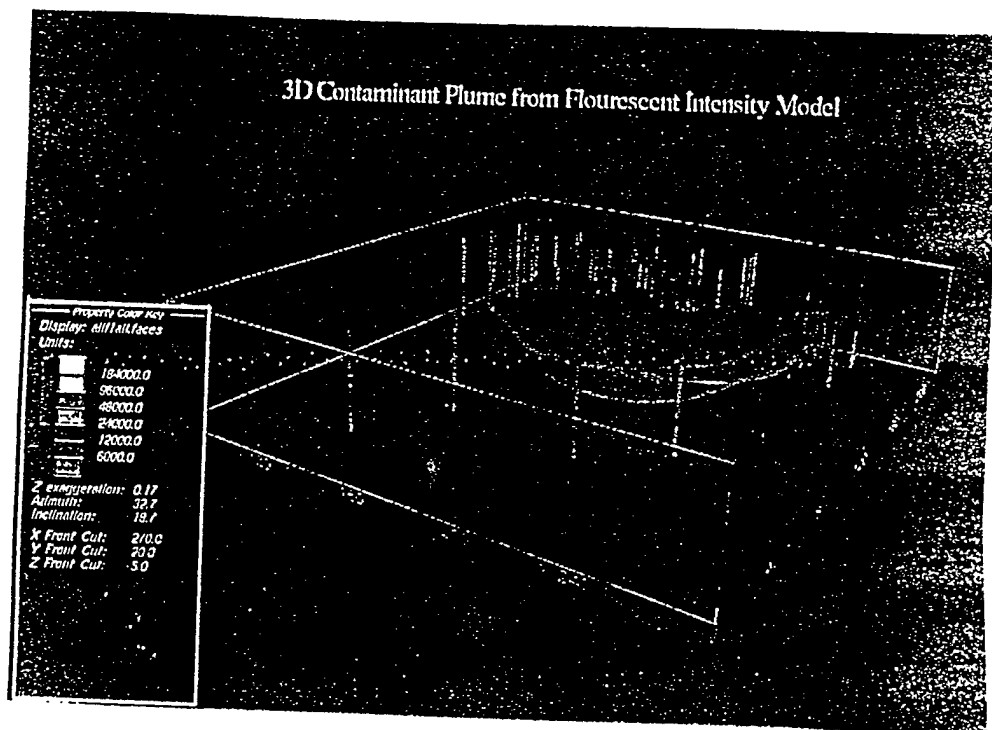
Figure 10. 3D Contaminant Plume from Alameda Site.
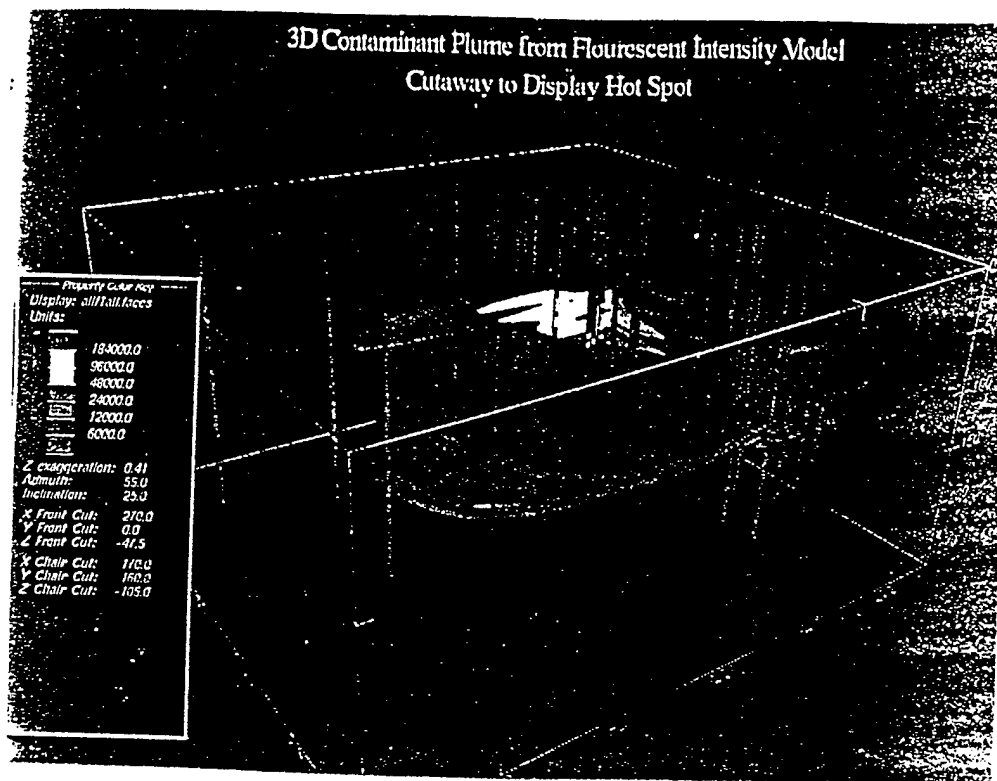
Figure 11. Alameda 3D Contaminant Plume Sliced to Hot Spot.
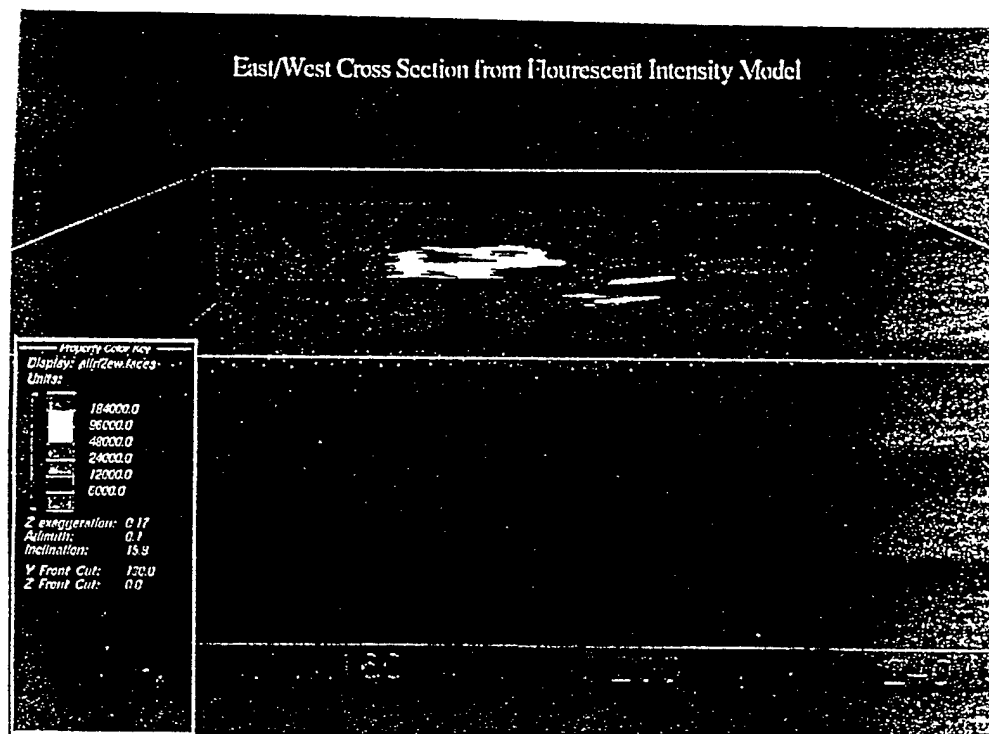
Figure 12. Cross Section Slice of 3D Contaminant Plume from Fluorescence Model.
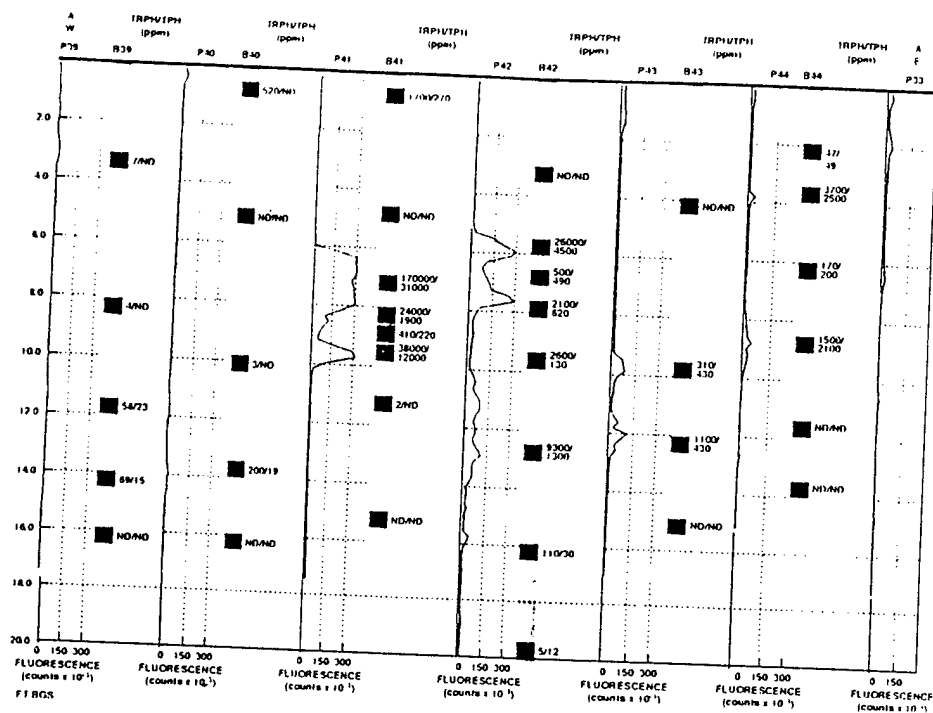
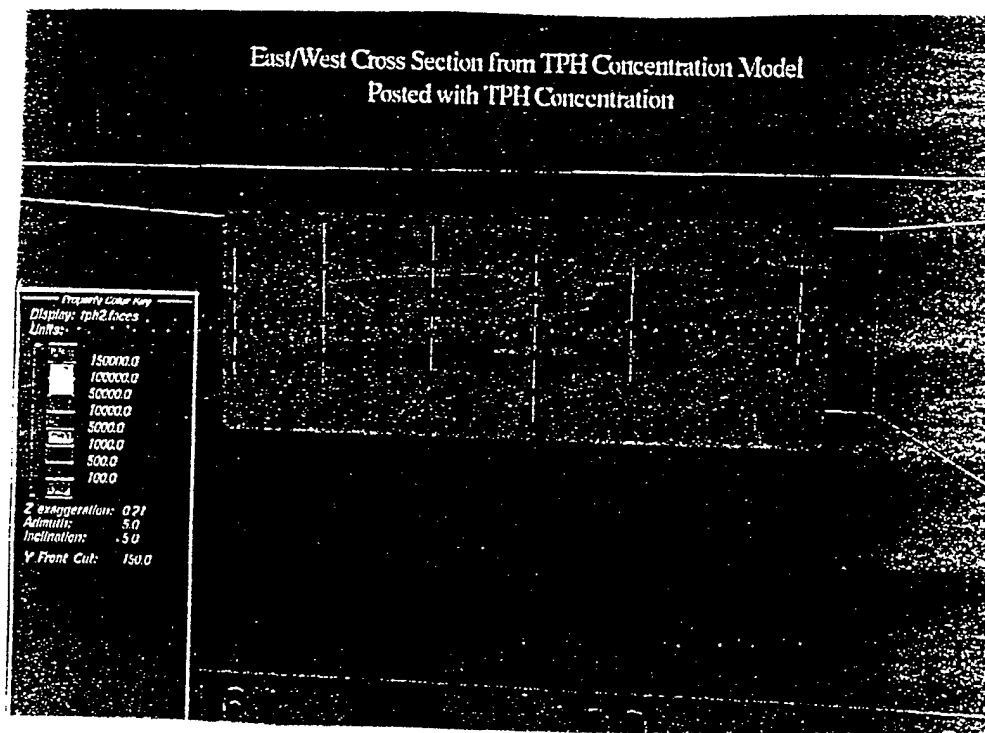Figure 13. SCAPS and Boring Data Cross Section for NAS, Alameda.
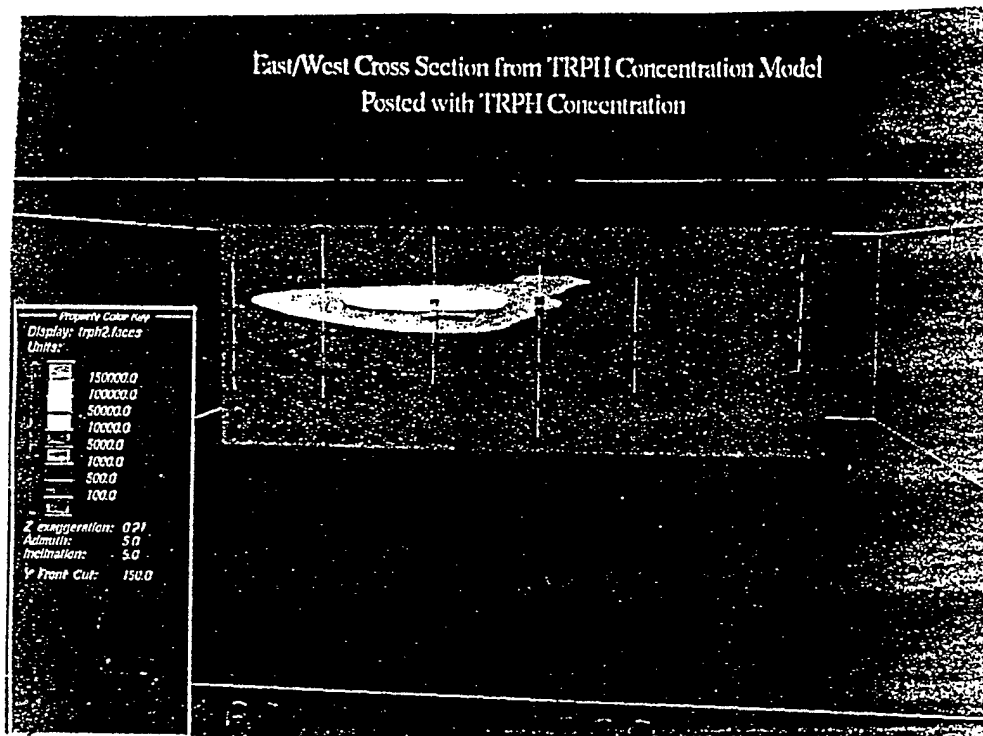

Figure 14. Cross Section of Contaminant Plume from TPH Model.

Figure 15. Cross Section of Contaminant Plume from TRPH Model.