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## RAPID DETECTION OF HYDROCARBON CONTAMINATION IN GROUND WATER AND SOIL

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### Abstract

In situ fluorometry is being developed as a method for rapidly detecting and quantifying hydrocarbon contamination in ground water and soil. The results of a fluorometry survey over a site having known fuel contamination are compared to results from a soil gas survey over the same site. The fluorometry data showed three additional contaminated areas that were not detected by soil gas measurements. Soil analyses confirmed the presence of the contaminated areas.

### Introduction

Hydrocarbon contamination from fuel leaks and spills is one of the most common ground water pollution problems in the United States. U.S. Environmental Protection Agency estimates indicate that there are over two million fuel storage tanks in the United States and any tank can potentially be a pollutant source (Valentinetti, 1989). Surveys of existing tank facilities indicate approximately 30% are leaking (Taylor, 1989). Leaks in underground storage tanks and underground fuel transfer lines are difficult to detect and locate. Often the leaks are so small that inventory studies are ineffective in locating the source of the pollutant. The rate of dissipation or natural degradation of fuel contamination in soil is extremely slow in many cases and even a small fuel leak can produce serious contamination that is extremely costly to remediate.

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In view of the magnitude and the continuing nature of the problem of hydrocarbon contamination, it is important that techniques for detecting and mapping hydrocarbon contamination in soil and ground water be continually improved. At present the major methods of locating hydrocarbon contamination in a site investigation involve the measurement of hydrocarbons in soil gas to determine the presence of volatile organic contaminants diffusing through the soil. However, all of the soil gas methods encounter the problem of irregular diffusion rates that vary due to changes in soil temperature, water content and atmospheric pressure changes. The correlation between the concentration of hydrocarbon vapor in soil gas and the concentration in soil is generally low (Marks and Singh, 1990).

An alternate method for locating and mapping hydrocarbon in soil has been developed based on the optical properties of petroleum contamination in soil. Initial trials suggest that in-situ fluorescence measurements made with a fiber-optic fluorometer mounted in a cone penetrometer offer significant advantages over soil gas measurements in mapping hydrocarbon contamination. The purpose of this report is to show the results of a soil contamination study done with a fiber-optic fluorometer and to compare the results with a soil gas survey done over the same area.

#### **Design of the Penetrometer/Fluorometer System**

Truck-mounted cone penetrometers are in routine use in the investigation of soil strength properties of foundations and roadway subgrades. The waste site investigation equipment was adapted from the design of a standard civil engineering penetrometer. The van body was modified to provide a separate instrumentation compartment that can be kept clean and for safety reasons is isolated from the compartment housing the rams and the penetrometer rods. Figure 1 shows the arrangement of the equipment. A complete description of the penetrometer unit is presented in Lurk et al. (1991).



Fig. 1. Photo of penetrometer truck and developed for investigation of hazardous waste sites.

The instrumentation built into the penetrometer rod includes the usual strain measurement systems for measuring vertical forces on the conical tip of the rod and the vertical forces on the friction sleeve mounted behind the cone. These two soil strength measurements taken together can provide an index of the soil type. Additionally, the cone is equipped with a sapphire window that allows light to be passed down an optical fiber and through the window to illuminate the soil immediately opposite the window. In measuring fluorescence, a 337 nm nitrogen laser is coupled to the fiber to furnish the illumination or excitation. Different petroleum products in the soil have different emission maxima depending on the characteristic types aromatic compounds present (Fig. 2). The major fluorophores are polynuclear aromatic compounds. The light passes back up through a second fiber and the energy distribution in the spectrum is determined using an optical multichannel analyzer. The position of the rod, the force on the tip, the sleeve friction, and the data from the spectral analysis are all recorded for each cm of the penetrometer push.

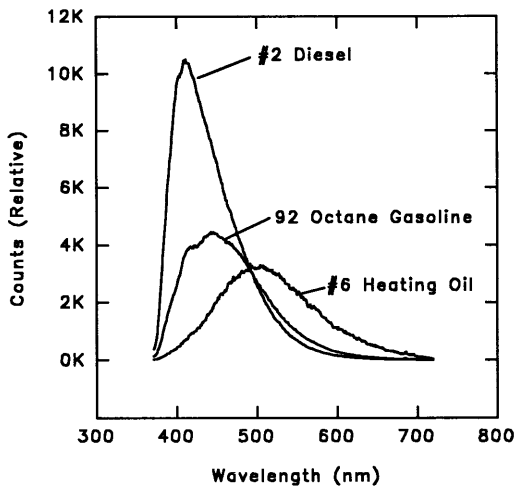


Fig. 2. Fluorescence spectra collected with the fiber-optic fluorometer from different hydrocarbon products. Each hydrocarbon was mixed in a moist (10% water) sand matrix.

A calibration curve is used to estimate the concentration of hydrocarbon present. The calibration curve presented in Fig. 3 was prepared using fresh diesel fuel in an Ottawa sand matrix. Note that the fluorometer can reliably locate diesel fuel down to concentrations as low as 500 ppm.

### Comparison of Soil Gas and Fluorometer Data

Figure 4 shows an oblique view of a three-dimensional plot of the volumes of soil contaminated at levels that provide a fluorescence intensity equivalent to or greater than that observed in soils contaminated with 500 ppm of diesel fuel. The surface area shown in Fig. 4 is approximately  $107 \text{ m}^2$ . The data are plotted in three dimensions to show the positions and the extrapolated shapes of the contaminated soil masses. The contour lines on the top side of the block show the results of a soil gas survey undertaken over the same area with a flammable gas meter calibrated on benzene. The soil gas survey and the fluorometer both show three major areas of hydrocarbon contamination on the east side of the site. Note that three additional areas on the west side of the study area were found with the penetrometer/fluorometer but did not appear in the soil gas survey data.

Soil samples collected from the northwestern end of the site showed up to 11,300 ppm hydrocarbon in the soil confirming the fluorometer data. Estimates of the hydrocarbon concentration from the soil fluorometer data taken from the same point ranged as high as 17,000 ppm. The soil gas survey showed no detectable hydrocarbon at this same point.

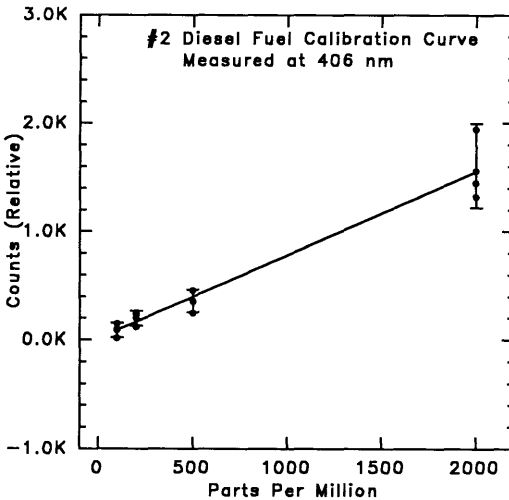


Fig. 3. Calibration curve for #2 diesel fuel mixed in sand. This type of curve allows the concentration of diesel-based pollutant in the soil to be estimated.

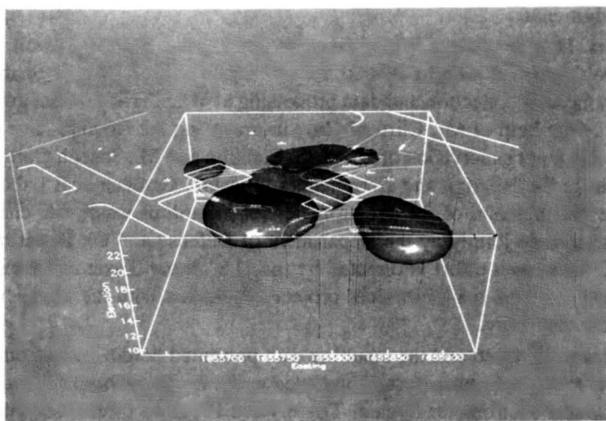


Fig. 4. Block view of a closed fuel storage/transfer area showing the soil that based on fluorescence has the equivalent of 500 ppm or more of diesel fuel contamination.

### Summary

This study offers an example of some of the basic features of the two soil survey techniques. The contrast between the two survey systems can be summarized as follows:

1) Low molecular weight hydrocarbons must be present for the soil gas system to be effective in locating contaminated soils. The fluorometer is most effective when heavy hydrocarbons with polynuclear aromatic components are present.

2) When the temperature and barometric pressure effects prevent the soil from outgassing, the soil gas measurements are ineffective. The fluorometer detects hydrocarbons directly in the soil regardless of the climatic or atmospheric conditions at the site.

3) Soil layers that have low permeability due to the presence of clay or due to a high water content can prevent the transmission of hydrocarbon vapor to the surface. Only direct measurement systems can operate consistently well if soil layering is complex. The cone penetrometer can map both the soil type and the contaminant concentration in a single push.

4) The soil gas survey can detect contamination from outgassing soils providing the location of a point on the surface above the hydrocarbon. The penetrometer sensor system can locate contamination at any depth down to approximately 50 m (in normally compacted soils) and can provide data on the depth, number and thickness of the contaminated soil layers.

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