

# **Use of Laser Induced Fluorescence to Detect DNAPL and Fluorophore Mixtures In-Situ**

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## **ABSTRACT**

We present results from laboratory investigations on the fluorescence of Dense Non-Aqueous Phase Liquids (DNAPL) and fluorophore mixtures, characterized using a Luminescence Spectrometer. Fluorophores such as aromatic compounds (e.g. benzene, toluene, ethylbenzene and xylenes, as well as other constituents of petroleum fuels, oils, lubricants and greases) are present as co-contaminants in many DNAPL spills. Concentration as low as 5% of fluorophore in the DNAPL solvent are easily detectable. Using the difference in characteristic fluorescence wavelengths for the various fluorophores, we are able to distinguish between naturally occurring fluorophores in the DNAPL solvent and introduced fluorophores. Field investigations using a Laser Induced Fluorescence (LIF) probe at several sites corroborate our laboratory results. Results to date indicate that the LIF probe will be applicable only for a qualitative assessment of DNAPL saturation, but may be useful in combination with other probes in the cone penetrometer for DNAPL source delineation.

**KEYWORDS:** DNAPL, site characterization, LIF, fluorophores, chlorinated solvents

## **INTRODUCTION**

To assess the risk of a Dense Non-Aqueous Phase Liquid (DNAPL) spill and design a remediation scheme, accurate site characterization is a prerequisite. Current methods for detecting DNAPLs in the subsurface are mostly "hit-and-miss". Split-spoon sampling is expensive, considering drilling, collection, handling and analytical work. It requires the collection of many samples which may have no contamination at all. Given the significant handling of split-spoon samples, there is a high probability of erroneous or inaccurate results using this method.

Soil vapors monitoring (Diem et al., 1988; Tolman and Thompson, 1989; Thomsen and Joyner, 1990; Rivett, 1995) may produce erroneous results since: (1) volatilization of dissolved halocarbons from the water table is not always detectable within the vadose zone; (2) vapor migration pathways do not necessarily match DNAPL distributions; (3) positive soil gas results do not provide any information about the

depth(s) of the DNAPLs; (4) there may be several layers of the aquifer contaminated by DNAPLs, which cannot be resolved from soil gas sampling; and (5) concentrations in soil gas may have only a weak correlation with the magnitude of the DNAPL zone, due to sorption and biodegradation processes

Laser Induced Fluorescence (LIF) probes have been used for several years to successfully pre-screen and characterize petroleum-contaminated sites (Chudyk et al., 1985; Lieberman et al., 1991; Luedeker et al., 1995; Lin et al., 1995; Xun et al., 1995; Nielsen et al., 1995). Several commercial probes are available, mounted on cone penetrometers (Litherland et al., 1986). There is no comparable tool to detect DNAPLs in the subsurface. The technique proposed here will address this issue and should result in an extension of the LIF probe capabilities for DNAPL site characterization.

## **OBJECTIVES OF THIS STUDY**

Our principal objective of our research is to develop in-situ tools for detecting DNAPLs in the subsurface. Our work builds upon existing LIF and cone penetrometer technologies, which can result in rapid implementation of our results. Since anecdotal evidence exists of the use of LIF probes for DNAPL detection, our research is directed towards providing a sound basis for the application of the technology, by performing a rigorous laboratory correlation between presence of DNAPLs with fluorophores and the fluorescence signal.

## **METHOD**

Mixtures of DNAPLs and common fluorophores (aromatic hydrocarbons, fuels, lubricants, greases and humic substances) were characterized in the laboratory using a Fluoromax-2 Spectrofluorometer (Jobin Yvon-Spex) to determine their fluorescence properties. Trichloroethylene (TCE) and tetrachloroethylene (PCE) were used as typical DNAPLs, based on their occurrence at contaminated sites. Humic substances were obtained by passing TCE through a loamy soil sample and characterized using GC/MS. The optimal excitation wavelength was identified to provide a high fluorescence signal for most of the fluorophore/DNAPL mixtures.

## **EXPERIMENTAL RESULTS**

Figure 1 presents spectra of mixtures of benzene and TCE at various concentrations. The mixture was excited at a wavelength of 290 nm, which results in a strong fluorescence at 292 and 306 nm. The fluorescence intensity is greater for pure benzene and decreases with the addition of TCE. Figures 2-6 present the relationship between fluorophore concentration and fluorescence signal intensity for mixtures of TCE and gasoline, diesel, motor oil, automotive grease and humic substances, at selected emission wavelengths where fluorescence intensity is highest (peak wavelength). The concentration of the fluorophore is indicated in the legend. All samples were excited at 325 nm.

## DISCUSSION

Fluorescence of aromatic compounds (e.g. benzene, toluene) in TCE or PCE increases with concentration. Fluorescence of common fuel, lubricant and humic substances is complex, given the large number of possible fluorophores. Signals are strong at low concentrations, but at higher concentrations of fluorophores in the DNAPL solvent self-absorption and self-quenching significantly reduces the signal. However, DNAPL mixtures are not expected to contain large fractions of these mixtures. High fluorescent intensities are seen for mixtures of common fuels, lubricants and humic substances using an excitation of 325 nm. GC/MS characterization of the mixtures indicates that even low concentrations of possible fluorophores (1-5%) in DNAPLs produce a significant signal. Background fluorescence of humics attached to soils is typically low and should not interfere strongly with the fluorescence of DNAPL/fluorophore mixtures. Humics are considerably more concentrated in DNAPL solvents than in soils. Further studies are under way to determine the effect of background noise. However, in commercial applications of the LIF/cone penetrometer technology to locate petroleum hydrocarbons, the background soil organic matter signal is significantly lower than the fluorescence of the contaminants in the organic phase.

## CONCLUSIONS

Strong fluorescent signals even at low fluorophore concentrations can be generated from mixtures of common fluorophores present in industrial and commercial settings (e.g. gasoline, diesel, motor oil and grease) and chlorinated solvents (e.g. TCE, PCE). DNAPLs may also fluoresce after they have extracted humic substances from the soil organic matter present in the subsurface, even for dilute solutions of humics in DNAPLs. Preliminary field testing using LIF to detect DNAPLs mixed with common fluorophores (Kram, 1998) indicates that this may be a feasible method to delineate the DNAPL source zones, and thus design better remediation processes. Additional laboratory work is planned using a LIF probe and precise soil sampling to correlate the presence of DNAPL/fluorophore mixtures with the LIF signal, and to determine the minimum detection level. The LIF probe is not expected to serve as a means of determining DNAPL saturation or fluorophore concentration; it may serve to indicate the possible presence of DNAPL.

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