

USE OF FLUOROPHORE/DNAPL MIXTURES TO DETECT DNAPLS IN-SITU

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ABSTRACT: 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 Dense Non-Aqueous Phase Liquid (DNAPL) spills or may be extracted by the flowing organic phase from the soil organic matter. From 10 to 25% of the carbon present in humic and fulvic acids (a major component of soil organic matter) is in aromatic rings and these naturally occurring compounds have specific fluorescence spectra. Chlorinated solvents have been used extensively at many military, industrial and commercial installations precisely to degrease and clean surfaces which contain fluorophores. The fluorophore/DNAPL mixture may be detected in-situ using Laser Induced Fluorescence (LIF) probes, allowing the detection and delineation of the DNAPL source zone(s). We present results from laboratory investigations on the fluorescence of mixtures of these fluorophores in DNAPLs, characterized using a Luminescence Spectrometer. Concentration as low as 5% of fluorophore in the DNAPL solvent are easily detectable with the current instrument. 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. Preliminary field investigations using a LIF probe at a former Fire Fighter Training Facility located on a military installation situated in the Central Valley of California corroborate our laboratory results. Further field testing is planned to determine the detection limits of the optimized LIF probe, corroborating with traditional sampling methods. Results to date indicate that the LIF probe will not be applicable for a quantitative assessment of DNAPL saturation, but may be useful in combination with other probes in the cone penetrometer for DNAPL source delineation. The information generated by the probe will significantly extend the ability to characterize a contaminated site, improving modeling, risk assessment and site management.

INTRODUCTION

Accurate site characterization is a prerequisite for designing a remediation scheme to remove the DNAPL source zone. DNAPLs can migrate horizontally as well as vertically during their travel through the subsurface (Schwille (1988), Mackay et al. (1985), Abriola (1989), Kueper and Frind (1991)). Current methods for detecting DNAPLs in the subsurface are mostly "hit-and-miss". Split-spoon sampling with no "pre-screening" of the site is expensive (considering drilling, collection, handling and analytical work) and requires the collection of many

samples which may have no contamination at all. Producing an accurate vertical and horizontal profile of the DNAPL source zone can be very expensive using this method.

An alternative is to monitor soil vapors (Diem et al., 1988; Tolman and Thompson, 1989; Thomsen and Joyner, 1990; Rivett, 1995), but this 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
- 5) concentrations in soil gas may have only a weak correlation with the magnitude of the DNAPL zone, due to sorption and biodegradation processes

LIF probes have been used successfully to pre-screen and characterize petroleum-contaminated sites (Chudyk et al., 1985, 1987, 1990; Vo-Dinh et al., 1990; Lieberman et al., 1991; Lurk 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

- Develop an in-situ tool for detecting DNAPLs in the subsurface that can serve to delineate the source zone (i.e. DNAPL residuals and DNAPL pools)
- Build upon existing Laser-Induced Fluorescence (LIF) and cone penetrometer technologies, for rapid implementation
- Provide 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

The fluorescence of mixtures of DNAPLs and common fluorophores (aromatic hydrocarbons, fuels, lubricants, greases and humic substances) was characterized in the laboratory using a Fluoromax-2 Spectrofluorometer (Jobin Yvon-Spex). Different concentrations of fluorophores in trichloroethylene (TCE) and tetrachloroethylene (PCE) were prepared, to determine the minimum threshold concentration needed to detect the DNAPLs. 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

Figures 1 and 2 present typical spectra of mixtures of benzene and TCE at various concentrations. In Figure 1, the mixture received excitation at a wavelength of 290 nm, which results in a strong fluorescence at 292 and 306 nm. Figure 2 presents the results of exciting the mixture with a wavelength of 325 nm, with peaks at 366 and 385 nm. The fluorescence intensity is greater for pure benzene and decreases with the addition of TCE. The lower excitation wavelength (290 nm) provides photons with the specific energy to generate a state transition and thus results in stronger peaks than the 325 excitation wavelength.

Figure 1. Benzene in TCE @ 290 nm

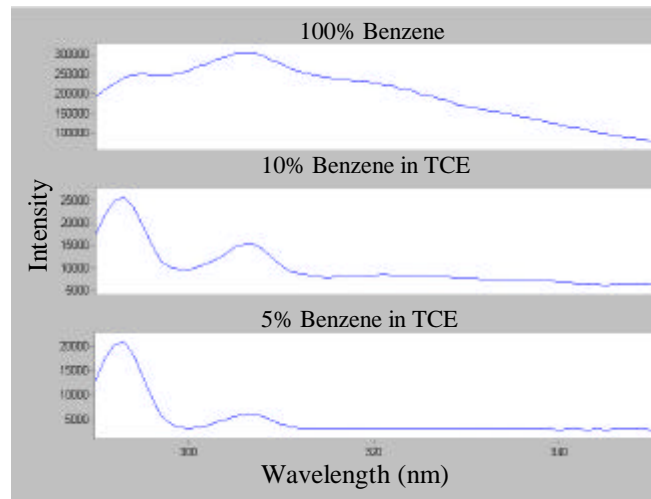
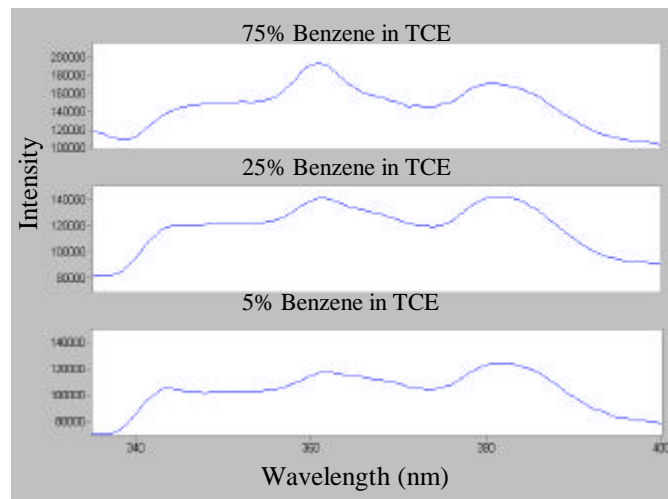


Figure 2. Benzene in TCE @ 325 nm



Figures 3-7 present the relationship between fluorophore concentration vs. fluorescence signal intensity for mixtures of TCE with (a) gasoline; (b) diesel; (c) motor oil; (d) automotive grease; (e) humic substances, at selected wavelengths. All samples were excited at 325 nm.

Figure 3. Gasoline in TCE

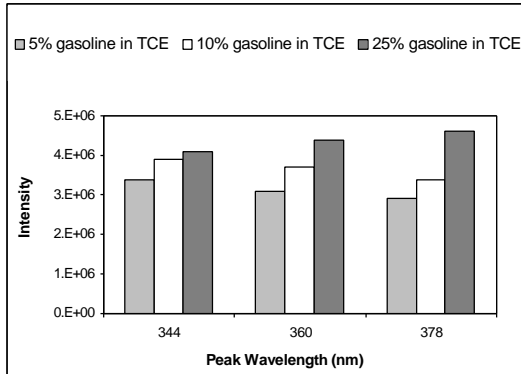


Figure 4. Diesel in TCE

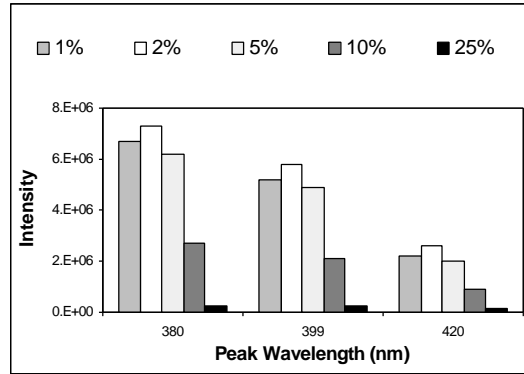


Figure 5. Oil in TCE

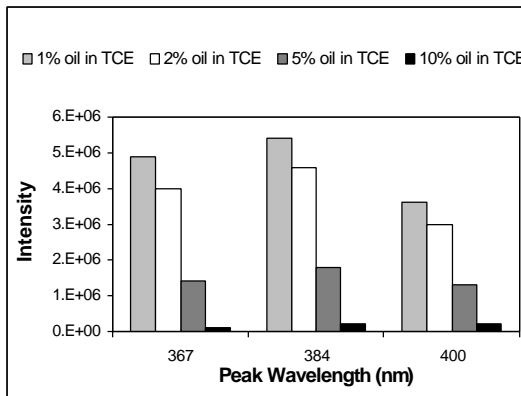


Figure 6. Grease in TCE

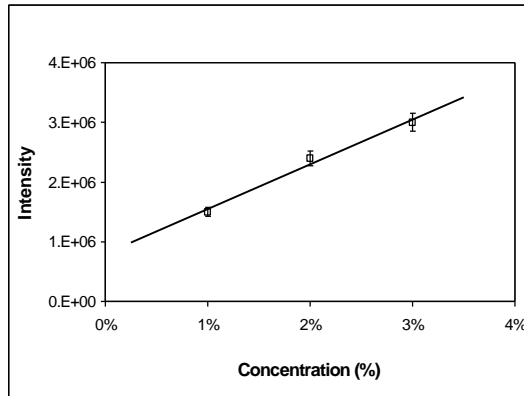
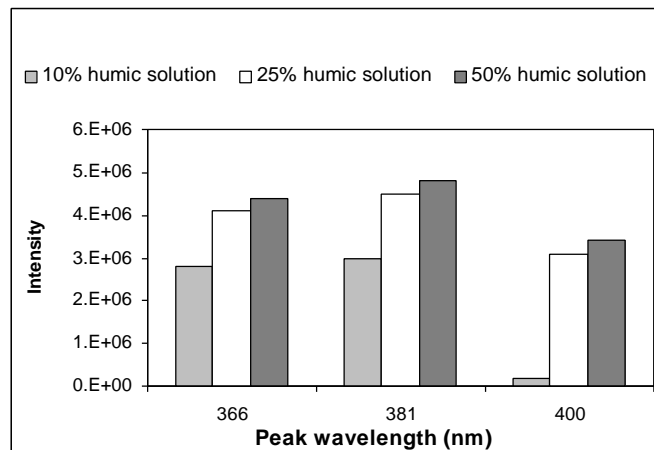


Figure 7. Humic substances in TCE



DISCUSSION

Fluorescence of pure aromatic compounds (e.g. benzene, toluene) in TCE or PCE increases monotonically with concentration. Fluorescence of common fuel, lubricant and humic substances is complicated by the large number of possible fluorophores. Fluorescent signals are very strong at low concentrations, but at higher concentrations self-absorption and self-quenching of the incoming and outgoing radiation significantly reduces the signal. However, DNAPL mixtures should not contain large fractions of these mixtures. Practical considerations in the design of the LIF probe (optical transmissivity of fiber optic cable is severely reduced below ~ 300 nm) directed our attention to wavelengths near the fluorescent region of multi-ring aromatics (325-340 nm). 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. Humics are more concentrated in DNAPL solvents than in soils.

CONCLUSIONS

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) produce strong fluorescent signals even at low fluorophore concentrations. DNAPLs may also exhibit fluorescence in the subsurface after they have extracted humic substances from the soil organic matter present. The fluorescence signal is discernible even for dilute solutions of humics in DNAPLs. Preliminary field testing using LIF to detect DNAPLs mixed with common fluorophores 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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