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PROCEEDINGS**

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CHARACTERIZATION OF HYDROCARBON-CONTAMINATED SITES USING DIRECT SENSING TECHNOLOGIES: ADVANTAGES AND LIMITATIONS

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Abstract

Understanding of nonaqueous-phase liquids (NAPLs) distribution in the subsurface is a fundamental component of any hydrocarbon-contaminated site remediation strategy. A recent trend in direct push (DP) technology is the use of direct sensing technologies such as Laser-Induced Fluorescence (LIF) and Membrane Interface Probe (MIP) in the investigation of hydrocarbon-contaminated sites. This study provides an overview of the key elements of LIF and MIP as screening tools for the contaminant spatial distribution characterization. Both technologies exhibit different advantages and limitations. In general, LIF enables the screening of residual and free-phase hydrocarbon petroleum products by detecting polycyclic aromatic hydrocarbons (PAHs). On the other hand, MIP enables detecting and distinguishing different zones of VOC contamination within a site. Overall, the qualitative to semi-quantitative information provided by these innovative techniques is highly valuable for the spatial characterization of hydrocarbon contamination, the development of a conceptual site model (CSM), and remediation activities.

Keywords: groundwater, contaminant distribution, petroleum hydrocarbons, remediation

INTRODUCTION

Petroleum hydrocarbons are among the most common groundwater contaminants, due to their widespread use (Alvarez and Illman, 2006). U.S. EPA (2003) listed about 440,000 sites impacted by gasoline releases only from leaking underground storage tanks. Other sources of hydrocarbon contamination include leaking pipelines, petroleum exploration, and disposal of refinery wastes. Once reaching the subsurface, this diverse group of compounds represents a persistent source of groundwater and geologic media contamination (Marić et al, 2015). Thus, an understanding of the hydrocarbon distribution is a fundamental component of any remediation of contaminated sites. The direct push (DP) technology pioneered by Geoprobe is the least expensive used drilling method in professional hydrogeology in the United States (Kresic and Mikszewski, 2013). A new trend in DP technology is the use of direct sensing technologies such as Laser-Induced Fluorescence (LIF), and Membrane Interface Probe (MIP). These innovative techniques can provide qualitative to semi-quantitative information about the spatial distribution of subsurface hydrocarbon contamination. This study aims to provide a brief overview of LIF and MIP key elements regarding their application at hydrocarbon-contaminated sites.

OVERVIEW of LIF and MIP TECHNIQUES

LIF technique

This innovative technology can be used for detecting residual and free-phase nonaqueous-phase liquids (NAPLs) containing polycyclic aromatic hydrocarbons (PAHs) (U.S. EPA, 2016). Although petroleum hydrocarbons are a mixture of different compounds, they nearly always contain enough PAHs for detection by LIF. However, it should be emphasized that LIF screening cannot detect the dissolved phased contaminants in groundwater (U.S. EPA, 2016). The probe is pushed or driven at a constant rate through the sediments, while ultraviolet light emitted through a sapphire window causes fluoresce of PAH compounds. The current LIF sensors cannot identify individual chemicals (U.S. EPA, 2016), but the relative product saturation in soil and product types present (gasoline, diesel, jet fuel, motor oil, cutting fluids, hydraulic fluid, and crude oil) (U.S. EPA CLU-IN, 2015b). Five of the six currently commercially available UV fluorescent systems in the United States use a technology developed wholly or in part by Dakota Technologies (U.S. EPA CLU-IN, 2015b). The key elements of the LIF technology available on the Dakota Technologies website are summarized in Table 1.

Table 1. The main advantages and limitations of LIF technology modified from <https://www.dakotatechnologies.com/learn-more/intro-to-lif/overview>

Key element	Description
<p style="text-align: center;">Contaminants and concentrations</p>	<p>LIF detects the PAH fluorescence in NAPL</p> <p>In general, LIF does not detect chlorinated solvent DNAPL because they aren't fluorescent molecules. The exception is chlorinated DNAPL that contains enough fluorophores.</p> <p>LIF does not detect dissolved phase VOCs or SVOCs.</p> <p>LIF does not detect BTEX and/or other VOCs, since their wavelength is incompatible with fiber optics.</p> <p>LIF lower detection limit ranges between 10 and 1000 mg/kg (TPH), depending on fuel type and soil matrix.</p>
<p style="text-align: center;">Geologic media and materials</p>	<p>LIF detects NAPL both in vadose and saturated zones.</p> <p>rix affects fluorescence response – sands and gravels may have as much as 10 times higher response than clays and silts.</p> <p>LIF's potential false-positive responses include shell hash, meadow mat, peat, wood, and calcareous sands. Relative waveform shape and generally low intensity nearly always identify these as a suspect.</p>
<p style="text-align: center;">Technology production and compatibility</p>	<p>Typical LIF production is 200-500 feet per day.</p> <p>LIF probe is logged continuously with depth (2cm/s). No data gaps should be expected.</p> <p>LIF is compatible with both DP and cone penetration tests (CPT) and technologies.</p>

MIP technique

The MIP is a semi-quantitative, field-screening tool for detecting VOCs and some SVOCs in the subsurface (U.S. EPA, 2016). It uses heat to volatilize and mobilize contaminants for sampling both from the sediment and groundwater. This technology should be used primarily to distinguish different zones of VOC contamination within a site (U.S. EPA, 2016). In other words, the use of MIP technology enables to focus on the most contaminated zones within the site. Moreover, MIP can help evaluate soil type and delineate groundwater contaminant locations in real-time (Kresic and Mikszewski, 2013). Key advantages and limitations of MIP technology, modified from (U.S. EPA, 2016) are summarized in Table 2.

Table 2. Key MIP elements, modified and summarized from (U.S. EPA, 2016)

Key Advantages	Key Limitations
Can detect the presence or absence of subsurface VOC contamination and relative degree of contamination both in vadose and saturated zones	Detection limits depend on soil type, temperature, and detector used. Finer soils tend to yield lower detection limits than coarser soils. (U.S. EPA CLU-IN, 2015c).
Can advance relatively rapidly (1 foot/min).	Cannot readily distinguish between high concentration soil levels and free-phase NAPL (ITRC, 2015)
Acquires and analyzes data in near real-time.	Contaminant carryover indicated on MIP logs as extended contaminated zone likely in NAPL or high-concentration zones (ITRC, 2015)
In combination with other probes or sensors, can provide simultaneous logging of precise three-dimensional delineation of source and plume areas.	Because the sample mass and volume are not known, MIP data should be considered estimates (Myers et al., 2002).

Both LIF and MIP are direct sensing tools - enhancements of the DP technology. The general limitations of a DP system are that most sites have a practical depth limitation of 50 ft or less, while only small-diameter wells (2 in. or less) can be installed (Kresic and Mikszewski, 2013).

ConclusionS

Due to the uncertain spatial distribution of the contaminants in the subsurface, the reliable characterization of contaminated sites is of paramount importance. Thus, the use of cost-effective investigation and remediation techniques is important both from the practical and scientific standpoint. A recent trend in DP technology is the use of direct sensing tools such as LIF and MIP in the investigation of hydrocarbon-contaminated sites. In general, LIF enables the screening of residual and free-phase hydrocarbon petroleum products by detecting PAHs, while MIP enables distinguishing different zones of VOC contamination within a site. Both technologies exhibit their advantages and limitations. When used simultaneously over an extended area, LIF and MIP can provide a valuable spatial characterization of hydrocarbon contamination in the vadose zone, sediments, and groundwater.

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