

Aleksandar Prvanović¹, Nenad Marić^{2*}, Zoran Nikić²¹Hull & Associates, Inc, Emerald Parkway, Dublin, Ohio, United States, ²University of Belgrade, Faculty of Forestry, Department of Ecological Engineering, Belgrade, Serbia

Scientific paper

ISSN 0351-9465, E-ISSN 2466-2585

<https://doi.org/10.5937/zasmat2202122P>

Zastita Materijala 63 (2)

122 - 127 (2022)

Use of laser-induced fluorescence method in characterization of the site contaminated by petroleum hydrocarbons in United States

ABSTRACT

Spatial characterization of the contamination is a fundamental component of any remediation approach. Compared to conventional investigation methods, the laser-induced fluorescence (LIF) is a faster screening tool and provides the detection of hydrocarbon contamination in real-time. This investigation was conducted at a hydrocarbon-contaminated site in Pennsylvania, US. The presence of light nonaqueous-phase liquids (LNAPL) was detected in 6 of 17 LIF borings, with the reference emitter responses ranging between 45% and 225%. The depth of the response was highly accurate and valuable and provided insight into the spatial distribution of contamination. The results indicated that no substantial amount of LNAPL existed along the LIF borings profile, thus excluding this area as a preferential LNAPL migration pathway. The obtained results contributed to the characterization and remediation of this industrial site.

Keywords: groundwater, petroleum hydrocarbons, spatial characterization, Laser-Induced Fluorescence

1. INTRODUCTION

Due to their widespread use, petroleum hydrocarbons are among the most common environmental pollutants [1-4]. Hydrocarbons are persistent contaminants in the subsurface [5], and a significant source of groundwater contamination [6,7]. An understanding of the hydrocarbon distribution is a fundamental component of any remediation strategy for contaminated sites. The use of direct sensing technologies as screening tools for the contaminant spatial characterization is a relatively new trend in contaminant hydrogeology. To be more precise, laser-induced fluorescence (LIF) / ultraviolet optical screening tool (UVOST) technology is both efficient and effective method of determining the distribution of light nonaqueous-phase liquids (LNAPL) in the subsurface. The probe uses a high-energy laser to produce an ultraviolet light source for the detection of polycyclic aromatic hydrocarbons (PAHs), which are commonly found in petroleum products (Figure 1).

*Corresponding author: Nenad Marić

Email: nenad.marić@sfb.bg.ac.rs

Paper received: 15. 10. 2021.

Paper accepted: 17.12. 2021.

Paper is available on the website: www.idk.org.rs/journal

Although petroleum hydrocarbons are a mixture of different compounds, they nearly always contain enough PAHs for detection by LIF [8,9].

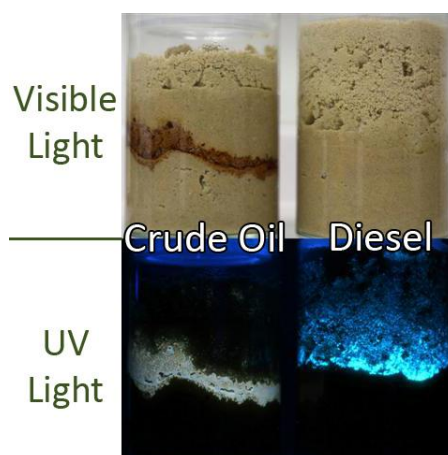


Figure 1. The utility of fluorescence for detecting petroleum. The different light colors emitted by the diesel vs. the crude oil are consequence of their PAH distribution/content [10]

Slika 1. Upotreba fluorescencije za detekciju nafte. Različite boje emitovane pri detekciji dizela i sirove nafte su posledica rasporeda i sadržaja PAH [10]

This investigation was conducted at a hydrocarbon-contaminated site in Pennsylvania,

US. It aims to provide insight into use of LIF as a screening tool for the contaminant spatial characterization.

2. MATERIALS AND METHODS

The LIF system used for the contaminated site investigation is the latest generation UVOST developed by Dakota Technologies, Inc. The system consists of a laser, fiber optic cables that are pre-strung through the direct push rods, an optical detection system, a laptop computer, and Shock Prevention Optical Cavity (SPOC). The screening was performed by pushing/hammering the SPOC into the soil at the average rate of two

cm/s. As the probe is advanced, the excimer laser generates energy which is transferred through the fiber optic cable to the optical cavity where the parabolic mirror reflects the energy through the sapphire window. Any PAHs that came in contact with the sapphire window then absorbed this photon energy. These PAHs then emit fluorescence in order to return to their base state. A portion of this fluorescence was carried back to the optical detection system via the second fiber optic. As the test proceeds, the total monitored fluorescence is recorded and displayed in real-time at one second intervals as a function of depth on the LIF/UVOST system computer (Figure 2).



Figure 2. The screening performed by pushing probe into the soil, while the LIF system displayed in real-time LNAPL fluorescence occurrence

Slika 2. Istraživanje izvedeno utiskivanjem sonde u sediment, dok je LIF system prikazivao prisustvo LNAPL u realnom vremenu

As a quality control check, the LIF/UVOST system response was evaluated prior to and upon completion of screening. This evaluation was completed using a Reference Emitter (RE) standard provided by Dakota Technologies, Inc.

The fluorescence intensity was presented as a percentage of the RE standard (% RE). Since various PAHs fluoresce at differing intensities, there are several compounds that fluoresce brighter than the RE standard, and therefore the total RE can exceed 100%. It should be emphasized that various LNAPLs have a unique waveforms signature based on the relative amplitude and shape of the channels (colored waveforms on LIF log). The fill color of the response waveforms on the primary graph is based on the relative contribution of each of the four channels' area versus the total waveform area. The characterization was completed using Dakota UVOST response to various random products saturated on wet sand for the expected wavelength

signature for common compounds [11]. Depth in feet was measured and recorded using a precision potentiometer. Measurements were recorded on the down stroke of the mast, as the tooling string was pushed into the ground (0.2 mm accuracy).

3. RESULTS AND DISCUSSION

3.1. Geology and hydrogeology of the study area

The study area is located within an industrial park in Pennsylvania. Its current and anticipated future use is commercial/industrial. Most of the study area is covered with asphalt or concrete pavement. Unconsolidated overburden material consists of subbase underlying the paved areas, and fill materials overlying the bedrock. Subbase consists of up to 0.6 m of sand, gravel and slag. Fill material underlies the subbase, consists of tight clay with varying amounts of silt, sand and gravel, and is up to 3.8 m below ground surface (bgs) in the northeastern portion of the site. At the central portion of the site fill is thinner (1.8 to 2.4 m bgs),

and consists of silt mixed with various amounts of clay and gravel. The predominant bedrock type underlying the site is thinly bedded and fine-grained shaley sandstone. The upper portion of the sandstone bedrock is weathered. Competent sandstone bedrock depth varies between 4.3 and 5.8 m bgs. Groundwater flow corresponds to the surface topography with groundwater generally flowing to the southwest. The NE-SW direction is consistent with the observed network of fractures interconnected with bedding planes. The bedrock water-bearing zone exhibited an apparent sub-artesian character. The average hydraulic conductivity K_{sat} based on pumping tests was 1.23 m/day. Using an average hydraulic gradient of

0.0085, and 15% as an assumed average effective porosity for sandstone, the average linear groundwater flow velocity was 0.064 m/day.

An unknown quantity of diesel fuel was released to the subsurface from an underground storage tank (UST) (Tank Field in Figure 3) due to the failure of an automatic tank gauge system riser cap. The accumulation of LNAPL within the UST cavity coupled with restrictive lateral and vertical migration pathways created LNAPL hydraulic head pressure. LNAPL infiltrated the more permeable weathered sandstone bedrock exposed in the sides of the UST cavity, which facilitated its release beyond the UST cavity (Figure 3).

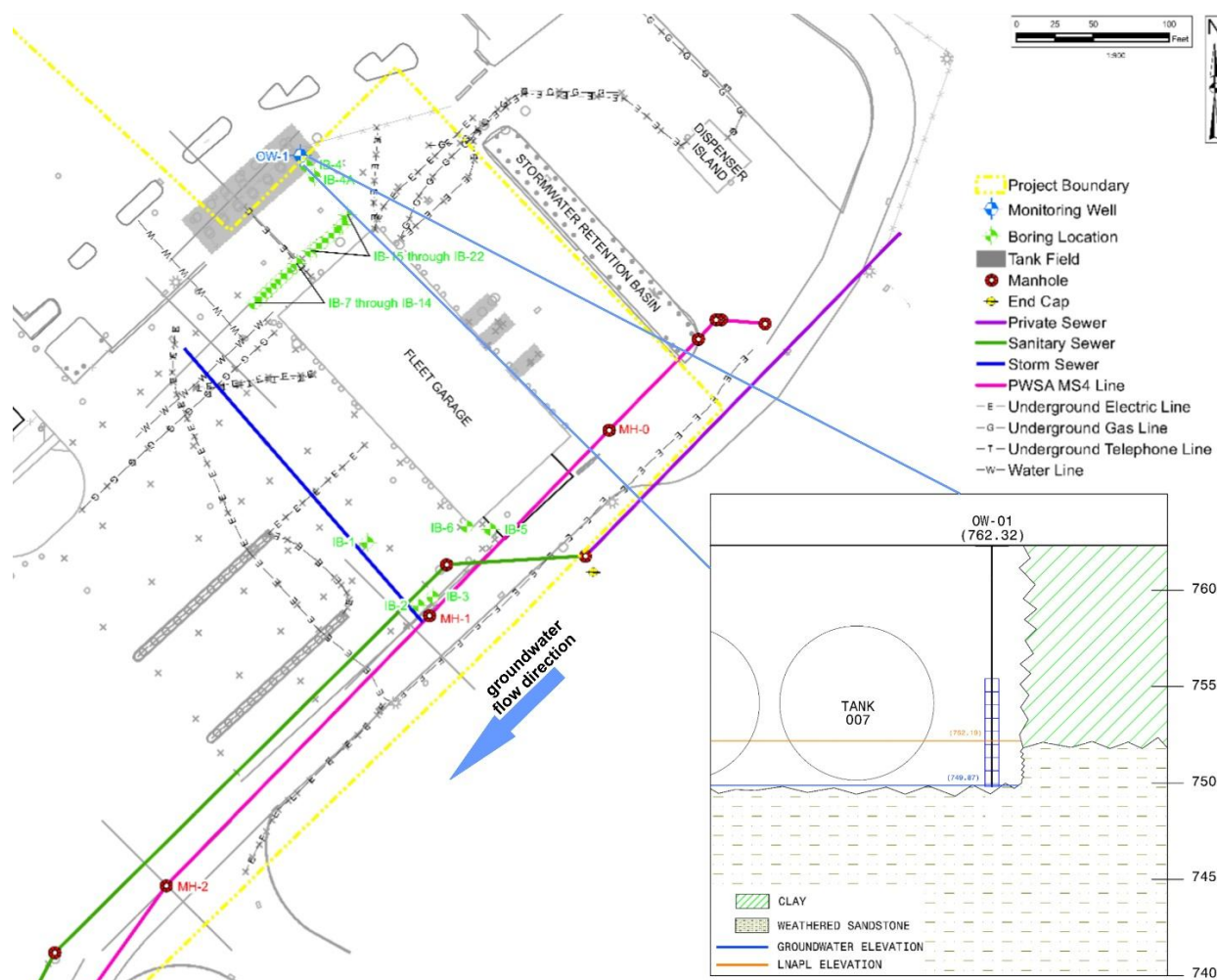


Figure 3. Site map and UST cross-section

Slika 3. Karta lokacije istraživanja i poprečni profil podzemnog rezervoara

The diesel migration primarily occurred via sub vertical and vertical fractures trending SW-NE and

SSE-NNW. It is apparent that while fractures played the primary role in bulk LNAPL migration,

bedding plane partings also played a role based on the pumping test analysis. Therefore, it was suspected that LNAPL migrated to, and accumulated within the storm sewer trench (MS4 line, Figure 3) through the bedrock and entered MS4 line via structural flaws, such as corroded collar joints and cracks. Further migration occurred through the MS4 line to the surface water feature where hydrocarbon sheen was initially observed.

3.2. LIF characterization

To determine if the MS4 line trench is the primary LNAPL accumulation feature and dominant migration pathway, the investigation consisting of 17 LIF/UVOST borings with depths ranging from 2.9 to 5.2 m bgs was performed. Individual LIF/UVOST logs (Figure 4) consist of a primary graph of total fluorescence versus depth and an

information box with waveform “callouts”. In the primary fluorescence graph, depth is plotted on the Y axis and the combined total fluorescence intensity of the four monitored waveforms is plotted on the X axis. Typical LIF responses in sand saturated with diesel fuel range between 200% and 300% of the RE.

Prior to advancing LIF borings, the centerline of the MS4 pipe was marked on the pavement and LIF boring locations were placed as close to the pipe as possible, thus, more likely to intercept adjacent fill material. Fifteen LIF borings were advanced adjacent the MS4 line. Two LIF borings (LIF-16 and LIF-11) were used as calibration points. A site map with results of LIF/UVOST investigation is shown in Figure 4.

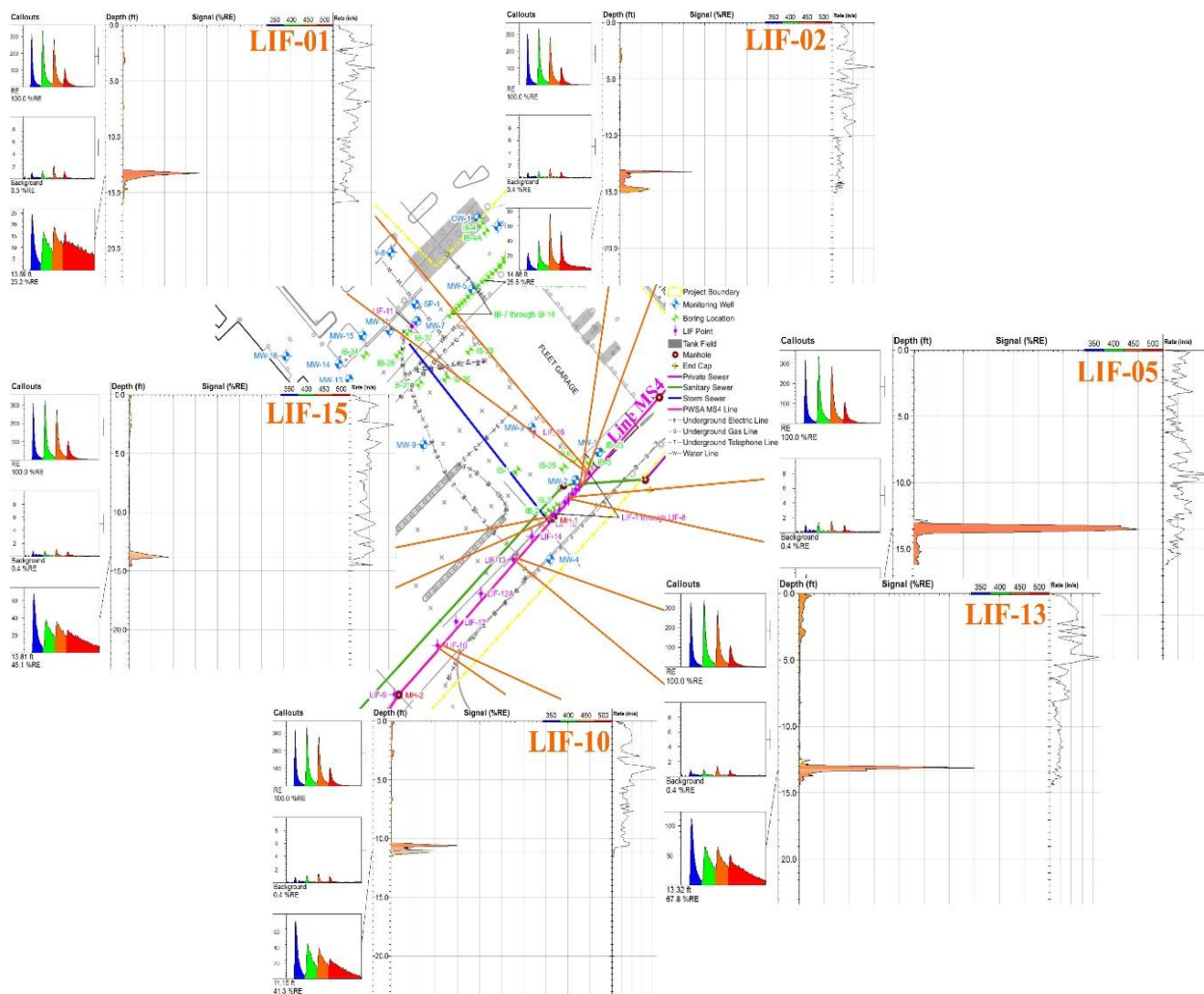


Figure 4. Results of LIF/UVOST investigation

Slika 4. Rezultati LIF/UVOST istraživanja

All borings were drilled through the overburden material and advanced until refusal, indicating that the top of bedrock is shallower near LIF-10. As shown on Figure 4, the results of the LIF/UVOST investigation indicated that LNAPL was detected in LIF borings 1, 2, 5, 10, 13, and 15 (3.9 to 4.6 m bgs). The exception was boring LIF-10 in which LNAPL was detected between 3.2 and 3.5 m. At the boring locations where LNAPL was detected, the RE responses ranged between 45% and 225%. The LNAPL detections were sporadic along the MS4 line, and indicated limited vertical extent of LNAPL concentrated mainly at the soil-groundwater interface. It was concluded that no substantial amount of LNAPL existed around the MS4 line, and that the MS4 line trench was not a conduit/preferential pathway for further downgradient LNAPL migration.

4. CONCLUSIONS

Understanding of NAPL distribution in the subsurface is a fundamental component of any hydrocarbon-contaminated site remediation strategy. This study emphasizes the potential of LIF in the investigation of contaminated sites. However, when different LNAPL types are present at the site, the system response should be considered only qualitative and not conclusively quantitative, due to the fact that different PAHs in different LNAPL types do not exhibit a linear correlation between the intensity of fluorescence and increase in concentration. On the other hand, the depth and the vertical extent of the response is highly accurate and may be relied upon to guide additional data gathering such as soil and/or groundwater sampling, and/or potential remediation design. The LIF/UVOST technology provided a quick and effective method of determining the presence and delineation of LNAPL in the subsurface of the study area. To be more precise, LNAPL was detected in 6 of 17 LIF borings, with the RE responses ranging between 45% (lower LNAPL saturation) and 225% (higher LNAPL saturation).

The LNAPL detections were sporadic along the MS4 line, and indicated limited vertical extent of LNAPL concentrated mainly at the soil-groundwater interface. Thus, the possibility of MS4 line trench serving as the preferential pathway for the bulk of released LNAPL was excluded. The obtained results provided crucial information for the subsequent study area characterization and remediation. Overall, this innovative technology can provide valuable insight into the spatial distribution of hydrocarbon contamination in the subsurface.

Acknowledgements

This research was supported by the Science Fund of the Republic of Serbia, Program DIASPORA, #Grant No. 6455306, GRACE.

5. REFERENCES

- [1] J.P.Alvarez, I.W.Illman (2006) Bioremediation and Natural Attenuation: Process Fundamentals and Mathematical Models, John Wiley & Sons, New York, NY.
- [2] R.Danovaro, N.Della Croce, M.Fabiano (1996) Microbial Response to Oil Disturbance in the Coastal Sediments of the Ligurian Sea (Nw Mediterranean), *Chemistry and Ecology*, 12(3), 187-198
- [3] G.Armiento, R.Caprioli, A.Cerbone, S.Chiavarini, C.Crovato, M.DeCassan, L.DeRosa, M.R. Montereali, E.Nardi, L.Nardi, M.Pezza, M.Proposito, J.Rimauro, A.Salerno, A.Salluzzo, F.Spaziani (2020) Current status of coastal sediments contamination in the former industrial area of Bagnoli-Coroglio (Naples, Italy), *Chemistry and Ecology*, 36(6), 579-597
- [4] L.Pang, S.Zhang, L.Wang, T.Yang, S.Wang (2021) Pollution characteristics and risk assessment of polycyclic aromatic hydrocarbons in the sediment of Wei River, *Environ Earth Sci* 80:203, <https://doi.org/10.1007/s12665-021-09483-z>
- [5] N.Marić, R.Petrović, Z.Nikić, V.Beškoski, P.Papić, I.Matić, M.M.Vrvić (2017) Natural attenuation of groundwater contaminated by petroleum hydrocarbons: mechanism, research concept and practical application, *Materials Protection Journal*, 58(4), 1–10.
- [6] U.S.EPA (2003) Data About The Underground Storage Tank (UST) Program, Washington, DC, Environmental Protection Agency. www.epa.gov/swerst1/pubs/ustfacts.pdf.
- [7] V.P.Beškoski, S.Miletić, M.Ilić, G.Gojgić-Cvijović, P.Papić, N.Marić, T.Šolević-Knudsen, B.S. Jovančićević, T.Nakano, M.M.Vrvić (2017) Biodegradation of Isoprenoids, Steranes, Terpanes, and Phenanthrenes During In Situ Bioremediation of Petroleum-Contaminated Groundwater, *Clean Soil Air Water*, 45: n/a, 1600023. doi:10.1002/clen.201600023
- [8] U.S.EPA CLU-IN (2015b) Hazardous Waste Cleanup Information, Laser-induced Fluorescence, Environmental Protection Agency. <http://www.clu-in.org/characterization/technologies/lif.cfm>.
- [9] U.S.EPA (2016) Expedited Site Assessment Tools For Underground Storage Tank Sites, Washington, DC, Environmental Protection Agency. <https://www.epa.gov/ust/expedited-site-assessment-tools-underground-storage-tank-sites-guide-regulators>.
- [10] <https://www.dakotatechnologies.com/learn-more/intro-to-lif/overview>
- [11] <https://www.dakotatechnologies.com/learn-more/intro-to-lif/data-interpretation>

IZVOD

UPOTREBA FLUORESCENCIJE INDUKOVANE LASERSKIM ZRAČENJEM (LIF) KAO METODE U SJEDINJENIM AMERIČKIM DRŽAVAMA

Prostorna karakterizacija zagađenja je ključna komponenta bilo kog remedijacionog pristupa. U poređenju sa konvencionalnim metodama istraživanja, fluorescencija indukovana laserskim zračenjem (LIF) je brža i omogućava trenutnu detekciju naftnog zagađenja. Ovo istraživanje je izvedeno na industrijskoj lokaciji zagađenoj naftnim ugljovodonicima u Pensilvaniji, SAD. Prisustvo "lake" faze zagađenja (LNAPL - dizel) je potvrđeno u 6 od 17 bušotina, lociranih duž rova u kojem je cev za odvod kišnice, sa intenzitetom LIF signala u rasponu između 45% i 225% (procenat referentnog emitera). LIF sistem je omogućio precizno definisanje dubine LNAPL faze omogućivši uvid u protostorni raspored zagađenja. Rezultati su ukazali da ne postoji značajan "rezervoar" LNAPL duž ispitivanog profila, isključivši mogućnost da pomenuti rov za odvod kišnice predstavlja glavni pravac migracije zagađenja. Sveukupno, dobijeni rezultati doprineli su karakterizaciji i remedijaciji ove industrijske lokacije.

Ključne reči: *podzemne vode, naftni ugljovodonici, prostorna karakterizacija, fluorescencija indukovana laserskim zračenjem*

Naučni rad

Rad primljen: 15. 10. 2021.

Rad prihvaćen: 17. 12. 2021

Rad je dostupan na sajtu: www.idk.org.rs/casopis