Geophysical and geochemical investigation of hydrocarbon subsurface contamination

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Abstract In Serbia as in many other countries, hydrocarbon contamination (such is Light Non-Aqueous Phase Liquid -LNAPL contamination of soils) near oil refinery or gas station remains a major problem of environmental concern. The detection of petroleum hydrocarbon contaminants such as LNAPL in the subsurface using geophysical and geochemical methods, has been the subject of considerable interest in recent years. Their surface non-invasive detection is based principally upon the electrical soil properties and processes related to biodegradation of the hydrocarbons. Geophysical investigation is conducted at the location of RNS (Refinery Novi Sad), Serbia. The objective of this study was to evaluate the possibilities of geophysical (Electrical Resistivity Imaging-ERI, and Ground Penetrating Radar-GPR) techniques in detecting and locating anomalies of hydrocarbon contamination. Geochemical investigation of LNAPL contamination at this site are compared with ERI and GPR interpretation results. Sediment samples at RNS were collected from both uncontaminated and contaminated locations. Samples were obtained using Eijkelkamp rig and stored in the laboratory refrigerator until measurements were made. Evidence, obtained from a joint geochemical and geophysical investigation approach, indicated that subsoil which has been saturated with hydrocarbon contamination for a long period (> 1 year) exhibits an increased conductivity or decreased resistivity.

Keywords: environmental pollution, LNAPL, ground penetrating radar, contamination, electrical resistivity imaging, soil sample chemical analysis

1. Introduction

The task of outlining the amount of LNAPL present in soils and water was a remarkable challenge for engineers who were involved in soil and water remediation. Hydrocarbons are partitioned into various phases (vapor, residual, free and dissolved) in the subsurface. These phases have different spatial and temporal natures. The distinct properties of these phases are making the characterization more difficult and complex for the problem of soil and water remediation (Atekwana *et al.*, 2010). Moreover, LNAPL and associated dissolved plumes are dynamic systems whose chemistry is changing in time and position within the plume. During time and seasonal recharge, the residual and free phase LNAPL zones move up and down in the aquifer with fluctuations in the water table. To overcome the LNAPL plume identification and characterization problem, engineers use geochemical techniques to analyze soils and water samples collected in boreholes and piezometers. These techniques are expensive. Geophysical techniques, as inexpensive and minimally-invasive, reduce the cost of subsurface LNAPL contamination investigation. As such, geophysical techniques including electrical resistivity (ER), ground penetrating radar (GPR), electromagnetic induction (EM), Self-Potential (SP), induced polarization (IP) and magnetic, have been applied to the hydrocarbon contamination investigation, e.g., (Atekwana *et al.*, 2010, Allen, 2007, Sauck, 2000). Numerous studies were published on the broad topic of electrical resistivity investigation in soil contamination detection. We were examining the ER and GPR signatures of LNAPL historical (long term) contamination, as a consequence of microbial processes that are the primary cause of the physical and chemical modification in the polluted environment. The theoretical basis for the use of geoelectrical methods (ER and GPR) for the detection of LNAPL contaminants in the subsurface is dependent on the contrasting electrical properties.

Recent hydrocarbon contamination is resulting in high resistivity anomalies, while mature oil contamination produces low resistivity anomalies (Sauck, 2000). Several months after the spill has occurred, oil contamination creates a low resistivity zone.

According to Sauck, 2000., the low resistivity anomaly is due to an increase of Total Dissolved Solids (TDS) in the acid environment, created by the bacterial action in the vadose zone or below the groundwater table (GWT). This zone is produced by a high TDS leachate which is non-periodically flushed down from the volume of intimately mixed hydrocarbon, water, oxygen and soil where microbial activity is a maximum. This leachate is a result of acidification of the heterogeneous free/residual product levels by organic and carbonic acids. This process is induced by the leaching and etching of the native mineral grains and grain coatings.

Two cases of contamination ware goal of this work (see Table 1).

Table 1. Two types of contamination at RNS and OC location

Contamination	RNS	OC
Type	Spills over the large surf. area	Point source spills
Age (years)	Several	> 10
Scale	Large	Small
Depth of GWL (m)	2-4	2
Cause of contamin.	Surface spills	Leaking underground storage tank

2. Geological settings

The RNS (Refinery Novi Sad, Fig.2a) is situated along the left bank of the Danube River. The terrain is formed of alluvial deposits, mostly sand and gravel, deposited in the zone of Danube meanders on a relatively flat field with low sides. The RNS was constructed along the natural terrain which is backfilled with sand to the elevation of 77.2 to 78.2 m above sea level (thickness of sand from 1 - 3 m). These sediments overlie the primary sandy aquifer.

Figure 1. Locations of the study area: a) RNS b) OC

Regarding the hydrogeology characteristics of the area, a permanent free aquifer is present in the sandy layers. The water level regime is related directly to the regime of the Danube and changes depending on the Danube's water level.

The groundwater flow direction is influenced by the regime of the Danube River. In the refinery, the prevalent flow direction is from North to South. The mean velocity of the groundwater flow is unknown, although the expected permeability in this lithological context is medium to high. Groundwater level in the Refinery area is usually between 2-4 meters below ground level, in backfilled sand.

The gas station OC (″Obrenovac centar″, Fig.2b) is located on the left bank of artificial canal Stara Tamnava. The terrain is made of alluvial sediments, mostly clay with sand (from the surface to the 2 m) and with small-grained sandy gravel above the impermeable clay layer.

The water level regime is directly related to the seasonal changes and is significantly lower than on the RNS locality. The depth of the aquifer is 2.5 meters maximum.

3. Methodology and results

3.1. Geophysical investigation

Geophysical methods are the decisive tool for the evaluation of the contamination in an indirect manner through the physical parameters such as resistivity, dielectric properties, chargeability, velocity, etc. In this work, a geophysical investigation had been performed using DC Resistivity and electromagnetic Ground penetrating radar (GPR) in sandy soil contaminated sites.

3.2. Electrical resistivity imaging (ERI)

The ABEM Terrameter LS has been used for data gathered up in this survey. The measurements were carried out using multiple gradient protocol electrode configurations along one profile at RNS location. The multiple gradient protocol provides detailed data related to limited depth with good vertical and horizontal resolution (Dahlin and Zhou, 2006). Wenner array was used at OC location. The applied current intensity was 100 mA. The data collected in the field are interpreted with RES2DINV software (Loke & Barker, 1996), which automatically subdivide the subsurface into a number of blocks, and then least-squares inversion scheme was used to determine the appropriate resistivity values for each block in 2-D.

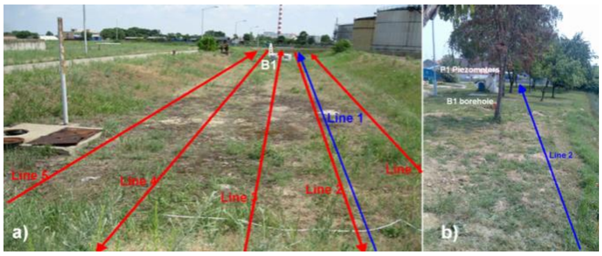

Figure 2. Profile position at a) RNS location (GPR-red line, ERI-blue line) and b) OC location (ERI-blue line).

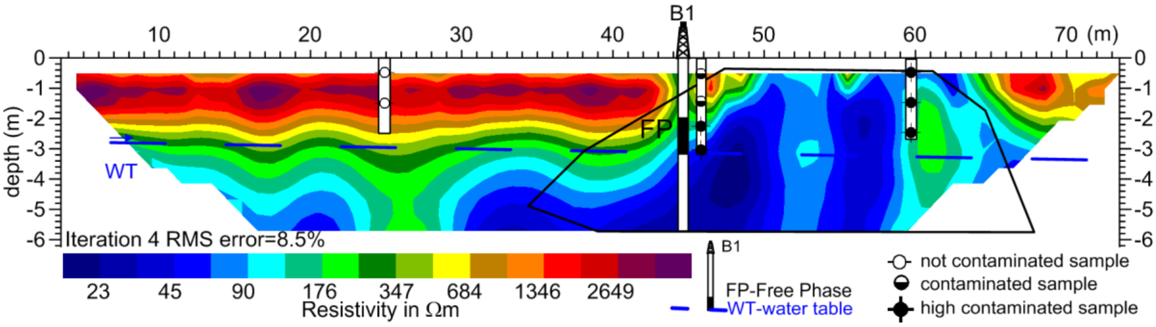

Figure 3. RNS location, ERI Inverse model resistivity section across hydrocarbon contamination plume.

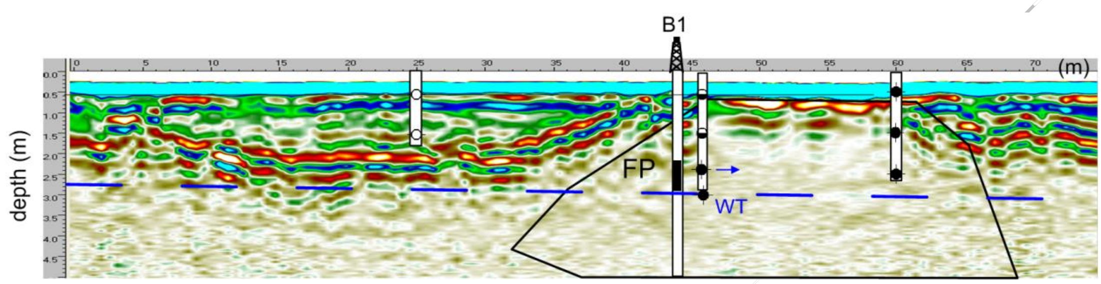

Figure 4. RNS location, line 2 GPR profile across a hydrocarbon contaminated site.

Two different sites of oil contamination were studied in Serbia. The RNS and pipeline accident at OC gas station, (see Fig.1 and Fig. 2).

3.3. Ground penetrating radar (GPR)

The TR-GEO-01 system ground penetrating radar was used in this work. The system is mid frequency video pulse georadar designed for sounding of various objects in grounds with low and moderate attenuation of radio waves. Among else, this system is suited for sounding and detection areas of leakage of oil products from the pipeline. The depth of detection in the wet sandy ground with clay loam and low moisture content is up to 5 m. The average frequency of video pulse spectrum is from 110 to 150 MHz. Prior to the producing time/depth section, the data were filtered to remove the DC current effect and then was multiplied by gain functions to overcome the attenuation effect of the earth materials. Measurements were made along five parallel lines (Fig.2a). Collected data, were processed using 'Radar' software to produce 2D radargram. GPR measurements were conducted on RNS location only.

3.4. Geochemical investigation

Geochemical investigation of LNAPL contamination at this site was conducted to confirm with geophysical investigation ERI and GPR. Sediment samples at RNS were collected from both uncontaminated and contaminated locations. Samples were obtained using the Eijkelkamp rig and stored in the laboratory refrigerator until the measurements were made.

4. Geoelectrical and geochemical data interpretation

Geophysical field experiments were conducted on the two sites to assess the efficiency of these nondestructive techniques to map hydrocarbon impacted areas, to recover the geometry and to detect the oil plume extent. In order to construct a 2D model of the subsurface, geoelectrical surveys were carried out in RNS 1 ERI profile and 5 GPR profiles (Fig.2a), and in OC gas station 1 ERI profile (Fig.2b). Inversion results of ERI data are depicted in Fig. 3 and Fig. 5. One from RNS, and the other from OC gas station. Long term contamination with hydrocarbons of the LNAPL type, in the permeable formation are exposed to microbial degradation which changes the original natural groundwater geochemistry and the distribution of gaseous components in the vadose zone. Baedecker, *et al*. (1993) reported in detail the geochemical processes connected with hydrocarbon degradation in the vadose zone, as well as in the upper part of the saturated zone. The most important characteristics of these processes are the formation of organic acids, the enrichment of ground water with Fe^{2+} and Mn^{2+} cations, outgassing of CO_2 and CH_4 into the vadose zone. Organic acids and the carbonic acid attack rock minerals and extract from them further cations like Ca^{2+}, Mg^{2+}, etc. All these geochemical changes have as a consequence the changes in physical properties of ground water below the spill and of the rock medium around the groundwater table. Geochemical investigation of LNAPL contamination at these two sites is compared with electrical resistivity imaging. Sediment samples at RNS and OC were collected from both uncontaminated and contaminated locations.

Ferrous iron Fe^{2+} was analyzed as well as Mg^{2+}, pH, Ca^{2+}, TPH (Total Petroleum Hydrocarbon), and electrical resistivity.

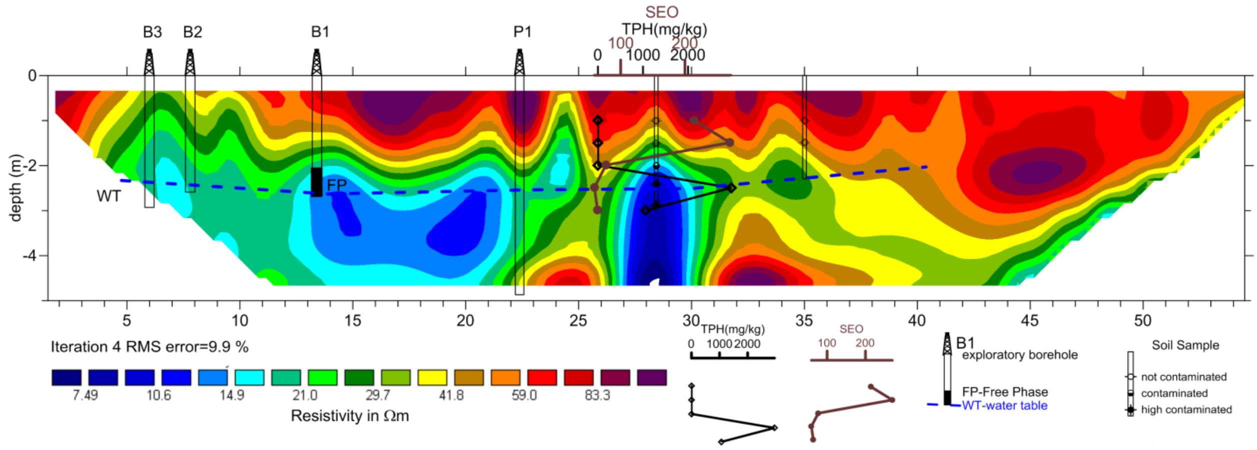

Figure 5. OC-ERI Inverse model resistivity section across hydrocarbon contamination plume.

These sites are different in contamination type, age, scale, depth of groundwater level (GWL), environment, surface conditions and the cause of contamination (Table 1). RNS contamination type is spilling over the large surface area, OC gas station is the point source spill caused by leaking underground gas storage tank. Long term contamination is present at both sites, OC several years RNS more than 10 years.

4.1. Location RNS

The resistivity survey measurements were made along one profile of 75 m long. Geoelectrical imaging surveys are carried out with multielectrode resistivity system using Gradient array at 1 m electrode spacing. In this survey, 81 electrodes were deployed in a straight line with constant 1 m spacing and connected to a 4 multicore cable. Each cable has 21 take outs. A computer-controlled system was then used to select the active electrodes for each measurement.

Figure 3 shows an electrical resistivity profile obtained in RNS (see Fig. 2a for profile 1 location).

The inversed resistivity imaging shows high resistivity that extends from near the surface to a depth of 2 m with the resistivity values ranging from 500 to 2600 Ωm (Fig. 3). Very high resistivity is closely connected to very dry sand.

The profile 2-RNS clearly shows a low resistivity anomaly at horizontal location 45-65 m (Fig. 3). The low resistivity anomaly is mostly prominent in the saturated zone, but extends from the surface into the vadose zone. The low resistivity anomaly is related to oil contamination confirmed in the borehole and analysed soil samples.

The total of 5 GPR lines was conducted (see Fig. 2a- for five profile's location). Profile 2 is presented as 2D radargram and interpreted in this paper. All of the GPR sections show the similar reflection pattern. Geologically, the discontinuous and shadow reflection zone represents oil contaminated sand. The presence of oil is detected in 45-65 m zone, especially above the water table at depths ranging from 1 to 3 m (Fig. 4). Clay and water with oil saturated layers reduce the apparent resistivities or increase the electrical conductivity of the environment to create a weaker GPR reflection pattern as compared to the uncontaminated layer on the left side of the profile (5-45 m), sometimes called the free-reflection zone.

The discontinuous reflection pattern is also known as the fuzzy or shadow zone and coincides well with the oil contaminated layer. The same pattern has also been reported in a previous study (Atekwana *et al*., 2000).

4.2. Location OC gas station

An equivalent electrical resistivity profile of 55 m long obtained in OC gas station by using Wenner array at 1 m electrode spacing using ABEM resistivity system with 32 electrodes (see Fig. 2b- for profile 2 location) is shown in Fig. 5.

The profile 2-OC gas station clearly shows a low resistivity anomaly at horizontal location 12-31 m (Fig. 5). The low resistivity anomaly is mostly prominent in the saturated zone, but don't extend to the surface into the vadose zone.

Figure 6 shows geochemical data collected from multi-level core samples across the LNAPL contamination plume. The high concentrations of Fe^{2+} a redox species is the evidence of biodegradation of LNAPL in the plume. Major ion chemistry suggests that enhanced mineral weathering is occurring inside the contaminated aquifer with elevated values of Ca^{2+} and groundwater specific conductance. During biodegradation, the pore fluid chemistry is changed by the degradation of the LNAPL (decrease in LNAPL concentration), the production of redox species (e.g., Fe^{2+} and Mn^{2+}), and production of metabolic byproducts such as organic acids (pH significantly decrease), and biosurfactants.

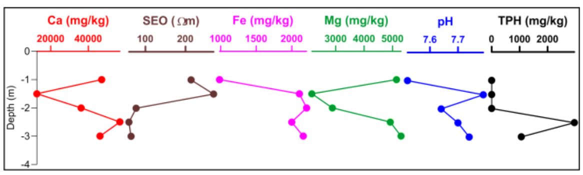

Figure 6. OC line 2 at 28 m (see Fig. 5), multi-level core samples geochemical analysis across contamination zone.

In both cases OC and RNS, geoelectrical methods give valuable information for planning and optimizing geochemical probing and remediation planning. Electrical-resistivity surveys can give more detailed maps of contamination zones than geochemical sampling.

5. Conclusions

The study pointed out the usefulness of two geoelectrical methods ERI and GPR in the characterization of underground leakage of hydrocarbons. Petroleum hydrocarbons naturally exhibit electrical resistive properties; however, this geophysical study, as well as many previous studies published before, has revealed electrically conductive characteristics of aged petroleum plumes.

Our experience with contaminated site characterization in Serbia shows that low resistivity anomalies caused by hydrocarbon contamination are possible to localize with the help of (ERI) as well as GPR and 2D data interpretation. Such contamination gives low resistivity anomaly as a result of petroleum biodegradation at shallow depth in the soil. The discontinuous GPR reflection pattern, i.e. shadow zone coincides well with the oil contaminated layer.

Experimental results, obtained from a joint geochemical and geophysical investigation approach, indicated that subsoil which has been saturated with hydrocarbon for a long period exhibits an increased conductivity. It suggests that electrical tomography could be useful for monitoring the effects of induced bioremediation through the repetition of the survey at different times. The strong conductivity anomaly, attributed to the hydrocarbon pollution zone, has been explained by increasing the organic activity and modification of the cation exchange capacity of the soil matrix.

Use of geophysical techniques (specifically geoelectrical) at hydrocarbon contaminated sites will become increasingly important not only in providing the characterization of the subsurface geology and contaminant distribution, but also in understanding the impacts of biogeochemical processes on the electrical properties of the sediments. Therefore, understanding the relationship between the geoelectrical properties of hydrocarbon-impacted sediments and ongoing physical and biogeochemical processes is a key to the successful application of geoelectrical methods.

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