Geo electrical Signature of Long Term Hydrocarbon Contamination in Serbia

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Abstract: *The detection of petroleum hydrocarbon contaminants such as light non-aqueous phase liquid (LNAPL) in the subsurface using geophysical methods, particularly electrical resistivity methods has been the subject of considerable interest in recent years. Their detection is based principally upon the electrical soil properties and processes related to biodegradation of the hydrocarbons. Direct current resistivity data were collected at the location of RNS (Oil Refinery Novi Sad) and "Obrenovac centar" fuel station site, Serbia. The objective of this study was to evaluate the possibilities of resistivity imaging techniques in detecting and locating anomalies of hydrocarbon contamination. Resistivity measurements were carried out utilizing the Wenner array configurations. In order to achieve good vertical and lateral resistivity distributions for the investigated site electrode spacing was 1 m. The interpretations obtained from 2D-modelling of the field data show a highly conductive region in areas with LNAPL contamination. This explanation was supported by the presence of free hydrocarbon phase floated on the surface of water filling the drilled boreholes and geochemical analysis of core sample collected on these two investigation site.*

Keywords: environmental pollution, LNAPL contamination, electrical resistivity imaging, Wenner array, soil sample chemical analysis.

1. Introduction

Subsurface contamination by LNAPLs is a worldwide problem and remains one of the most widespread and prevalent sources of groundwater contamination. In the United States, more sites are contaminated by petroleum hydrocarbons than any other type of contaminant [10]. Gasoline spills are among the most frequent causes of groundwater pollution in Belgium [11].

In Serbia as in many other countries, LNAPL contamination of soils near oil refinery or gas station remains a major problem of environmental concern.

During the Balkan Wars and NATO bombing a lot of the large – capacity of oil tanks were directly hit and inflamed (Fig.1). During the hostilities app.74000 tons of crude oil and petroleum products escaped in the RNS. From this amount app. 90% burned away and remaining 10% infiltrated in the collecting drainage channels or in the soil environment (about 2700 m^3).

The task of delineating and quantifying the amount of LNAPL present in soils and water was significant challenges to engineers and scientists involved in soil and water cleanup and remediation. Hydrocarbons are partitioned into various phases (vapour, residual, free and dissolved) in the subsurface. These phases have different spatial and temporal natures. The different properties of these phases make the characterization more difficult and complex the problem of soil and water remediation [5].

Numerous studies have been published on the broad topic of electrical resistivity investigation in soil contamination detection. However, in this paper we focus primarily on LNAPL contamination. We examine the geoelectrical signatures of LNAPL historical (long term) contamination resulting from microbial processes and are example of case studies that illustrate and capture the physical changes in the contaminated environment.

Figure 1: RNS after oil tanks were directly hit and inflamed.

To overcome the LNAPL plume characterization problem, engineers usually analyze soils and water samples collected in boreholes and piezometers. Based on these analyses, they extend the results to estimate the plume extent on the whole site. One major limit of this invasive technique lies in the high costs of drilling operations, sampling and analyses. This often leads to limit the number of investigations. The plume extent is therefore often poorly delineated. Geophysical techniques hold great promise as inexpensive and minimally-invasive sensors of subsurface LNAPL contamination. As such, geophysical techniques including magnetic [16], electromagnetic induction, ground penetrating radar (GPR), electrical resistivity, Self-Potential (spontaneous potential) and induced polarization have been applied to the hydrocarbon-impacted zones detection in the subsurface, e.g., [5], [6], [12], [17], [18].

The theoretical basis for the use of geoelectrical methods for the detection of LNAPL contaminants in the subsurface is dependent on the contrasting electrical properties of the LNAPL versus the pore and ground water displaced by the LNAPL.

Recent hydrocarbon contamination results in high resistivity anomalies, while mature oil contamination produces low resistivity anomalies [17]. Several months after the spill has occurred, oil contamination creates low resistivity zone [5], [18]. The formation process of a hydrocarbon contaminated is linked to chemical reactions and variations in physical characteristics of the affected medium. According to Sauck, 1998, 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 and is produced by the leaching and etching of the native mineral grains and grain coatings.

2. Background and Geological Setting

The Novi Sad Refinery is located on the left bank of Danube River, close to the artificial canal Danube-Tisa-Danube (Fig.2 - upper). The terrain is made of alluvial sediments, mostly sand and gravel, deposited in zone of Danube meanders on relatively flat area with low slopes. These fluvial deposits are partly covered with organic rich formations with residual of dissolved calcium carbonate. The natural terrain on top of which the facilities of Novi Sad refinery were constructed was 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 basic sandy aquifer. Thickness of the less permeable layer is between 0.5 and 2.5 m, but locally where the thickness reaches 4-6 m.
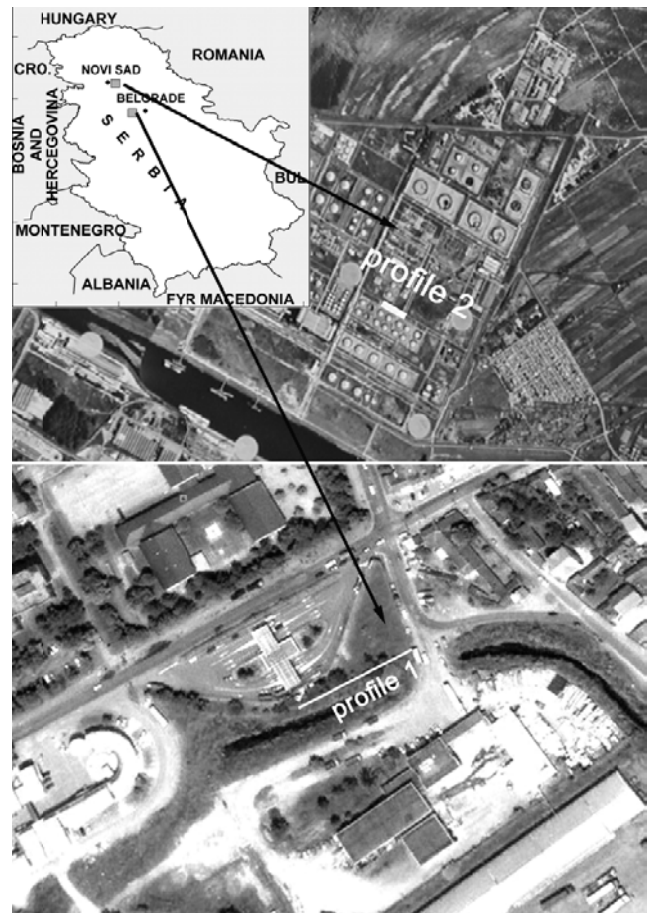

Figure 2: Site location map. Oil Refinery Novi Sad (RNS) upper, and Gas station ″Obrenovac centar″ down

The site specific geology can be derived from the many drillings performed on the site provided the following representative stratigraphy is as follows:

- 0 to 1.1 m: sand, fine to medium grained, grey, dry;
- 1.1 to 2.3 m: silty sludge, dark brown, bound;
- 2.3 to 4.2 m: gray-brown sandy silt with clay fractions, bound, wet;
- 4.2 to 5.0 m: fine grain to silty sands, grey, weakly bound;
- 5.0 to 25.0 m: different middle to fine grain quartz sands, with small-grained gravel.

As regards to the hydrogeology characteristics of the area, a permanent free aquifer is present in the sandy layers. The water level regime is directly related to the regime of the Danube and changes depending on Danube's water level. At the morphologically lower parts of the alluvial plain the groundwater emerges to the surface and floods the plain. The total thickness of the aquifer is 25 meters on average, the upper layers (average thickness from 5-15 m) are mostly made of sand, while the lower part is consist of gravelly deposits (5-10 m thick).

The groundwater flow direction is influenced by the regime of 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 1-2.5 meters below ground level, in backfilled sand.

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The gas station ″Obrenovac centar″ is located on left bank of artificial canal Stara Tamnava (Fig.2 – down). The terrain is made of alluvial sediments, mostly clay with sand (from the surface to the 1.4 m) and with small-grained sandy gravel above the unpermeable clay layer.

The water level regime is directly related to the seasonal changes. The depth of the aquifer is 2.5 meters on average.

3. A conceptual model for the geoelectrical response of LNAPL plumes

Until recently, it has commonly been assumed that hydrocarbon-impacted sediments can be effectively imaged only by their higher resistivities compared to ″background″ due to the partial replacement of conductive soil and pore water by highly resistive petroleum compounds (e.g., [9]; [14]). This premise is correct as long as the hydrocarbon is fresh, or has not been physically, chemically, or biologically altered.

There is ample evidence in the geochemical and microbiological literature to suggest physical and chemical alteration of hydrocarbons in contaminated sediments by indigenous microorganisms (e.g., [8]). Because of the partitioning of hydrocarbons into different phases (free, dissolved, and residual) in the subsurface and the time-dependent biological transformation of hydrocarbons, the chemical and physical properties of hydrocarbon-contaminated sediments are expected to vary with time and in space at contaminated sites.

Geomicrobiology is a field of emerging interest. Few studies have investigated the biological impact on subsurface geophysical properties [1], [2], [4], [18]. The common model for the geophysicist has been based upon the physical properties of the pure hydrocarbon liquid phase; i.e., that it has very high electrical resistivity. Oils and other hydrocarbon products have been used for years as electrical insulators, as for example in transformers. This has led to a number of attempts to look for a high-resistivity free product zone just above the water table at hydrocarbon contaminated sites.

Microbial processes and products at LNAPL-contaminated sites cause changes in the physical properties in the contaminated environment which are not used in routine geophysical investigations. These include, but are not limited to biogenic gases, precipitation of magnetic minerals, and temperature effects. The production of biogenic gases (e.g., CO_2, H_2S, H_2, and CH_4) can cause changes in the rheological properties of the contaminated region. Production of gases affects bulk electrical conductivity. The transport of the contaminants through the aquifer is strongly influenced by the aquifer properties.

Figure 3 is a Scanning electron microscopy (SEM) image of a mineral grain obtained from a LNAPL contaminated ″Obrenovac centar″ gas station site, on a samples in the anaerobic portion of the dissolved plume (profile 1). SEM image shows bacteria attached to a mineral surface (Fig.3a-d). Changes in surface area and surface roughness occur

primarily from microbial mediated processes such as attachment to mineral surfaces (Etch pits, Fig.3c and d). This is evidence that implicates microbes in the alteration of the surfaces of the mineral grains. The process of dissolution can remove interspatial cements or mineral precipitates which will increase porosity. Changes in porosity will lead to variations in the bulk electrical conductivity which can be measured by the DC resistivity.
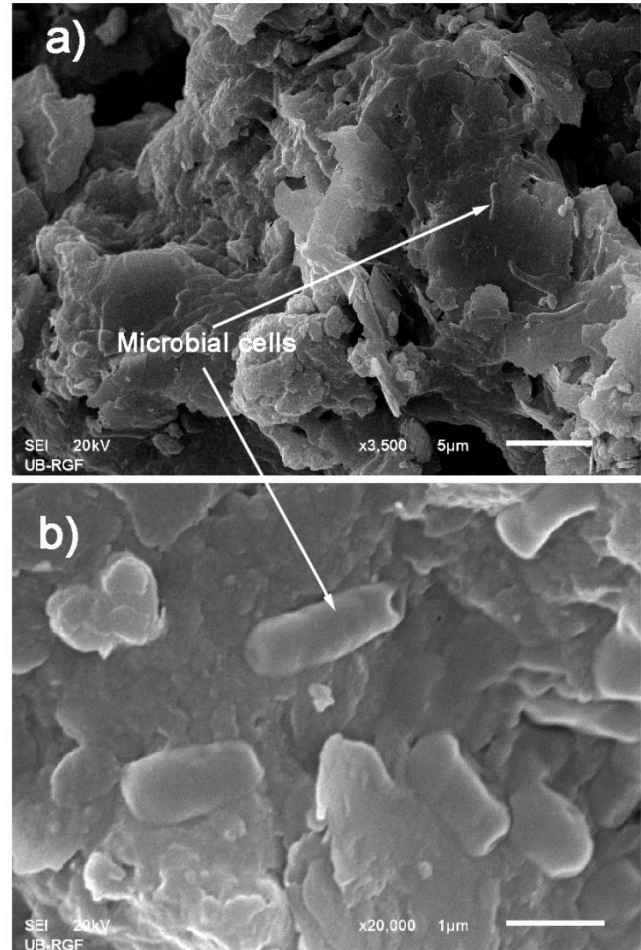

Figure 3: a) and b) Scanning electron microscopy image of sand from a light non-aqueous phase liquid (LNAPL) contaminated in two magnifications

Organisms capable of degrading hydrocarbons are present in vast numbers in natural soils and rock. Ridgeway et al. 1990 identified more than 300 kinds of gasoline-degrading bacteria isolated from well water and core material in shallow contaminated coastal aquifer.

The near subsurface is generally described as a porous medium and divided into a water saturated zone below the water table and a vadose zone above the water table [3]. The interface between the saturated and vadose zones contains the capillary fringe and transition zones. The capillary fringe is a tension saturation zone above the water table and can vary in thickness (being greater for finer grained material).

The physical and chemical properties of the aquifer and physical and chemical properties of the saturating fluids (water, contaminant, or air) control the geophysical signatures.
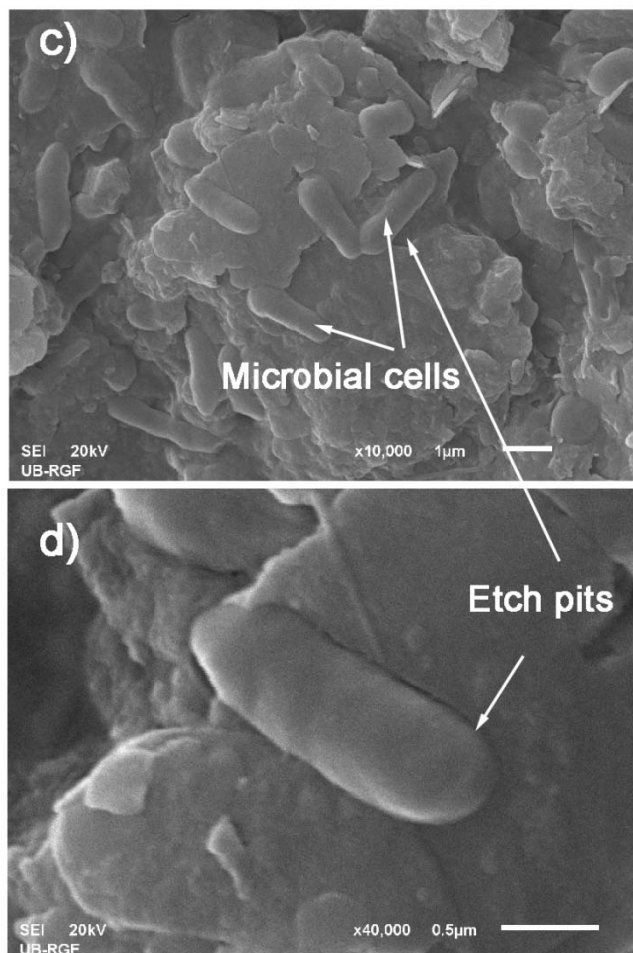
Figure 3: b) and d) Scanning electron microscopy image of sand from a light non-aqueous phase liquid (LNAPL) contaminated site showing bacteria attached to send surface and dissolution features such as etch pits.

During and shortly (weeks to several years) after a spill, the LNAPL partially displaces air and water in the formation. Due to its lower density than water, LNAPL will float on water and will partially displace water and air in the capillary fringe and transition zone. The free phase can also extend laterally for several tens to hundreds of meters.

The vapor phase consists of the volatile fractions of the hydrocarbon and is typically found in the upper parts of the vadose zone above the residual and free phase hydrocarbon zones.

The dissolved phase occurs in the saturated zone. The concentration of the LNAPL in the aqueous phase is determined by the solubility of the different fractions which are typically low.

With time and seasonal recharge, the residual and free phase LNAPL zones move up and down in the aquifer with fluctuations in the water table. Free LNAPL is trapped in the residual zone and the upper portion of the saturated zone causing a distinct smear zone [19].

The LNAPL contaminated subsurface is a dynamic and complex bio-physicochemical environment and its geophysical response will depend on factors such as: the type of the LNAPL (crude oil, jet fuel, diesel fuel), LNAPL release history (e.g., continuous release or single release), the distribution of the LNAPL relative to air in the vadose zone or water in the saturated zone, hydrologic processes (e.g., advective transport, seasonal recharge), the saturation history of the contaminated media, biological processes, etc.

4. Geoelectrical data and Measurements on Soil Samples interpretation

Two different sites of oil contamination were studied in Serbia. The Refinery Novi Sad (RNS) and pipeline accident at ″Obrenovac centar″ gas station, Fig. 2. 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 oil plume extent. In order to construct a 2D model of the subsurface, resistivity surveys were carried out in RNS and on Obrenovac centar gas station.

These sites are different in contamination age and scale, depth of groundwater level (GWL), environment, surface conditions and the cause of contamination.

Figure 4 shows an electrical resistivity profile obtained in RNS (see Fig. 2- for profile 2 location). The survey consisted of a Wenner resistivity array at 1 m electrode spacing using abgraded ABEM resistivity system with 32 electrodes.

An equivalent electrical resistivity profile obtained in ″Obrenovac centar″ gas station (see Fig. 2- for profile 1 location) is shown on Fig. 5.

A two-dimensional interpretation using software RES2DINV [13] was applied to several geoelectrical profiles. Two of them are depicted on Fig. 4 and Fig. 5. One from RNS, and one from ″Obrenovac centar″ gas station.

Long time residual hydrocarbons of the LNAPL type in permeable formation are exposed to microbial biodegradation, which changes the original natural ground water geochemistry and the distribution of gaseous components in the vadose zone. Baedecker, et al. (1993) described 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 features of these processes is the creation 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, Mg, 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.
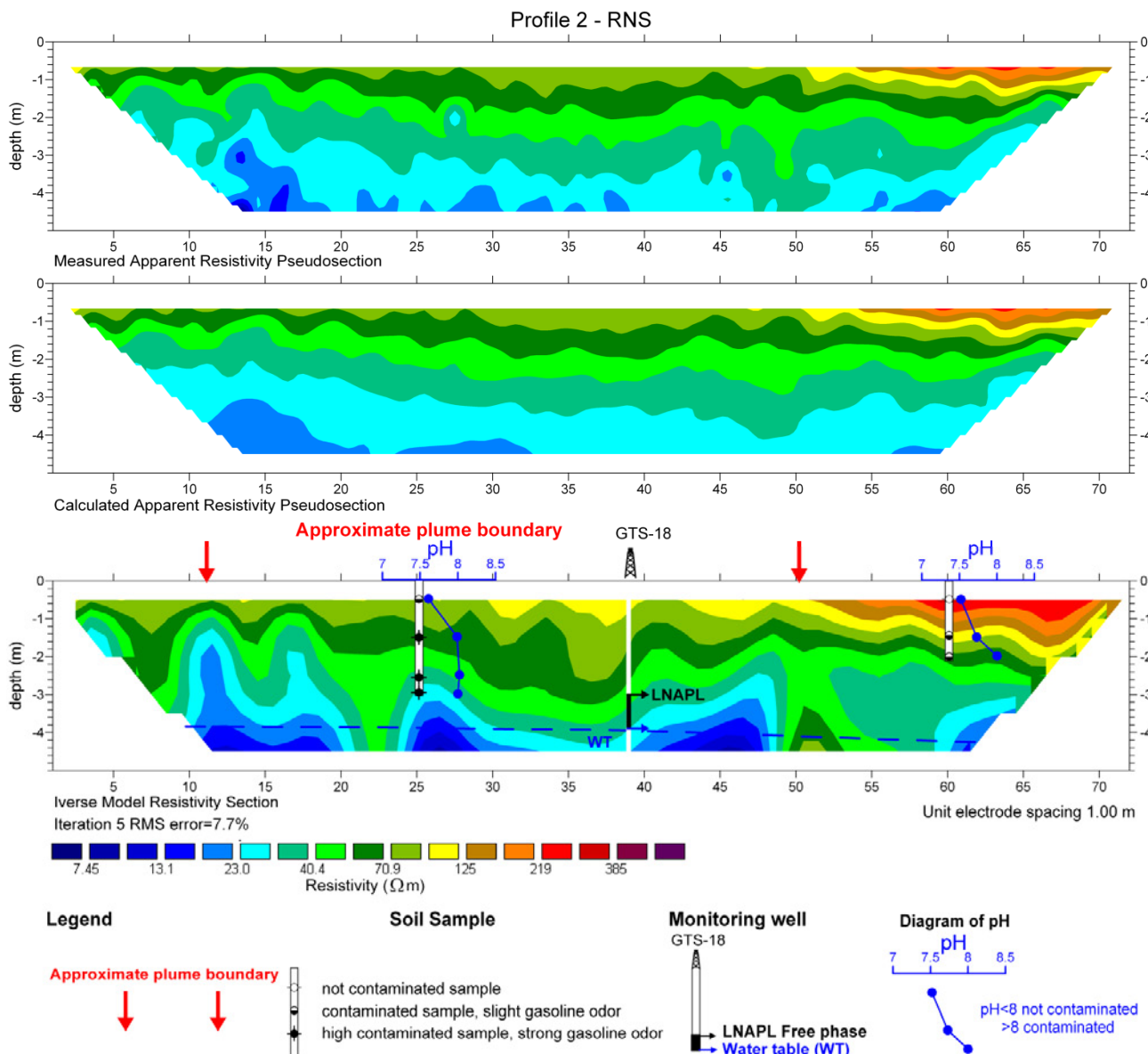
Figure 4: Inverted Wenner resistivity profiles 2 along the contaminant plume.

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Geochemical investigations of LNAPL contamination at this site are compared with electrical resistivity imaging. Sediment samples at RNS were collected from both uncontaminated and contaminated location. Samples were obtained using Eijkelkamp rig and stored in the laboratory refrigerator until measurements were made.

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

Increasing level of Iron in the contamination plume is explained by anaerobic biodegradation – Fe (III) reduction:
$60H^+ + 30Fe (OH)_3 + C_6H_6 = 6CO_2 + 30Fe_2^+ + 78H_2O$
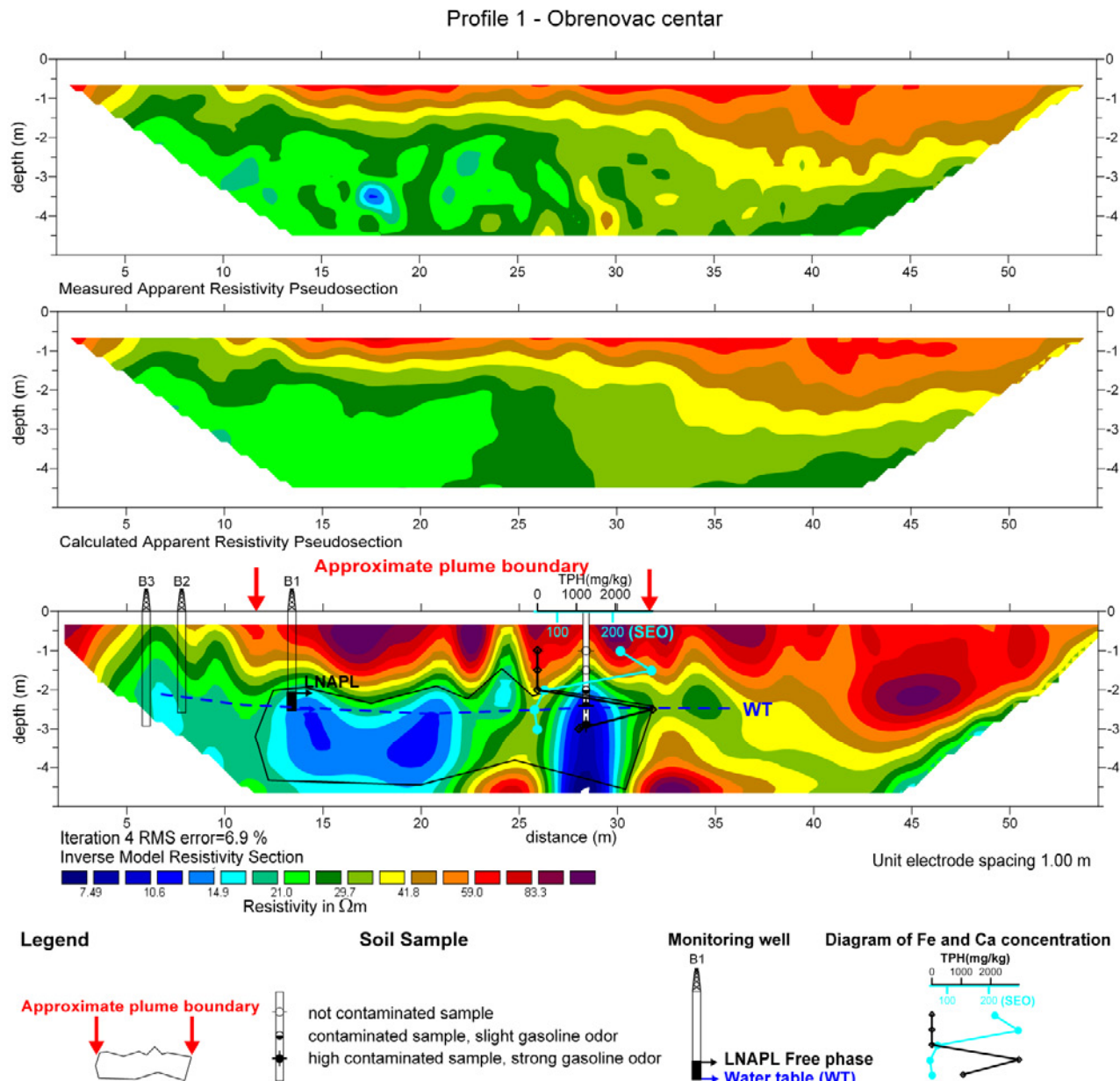
Figure 5: Inverted Wenner resistivity profile 1 along the contaminant plume

Figure 6 shows geochemical data collected from multi-level core samples across and beyond the LNAPL contamination plume. The high concentrations of Fe^{2+} a redox species is evidence of biodegradation of LNAPL in the plume. Major ion chemistry suggests that enhanced mineral weathering is occurring within 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), decrease in the concentration (e.g., NO_3^-, SO_4^{2-}), the production of redox species (e.g., Fe^{2+} and Mn^{2+}), and production of metabolic byproducts such as organic acids (pH significantly decrease), biosurfactants, and biogenic gases (e.g., CO_2, H_2, CH_4, H_2S).

The profile 2-RNS clearly shows a low resistivity anomaly at horizontal location 10-50 m (Fig. 4). The low resistivity anomaly is mostly prominent in the saturated zone, but extends from the surface into the vadose zone.

The profiles from both location show anomalously low electrical resistivity across the plume.

The profile 1-″Obrenovac centar″ 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 not extends to the surface into the vadose zone.

In both cases geoelectrical methods give valuable information for planning and optimizing geochemical probing. Electrical-resistivity surveys can give more detailed maps of contamination zones than geochemical sampling.
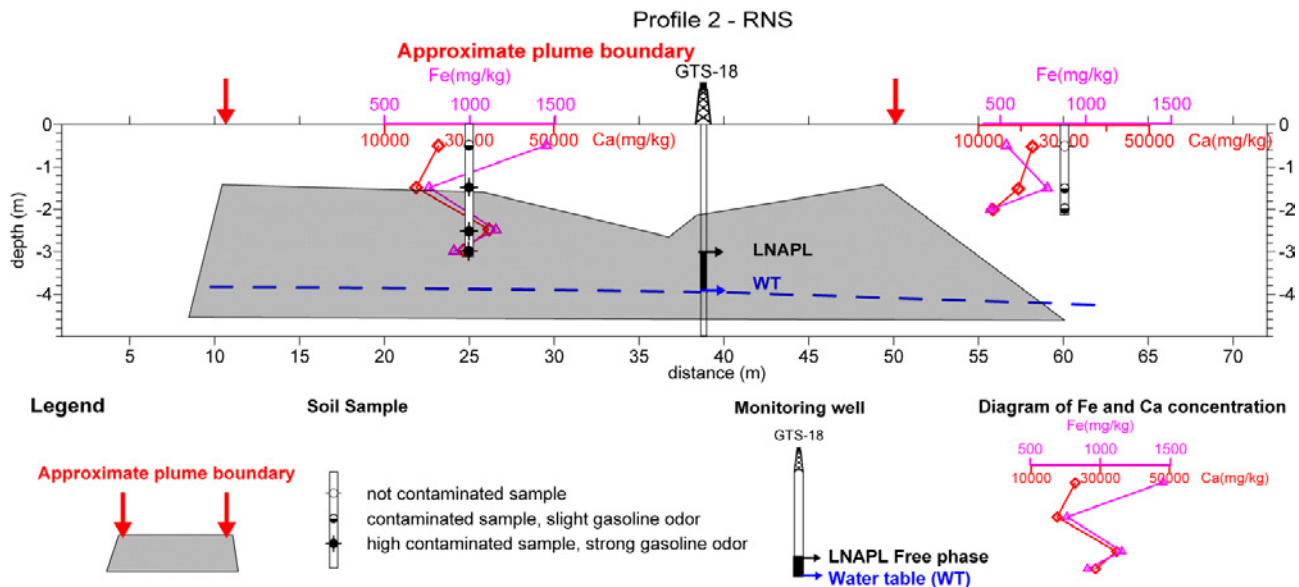
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Figure 6: Depth variations of selected chemical parameters at two sites along electrical profile 2 – RNS

Our experience with contaminated sites characterization in Serbia shows that low resistivity anomalies caused by hydrocarbon contamination is possible to localize with the help of Electrical Resistivity Imaging (ERI) and 2D data interpretation. Such contamination gives low resistivity anomaly as a result of petroleum biodegradation at shallow depth in the earth.

5. Conclusions

Petroleum hydrocarbons remain one of the most prevalent groups of soil contaminants. Consequently, a variety of geophysical techniques have been used and recently published to detect their presence and distribution in the subsurface.

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

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 biodegradation (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.

We believe that the use of geophysical techniques (specifically geoelectrical) at hydrocarbon contaminated sites will become increasingly important not only in providing 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 as proxies of these processes.
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