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DETECTION AND MONITORING OF HYDROCARBON POLLUTION SOURCES IN THE PETROMIDIA REFINERY AREA

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Abstract

The detection and spatiotemporal monitoring of hydrocarbon contamination in the geological environment (soil, geological formations, and groundwater) represent the main objective of the study, conducted during the period of 2023-2024. The study focused on areas adjacent to the Petromidia refinery with industrial activity exceeding five decades, located in the vicinity of the city of Navodari. Both `classic` geophysical techniques (VES - Vertical Electrical Sounding, IP - Induced Polarization) and recently introduced techniques on a global scale (GPR - Ground Penetrating Radar) were employed. Electrical and electromagnetic measurements were complemented by magnetic investigations, drilling works, and geological and hydrogeological observations. The most effective geophysical measurements, both for detecting and monitoring underground hydrocarbon contamination, were the geoelectrical resistivity ones, due to the significant contrast in electrical resistivity between the highly resistive pollutant substances and the affected geological environment, consisting of rocks and fluids with much higher electrical conductivity. The geological and hydrogeological data from shallow boreholes were used for the correct interpretation of geophysical anomalies, while the results of magnetic measurements indicated the routes of buried pipelines, and potential sources of pollution.

Key words: *electrometry, hydrocarbon, pollution, soil.*

INTRODUCTION

Contamination with hydrocarbons of the land and groundwater in the vicinity of refineries, fuel depots, oil wells, and even transportation pipelines, constitutes one of the significant environmental protection issues (Onutu & Tita, 2018). The localization and determination of the spatial-temporal distribution of contamination currently rely exclusively on the use of direct methods of biochemical analysis of soil and water samples taken from the surface or from boreholes.

The information obtained in this way is point-based and therefore cannot provide an overall picture of land and groundwater contamination. Analyses are costly and require an extended period for observations to be made.

The integration of point-based information into a three-dimensional spatial-temporal image of areas contaminated with hydrocarbons and residual waters becomes possible through the appropriate use of geophysical methods, supported by hydrogeological information.

The main objective of the geophysical investigation was to develop a geophysical monitoring of hydrocarbon contamination resulting from refining, storage, and transportation activities of petroleum products in the vicinity of refinery located in the area of the city of Navodari.

MATERIALS AND METHODS

1. Physical-geographical characterization

The target under investigation is located on the coastal strip separating the Black Sea from the Gargalac (Corbu) and Tașaul lakes, an integral part of the Central Dobrogea Platform.

The relief generally exhibits the characteristics of a high hilly plain, with wide valleys and terraces, reaching heights of up to 100 meters.

The average relief energy is 50 meters. Genetically, the area represents a paneplain (nearly flat land surface resulting from long-continental erosion and denudation) of the Caledonian mountains (Green Shale Formation), covered in the Quaternary by a loess cover.

Beneath this cover of aeolian deposits, patches of eroded Jurassic limestone emerge, featuring karstic landforms such as caves and gorges.

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Towards the coastal zone, the relief is lower, featuring lagoons, fluvio-marine estuaries, and sandy coastal barriers.

The climate is typically continental, with the sea exerting its influence over a coastal strip 10-15 kilometres wide. The basin of Lake Taşaul is situated on the contact zone between Jurassic limestone and the Proterozoic substrate of the Green Shale Formation. Along this stratigraphic contact, the course of the Casimcea River has insinuated itself, more active during cold, glacial periods of the Quaternary (Chitea, 2011). From a geomorphological perspective, the studied objective is situated on the "complex barrier beach" (barrier beach) of Taşaul - Corbu, which extends southward to the Mamaia complex barrier beach.

2. Aspects of historical hydrocarbon contamination in the Petromidia refinery area

The pollution phenomenon with petroleum products from industrial areas related to the extraction, transportation, and processing of oil in Romania, noted in the last 40 years, especially through its harmful effects on the quality of some drinking and surface water sources, as well as on the productivity of soil in some agricultural lands, has been the subject of special research initiated in the 1960s.

These studies were prioritized through hydrogeological and geophysical investigations conducted in the vicinity of refineries and fuel transportation pipelines by ISPIF Bucharest and the University of Bucharest starting from 1975.

The contamination with hydrocarbons of land, groundwater, and surface water near major pollution sources (refineries, fuel depots, oil and fuel transportation pipelines, oil extraction rigs, petroleum residue ponds, etc.) represents one of the largest and most challenging environmental protection issues in Romania (Paraschiv, 1979).

The placement near Navodari city of the country's most important sources of petroleum pollution (the Petromidia refinery, petroleum and fuel depots, and petroleum product transportation pipelines) makes this area the subject of numerous research endeavours and the primary motivation for selecting this perimeter for implementing hydro-geophysical research (Figure 1).

Figure 1. Petromidia refinery

The pollution sources in the Petromidia refinery area are classified as follows:
- systematic losses of petroleum products in the technological processes of extraction, transportation, and storage;
- accidental losses of petroleum products in the transportation and refining processes (explosions, fires, pipeline corrosion, earthquakes, technical accidents, pipeline breakages for fuel theft);
- slow leaks of products through cracks in pipelines, tanks, ponds, basins, sewers;
- losses of petroleum products during long-distance transportation of pollutants through watercourses, rainwater, and wind.

The migration of hydrocarbons, immiscible with water, occurs in two ways:

a) In unsaturated conditions, under the influence of gravity and meteoric waters (within refinery);

b) In saturated conditions, at the surface of groundwater in the form of a laminar contamination plume, laterally advancing in the direction of groundwater flow (outside refinery, in the direction of groundwater flow).

An example of contamination in saturated conditions at the level of the groundwater table is represented by the area southeast of the Petrobrazi refinery, where the boundary of the spread of groundwater contamination with petroleum products covered an area of approximately 11 km^2 in January 1981, separated into two distinct sectors according to the degree of pollution:

A central sector, affected by intense pollution, with significant concentrations of pollutants in the form of a lens-shaped layer above the groundwater, ranging from 1 cm to 5 m in thickness, predominantly spreading within the refinery premises and extending south-eastward to approximately 2.5 km away; A sector with reduced pollution, with thin films, iridescence, or a specific petroleum smell in the groundwater, with the boundary located approximately 3.5 km from the refinery. In the Petromidia refinery case, the depths of the petroleum layer were frequently recorded at values of 2 - 6 m and are variable over time, depending on the vertical oscillation of local groundwater levels. The general propagation direction of the petroleum pollution front is similar to that of the predominant groundwater flow (NW - SE), but the advancement speed differs from that of water, being slower in the case of petroleum pollutants due to the different physical-mechanical characteristics (higher viscosity and adhesion of petroleum products) and the specific horizontal and vertical migration mechanism of petroleum products (depending on the action of capillary forces in the porous medium).

3. Geoelectric detection of hydrocarbon contamination

The use of various geoelectrical techniques for detecting underground hydrocarbon pollution is an efficient and non-invasive method for soil investigation in search of contamination. Among these techniques are VES (Vertical Electrical Sounding), IP (Induced Polarization), ERT (Electrical Resistivity Tomography), and GPR (Ground Penetrating Radar). Measurements of VES (Vertical Electrical Sounding) conducted with instruments such as AGI MINISTING (Figure 2) is extremely useful in identifying zones of hydrocarbon contamination.

VES involves measuring the electrical resistance of the soil in a vertical manner, allowing for the determination of the vertical distribution of the electrical properties of the subsurface. These techniques are particularly effective when placed on profiles that traverse areas of interest, such as refineries or other potential sources of hydrocarbon pollution.

By combining data obtained from various geoelectrical techniques, a more comprehensive picture of the distribution and characteristics of subsurface contamination can be obtained, which can better guide strategies for remediation and environmental monitoring (Greenhouse, 1993).

Figure 2. Geoelectric data acquisition using Ministing system from AGI

The observation data has been processed and interpreted using specialized software such as Res2DInv, EarthImager, as well as programs developed by the research team members. Analysing the curves of the vertical electrical soundings conducted in the area of the four refineries, it was observed that from a geoelectric standpoint, two main modes of electrical resistivity distribution in depth can be distinguished in the investigated region (Figure 3):

- VES curves representative of type H (for example-yellow colour) in the northeastern area, where the Petromidia refinery is located;
- VES curves representative of type K (for example-blue colour) in the southwestern area, where the Petromidia refinery is located.

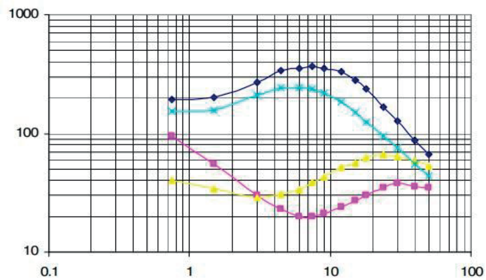

Figure 3. Representative VES curves

The main difference between the two separately identified sectors, with distinct variations in electrical resistivity, lies in the presence of a clay layer electrically conductive at the upper part of the geological structure in the northeastern part of investigated area (type H VES curves), a layer absent in the south-western part of investigated area (type K VES curves). The mentioned clay layer, intercepted in shallow boreholes, largely protects the northeastern area, with hydrocarbon contamination significantly lower compared to the southwestern area. The rapid increase in electrical resistivity in the electrical soundings conducted in the investigated area is due to the presence at shallow depths (1.5-4 m) of the resistive layer containing the pollutant film and geological formations impregnated with petroleum products. The processing and quantitative interpretation of VES data have resulted in obtaining resistivity sections down to a depth of 4 meters along the profiles in the investigated areas. The outlined anomalies of maximum resistivity (Figure 4 - red colour) illustrate the presence of hydrocarbon contamination plumes at depth.

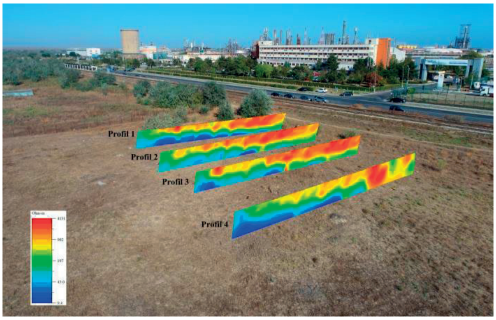

Figure 4. Apparent resistivity sections-Perimeter I

Figure 4 shows the distribution of electrical resistivity along profiles I, II, III and IV (Perimeter I), which traverses the north-south direction of the pollution zone associated with the Petromidia refinery. The elongated anomaly of maximum resistivity located at depths of 1.5-3 meters is interpreted as being due to the presence of the hydrocarbon contamination plume located at the aquifer's surface. Interruptions or variations in the thickness of the resistive layer are interpreted as being caused by variations in the compaction of the contaminated gravel (Berkowitz, 2008).

The thickness of the resistive layer (Figure 4 - red colour), greater than the contaminant film at the aquifer's surface, also includes that of the gravel impregnated with hydrocarbons during seasonal variations in the hydrostatic level (historical contamination). The interpretation of these resistivity anomalies was supported by direct information from recently executed hydrogeological boreholes and from artisanal excavations present in the immediate vicinity of the investigated perimeters (McNeill, 1980).

In order to obtain detailed information on the distribution of resistivity in depth in areas significant for understanding the relationships between the contaminant and the polluted geological environment, VES measurements were conducted on Perimeter II (Figure 5).

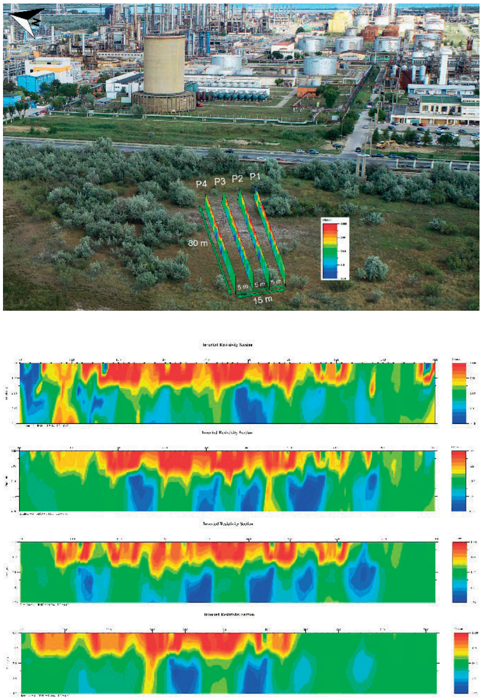

Figure 5. Apparent resistivity sections - Perimeter II

The electrical resistivity section obtained down to a depth of 4 meters illustrates details of anomalies of maximum resistivity associated with the hydrocarbon contamination plume on each profile. Variations in the intensity of resistivity anomalies can be interpreted as

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variations in contaminant concentration, while interruptions in the major resistivity maximum anomaly can be attributed to the effects of local tectonic accidents.

4. Georadar detection of hydrocarbon contamination

The georadar investigation at the Petromidia refinery in the southeastern sector revealed some interesting findings. The underground limit interpreted as the water table suggests the presence of groundwater at that depth. Additionally, the zones of weak electromagnetic signal could indicate the presence of a hydrocarbon plume within the upper aquifer. This suggests the possibility of hydrocarbon contamination in the groundwater, which is a concern for environmental and remediation efforts. Further investigation and monitoring would likely be necessary to assess the extent of the contamination and develop appropriate mitigation measures (Fuente, 2021).

In the Petromidia refinery area, 10 longitudinal profiles and 6 transverse profiles were continuously recorded using a 100 MHz antenna (Figure 6).

The analysis of the recordings on the longitudinal profiles shows the existence of a well-defined geophysical boundary located at 0.75 m (Figure 7). The detected interface is practically continuous along the entire length of the measurement profiles. Correlating these observations with archive data obtained from previous boreholes, the following values for velocity and permittivity are obtained:

- a velocity of 6.5-7.6 cm/ns for the medium above the first georadar limit, considering this interface as the water level (Schon, 2004);
- the permittivity varies in the range of 15.58-21.30 (Kapicka, 1997).

Considering that the permittivity of a sandy medium saturated with water is around 25, and the reflection sign is negative, we can conclude that the interface encountered at 0.75 m (Figure 7) is due to the level of petroleum product. Electric permittivity (or dielectric constant) is a quantity, denoted by ε, which indicates the resistance to electric polarization of a dielectric material (Tezkan, 2005).

In practice, a dimensionless quantity expressed by the ratio of the permittivity of a medium to that of vacuum is used. The groundwater level is located at depths of 1.5-2 m. Below the first detected georadar limit, the value of electromagnetic wave velocity decreases due to the presence of water in the propagation medium. By decreasing the velocity, the travel time of the wave increases.

Areas where reflection coefficients have high values and do not allow the delimitation of a reference radar horizon have been interpreted as being due to hydrocarbon intrusions (yellow zones - Figure 8).

Figure 6. Georadar acquisition data with 100MHz antenna

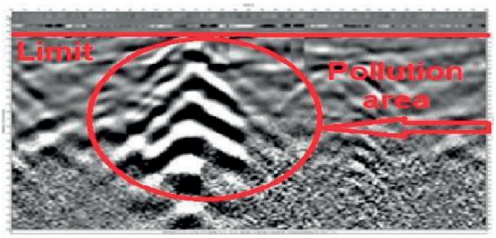

Figure 7. Georadar data (radargram) in the Petromidia refinery area

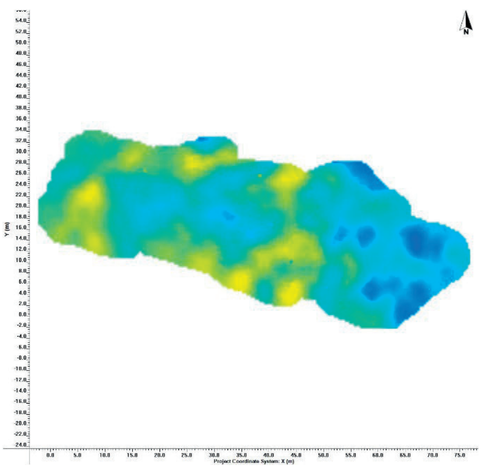

Figure 8. Georadar section

RESULTS AND DISCUSSIONS

Geophysical monitoring of the temporal and spatial evolution of hydrocarbon contamination plumes has been studied in the Petromidia refinery area. The hydrocarbon contamination plume, resulting from the temporal overlay of historical contamination with current contamination, is largely influenced by the regional dynamics of the aquifer. Geoelectrical VES measurements conducted for monitoring has investigated the central part of perimeter I and II.

The results of monitoring measurements were analysed in the form of resistivity pseudo sections to avoid disturbances caused by quantitative interpretation programs. The observed changes in resistivity during monitoring, considered for interpretation, are due to variations in moisture in surface layers (soil, paleosol, loess), fluctuations in the water table level, and some quantities of pollutants recently introduced into the geological environment in the refinery area (Figures 3, 4 and 5). The fragmentation of the major resistivity maximum anomaly is due to active processes of surface water infiltration along a fault system, which affects the geological structure and the soil layer (Figures 3, 4 and 5).

The results obtained from the georadar investigation were presented in the form of radargrams or depth sections, which can highlight geological structures at shallow depths, including the localization of tectonic features with local significance, as well as the delineation between hydrocarbon-saturated and unsaturated zones (Manescu, 1994).

CONCLUSIONS

The results of geophysical investigations dedicated to the detection and monitoring of hydrocarbon contamination plumes near the Petromidia refinery have shown that VES geoelectrical resistivity measurements are the most effective. Elongated anomalies of maximum electrical resistivity, located at depths where the first aquifer is localized, illustrate the presence of contamination plumes due to the hydrocarbon film and the geological environment impregnated with contaminants during seasonal variations in the water table level. Interruptions in the maximum resistivity anomalies are due to variations in the compaction of gravel or local tectonic accidents. The geoelectric monitoring of hydrocarbon contamination plumes was conducted using vertical electrical soundings, through the sequential analysis of resistivity pseudo sections. The geoelectric effect of hydrocarbon contamination is evident even under significantly different seasonal climatic variations, with the maximum resistivity anomaly determined by the presence of hydrocarbons being well delineated through repeated geophysical measurements.

This resilience in detection is particularly significant in delineating the maximum resistivity anomaly associated with subsurface hydrocarbon contamination (Allred, 2010). Repeated geophysical measurements serve as a reliable tool in accurately mapping out these anomalies, aiding in the assessment and management of hydrocarbon contamination in diverse environmental conditions. It's interesting to hear that geophysical investigations near the Petromidia refinery have identified VES (Vertical Electrical Sounding) geoelectrical resistivity measurements as the most effective method for detecting and monitoring hydrocarbon contamination plumes. Geophysical methods play a crucial role in environmental studies, especially when dealing with issues such as pollution and contamination. VES involves measuring the electrical resistivity of subsurface materials at different depths using a vertical electrode array. In the context of hydrocarbon contamination, variations in resistivity can be indicative of changes in the subsurface caused by the presence of hydrocarbons (Vafidis et al., 2014).

Here are some reasons why VES geoelectrical resistivity measurements might be effective in this scenario:

Contrast in Resistivity - hydrocarbons generally have a lower electrical resistivity than the surrounding soil or rock. This contrast allows for the detection of hydrocarbon plumes in the subsurface.

Depth Profiling - VES provides information at different depths, allowing for a vertical profile of subsurface resistivity. This can help in understanding the depth and extent of the contamination plumes.

Spatial Resolution - VES can offer good spatial resolution, helping to map the lateral extent of contamination. This information is crucial for effective remediation strategies.

Cost-Effectiveness - compared to some other geophysical methods, VES can be relatively cost-effective, making it a practical choice for large-scale monitoring projects.

Non-Invasive Nature - geoelectrical methods are non-invasive, meaning they don't require drilling or excavation. This minimizes disturbance to the site and provides a more environmentally friendly approach.

Real-Time Monitoring - VES measurements can be conducted periodically, allowing for real-time monitoring of changes in subsurface resistivity. This is important for tracking the dynamic nature of contamination plumes.

It's essential to note that the effectiveness of geophysical methods can vary based on site-specific conditions. Additionally, integrating multiple geophysical techniques can provide a more comprehensive understanding of subsurface conditions.

If VES has proven to be the most effective in this case, it demonstrates the importance of selecting the right geophysical tools for the specific challenges posed by hydrocarbon contamination near the Petromidia refinery. The GPR data was obtained using a NOGGIN system with 100, 250, and 500 MHz antennas. The 100 and 250 MHz antennas provided the best results in terms of spatial resolution and depth, while the shallow groundwater level provided excellent conditions for GPR.

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