

ASSESSMENT OF HYDROCARBON CONTAMINATION USING 2D RESISTIVITY IMAGING METHOD AND GEOCHEMICAL ANALYSIS IN IBADAN SOUTHWESTERN, NIGERIA.

ABSTRACT

The study examined the use of 2D resistivity imaging survey and geochemical analysis to map and assess the level of soil contamination due to hydrocarbon spillage in Araromi Auto Spare Parts Market Ibadan, Southwestern Nigeria. The objectives are to provide 2D inverted resistivity sections beneath the study area, delineate anomalously low resistivity zones indicative long-term hydrocarbon contamination in the sections, and determine concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the suspected soils. Five traverse were traversed using Wenner array with electrode spacing varied from 5 m to 15 m and station increment of 5 m. The resistivity data were processed by using 2D inversion procedure to generate the 2D inverted resistivity sections. Geochemical analysis was conducted on five soil samples collected at 1 m depth in the low resistivity zones delineated on the 2D inversion sections, to determine the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) to assess the level of contamination. The 2D inverted sections delineated low resistivity anomalies, ranging from 1.25 Ω m to 5.54 Ω m, characteristic of mature biodegraded hydrocarbon contamination. The results of geochemical analysis revealed total PAH concentration of 1390 μ g/kg to 16140 μ g/kg suggesting that the study area is highly contaminated by the used motor oil. The combined use of 2D resistivity imaging and geochemical analysis has shown that soils beneath the study area has been heavily contaminated by the used motor oil, and may constitute potential health risk to the soil and groundwater systems in its vicinity. The results are expected to serve as usefully guide in planning remediation programme.

Keywords: hydrocarbon contamination, resistivity imaging, geochemical analysis, polycyclic aromatic hydrocarbons

Content Nature terms of use

1. INTRODUCTION

Indiscriminate disposal of used hydrocarbons/used motor oil into the environment from industrial sites is a serious cause for concern as they negatively impact soil and groundwater systems and constitute potential health risk to human population mainly due to the polycyclic hydrocarbons (PAHs) contained in them [1, 2, 3, 4].

PAHs are a class of hazardous organic compounds made up of two or more benzene rings in linear, angular, or cluster forms [5, 6]. They are ubiquitous pollutants, found as mixtures of different chemical compounds, that are discharged into the environment from anthropogenic sources activities mostly incomplete combustion of fossil fuels.

When waste oil seeps into the ground, the PAHs cling to the soil particles in the topsoil and later roam vertically and laterally with rain water that percolates from the surface. Migration of PAHs through soil is usually slow because they do not dissolve easily in water. They are biodegraded by microorganisms after a period of maturity ranging from 4 months to 1 year in soil, releasing by-products which flow with water to form contamination plumes along their paths within the soil and subsequently contaminate the groundwater [7].

Investigation of hydrocarbon-impacted site is important since contamination of the topsoil would eventually reach the entire subsurface strata and groundwater resources in a matter of time. The speed of migration of the contaminants depends on the prevailing geologic conditions of the soil and the underlying rock [8].

The traditional techniques for assessing soil contamination and pollution are drilling, sampling and geochemical analysis to determine the concentrations of the chemical constituents of the contaminants. These techniques are, however, point specific and can only reflect scattered local information. They are also invasive, expensive and time-consuming [9].

Geophysical surveys can provide continuous subsurface information in hydrocarbon-contaminated areas, and have more advantages in being non-invasive and cheaper compared to drilling and sampling [10, 11, 12]. Fresh hydrocarbon spills manifest as high resistivity anomalies in resistivity sections [13]. Biodegradation of mature hydrocarbon plumes undergoes results in increased total dissolved solids (TDS) and consequent decrease in resistivity presented as low resistivity anomalies [7, 14, 15].

Electrical resistivity tomography (ERT) is widely used in the characterization of hydrocarbon-contaminated sites to detect and delineate contamination plumes and determine to which extent the soil and groundwater have been affected [16, 17, 8, 18]. The technique relies on the resistivity contrast between the contaminated zone and the background geologic 'clean' zone [19, 20, 21]. It is capable of delineating linear geologic features, such as fractures and faults which can serve as conduit for the downward migration of contaminants into the aquiferous units [22, 23]. An integration of geophysical techniques with geochemical data can provide a reliable assessment of the areal extent and level of hydrocarbon contamination [7, 9, 24].

Used hydrocarbons have been indiscriminately poured on the ground at Araromi Auto Spare Parts Market located at Agodi gate, Ibadan southwestern Nigeria, for over five decades, as old motor parts are disassembled to find reusable parts for sales to prospective buyers. The engine oil wastes are left in contact with the topsoil in which it clings to the surface of soil particles and subsequently migrate with surface/rain water to nearby aquifer units. Assessment of the extent of contamination within and around the location is thus important considering the hazardous effects which the contaminants may have on the soil and groundwater. The findings of the assessment may provide clues for appropriate remediation.

The aim of the study is to carry out 2D resistivity imaging survey and geochemical analysis to map and evaluate the level of soil contamination due to hydrocarbon in Araromi Auto Spare Parts Market Ibadan, Southwestern Nigeria. The objectives are to provide 2D inverted resistivity sections beneath the study area, delineate anomalously low resistivity zones indicative long-term hydrocarbon contamination in the sections, and determine concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the suspected soils using geochemical analysis.

2. METHODOLOGY

2.1. Study Area

The study area is located within latitude $3^{\circ} 55' 12''\text{N}$ - $3^{\circ} 55' 19''\text{N}$ and longitude $7^{\circ} 23' 37''\text{E}$ - $7^{\circ} 23' 44''\text{E}$ (Fig. 1). Its climate is tropical with distinct wet and dry seasons and a mean annual temperature of 27.1°C [25]. The rainy season occurs between March and October, when the moist maritime southwest monsoon winds blow inland from the Atlantic Ocean, while the dry season occurs from November to February when the dry dust-laden winds blow from the Sahara Desert.

The underlying geology is granite gneiss, a Precambrian basement complex rock of metamorphic origin (Fig. 2). Granite gneiss is a metamorphic rock formed by changing schist, granite, or volcanic rocks through intense heat and pressure. The rock is foliated and often has a high luster due to large crystals within the rock [26].

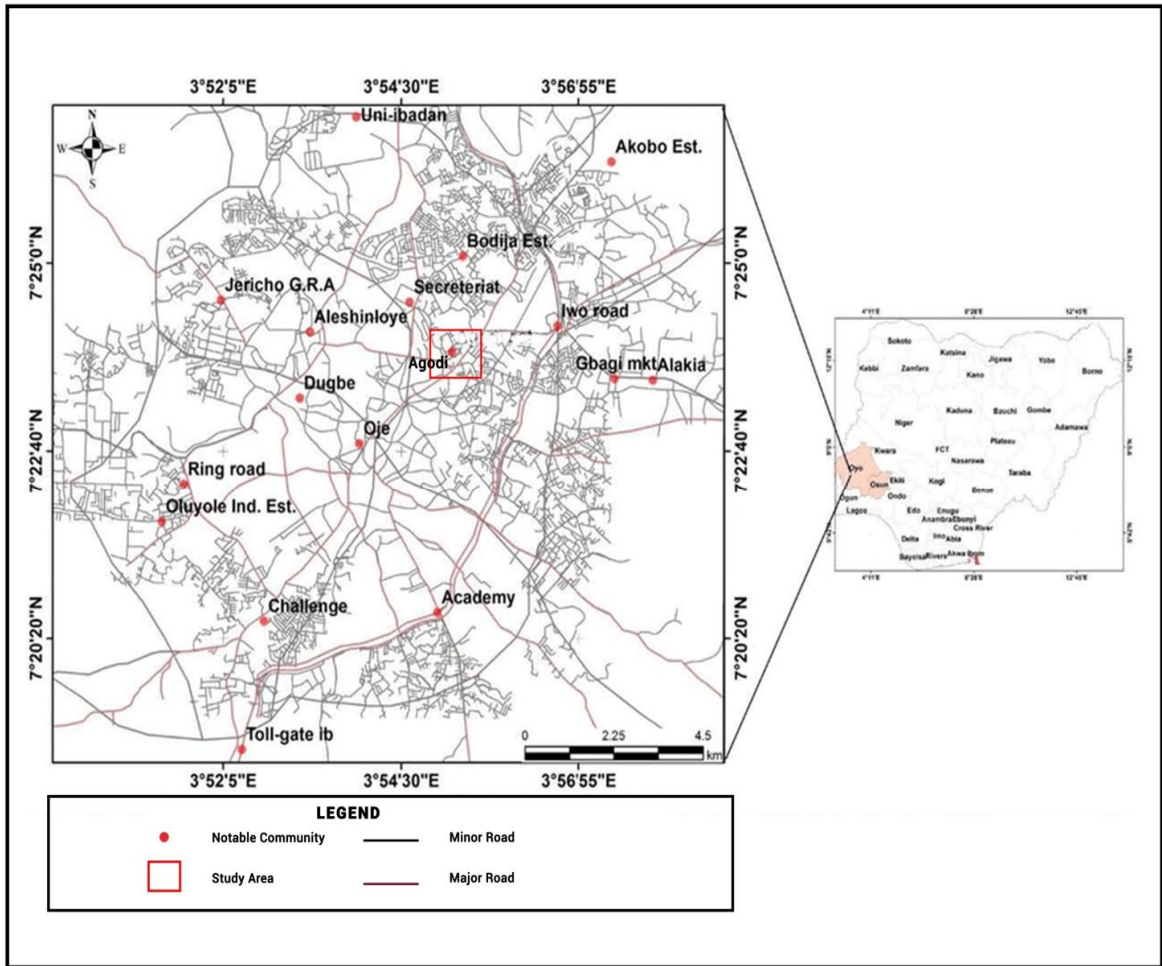


Fig.1: Location map showing the study area

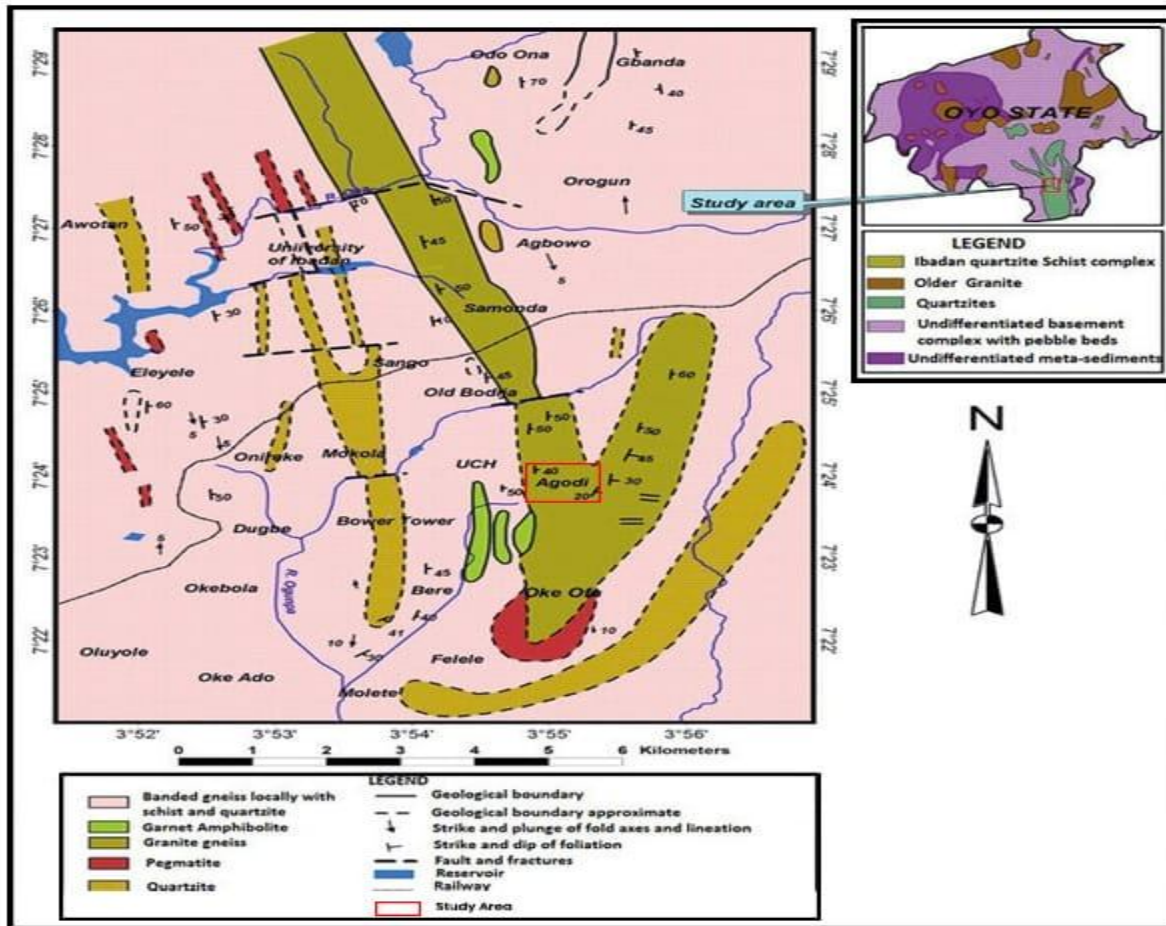


Fig. 2: Geological map showing the study area

2.2. 2D Resistivity survey

2D electrical resistivity survey was employed using Wenner electrode array with electrode spacing of 5m, 10m, and 15m and station increment of 5m along 5 traverses of lengths ranging from 85 m to 200 m (Fig. 3). The data were acquired with a resistivity meter and its accessories, and processed by using 2D inversion procedure to generate the 2D inverted resistivity earth sections. The program used a forward modelling subroutine to calculate apparent resistivity values from field data, which were then inverted using a nonlinear least-squares optimization technique [27]. Anomalously low resistivity zones indicating the mature hydrocarbon-contaminated soils were delineated on the 2D inverted resistivity sections.

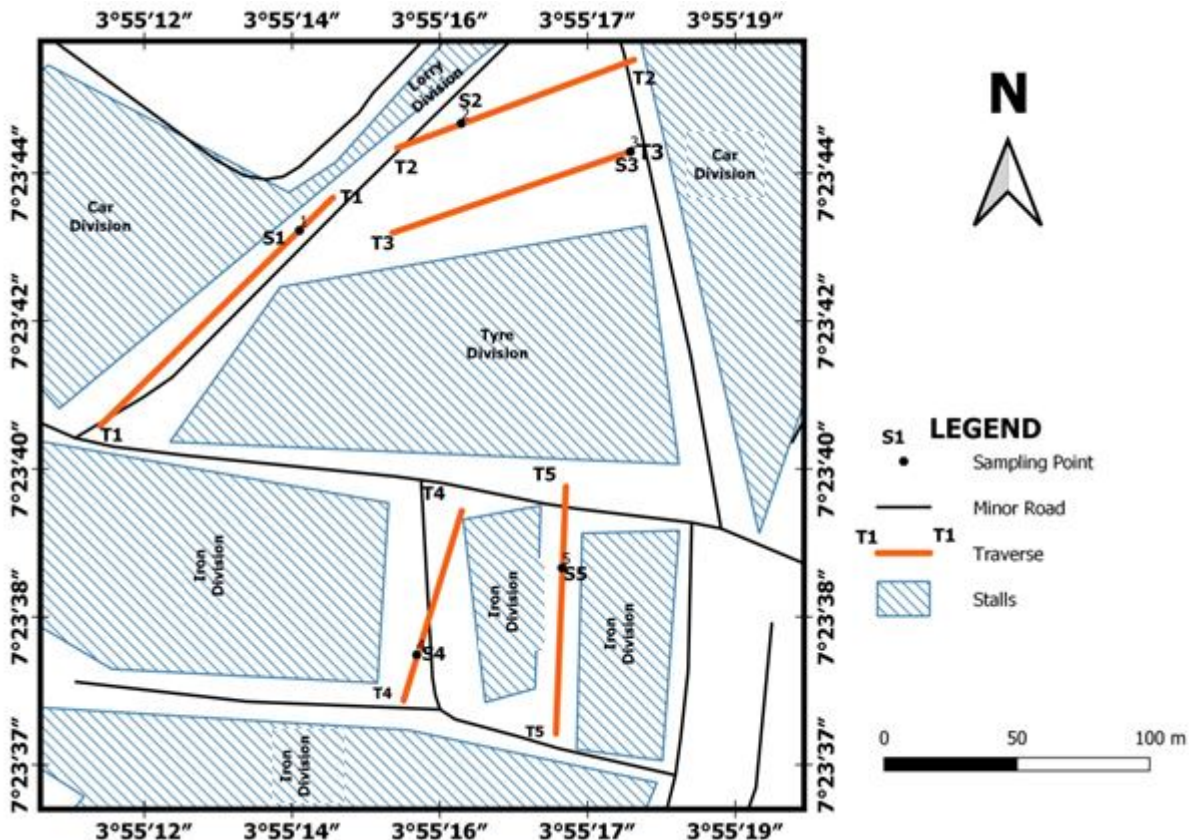


Fig. 3: Field layout of the geophysical traverses and soil sampling points

2.3. Geochemical Analysis for PAHs

Oil-stained soil samples were collected from test pits dug along the traverses to the depths of the observed resistivity lows. The samples were air-dried for 8 days in the laboratory, free of dust and chemical fumes. They were pulverized and 100g of each was measured into sample bottles. Extraction was done in a sonicator using 40ml of dichloromethane for 40 minutes. The procedure was repeated three times.

The extract was obtained and kept in a clean dust-free laboratory for 12 days to enable vaporization of the solvents after which the concentrations of the polycyclic aromatic hydrocarbons (PAHs) in each sample was determined by using Gas Chromatography–Flame Ionization Detection(GC-FID). The total concentration of the PAHs in each sample was computed and used to classify the levels of contamination in the study area.

3. RESULTS AND DISCUSSION

3.1. 2D Resistivity Imaging

The 2D inverted resistivity sections beneath the Traverses run across the study area show subsurface heterogeneity with characteristic lateral and vertical resistivity variations. Mature hydrocarbon-contaminated zones are characterized by anomalous low resistivity values, generally less than 10 Ωm , indicating the presence of high ionic contents and increased conductivity resulting from biodegradation of the polycyclic aromatic hydrocarbons contained in the used motor oil.

Traverse 1 is underlain by clayey overburden whose resistivity ranges from 10.8 Ωm to 45.1 Ωm and weathered bedrock with resistivity varying from 64.1 Ωm to 282 Ωm (Fig. 4). The high resistivity values in the topsoil probably indicate contamination by used oil spillage. Resistivity of the bedrock ranges from 433 Ωm to 13971 Ωm . Depth to the bedrock is about 2 m.

The bedrock is fractured beneath stations 7 to 15, 21 to 27 and 31 to 36, providing pathways for the migration of contaminants through the rocks. Low resistivity anomalies of values ranging from 1.85 Ωm to 12.5 Ωm occurring within the fractures at depths below 2.5 m suggest contamination plumes of mature hydrocarbons. Similar low resistivity values have been reported for mature hydrocarbons contaminated sites in previous studies such as [20], [21] and [23].

The 2D inverted resistivity section beneath Traverse 2 (Fig. 5) reveals overburden resistivity varying from 13.5 Ωm to 30.9 Ωm and bedrock resistivity ranging from 46.5 Ωm to 828 Ωm indicating intensely/fairly weathered bedrock. The bedrock is fractured beneath stations 6 to 10. The fracture hosts a zone of anomalously low resistivity (2.42 Ωm – 5.54 Ωm) from about 2.5 m depth downwards, representing suspected mature hydrocarbon contamination. The resistivity lows beneath stations 1 to 6 and stations 16-17 may be due to uncontrollably disposed pieces of waste metallic substances buried over time within the topsoil. The zone of relatively high resistivity (163 Ωm – 518 Ωm) beneath stations 9 to 11, from surface to about 4 m, probably suggests contamination by used hydrocarbons not yet biodegraded.

The resistivity distribution beneath Traverse 3 delineate overburden resistivity ranging from 14.7 Ωm to 89.6 Ωm typical of clay (Fig. 6). The relatively higher resistivity (196 Ωm – 242 Ωm) beneath stations 6 to 7 may be due to fresh contamination by used oil spillage while the resistivity

Traverse 1 (2-D Resistivity Structure)

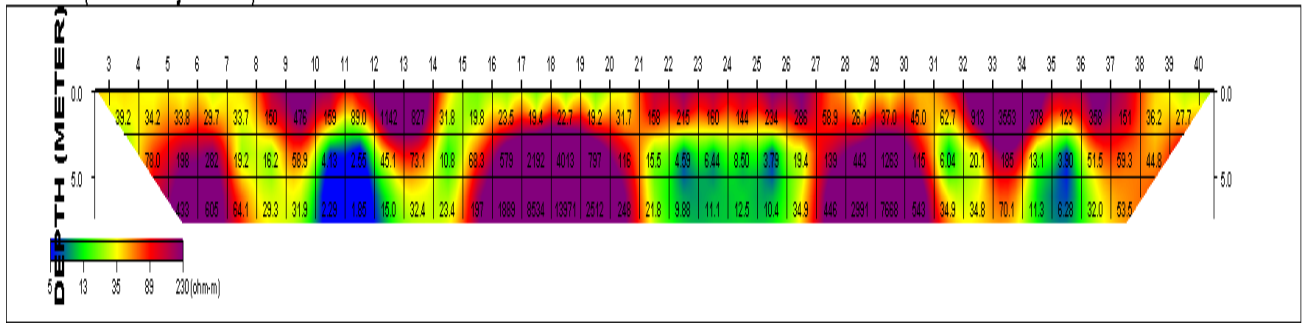


Fig.4: 2D inverted resistivity section beneath Traverse 1

Traverse 2 (2-D Resistivity Structure)

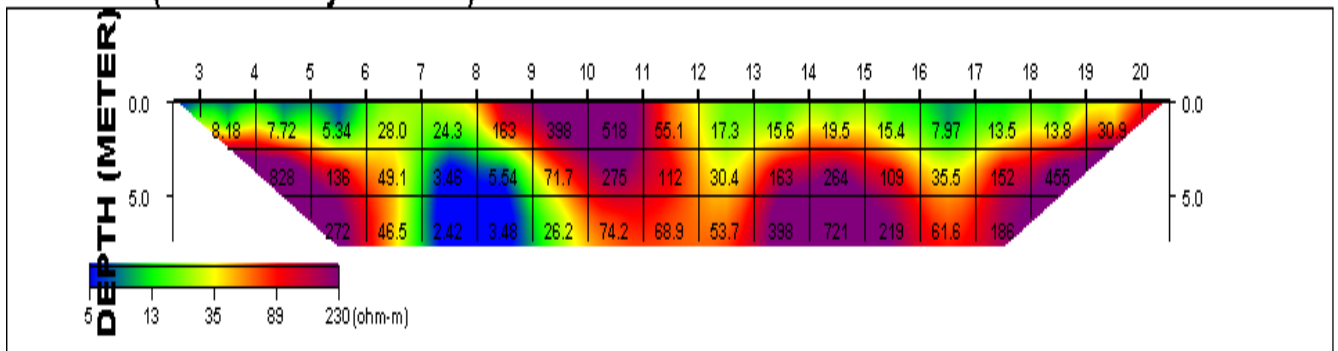


Fig. 5: 2D inverted resistivity section beneath Traverse 2

Traverse 3 (2-D Resistivity Structure)

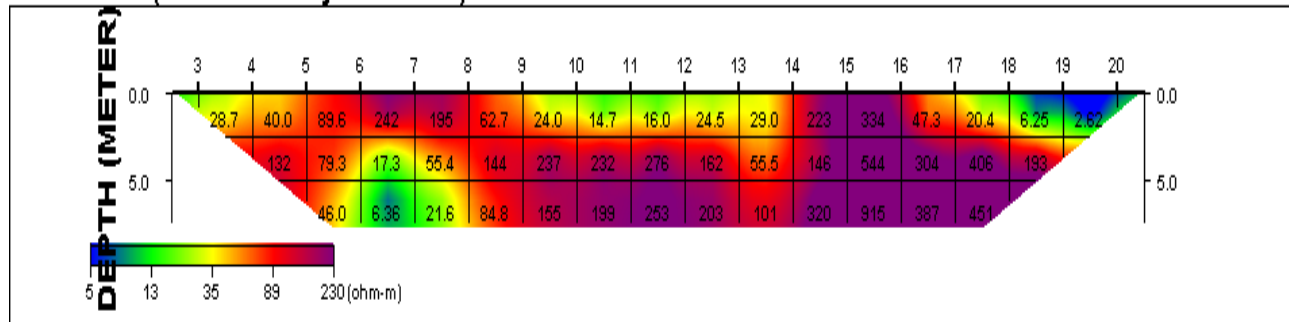


Fig. 6: 2D inverted resistivity section beneath Traverse 3

lows (2.62 Ωm – 6.35 Ωm) beneath stations 18 to 20 possibly indicate buried pieces of uncontrollably disposed waste metallic substances. The resistivity of the bedrock (132 Ωm – 544 Ωm) suggests intense weathering. Depth of the bedrock is about 3 m and it outcrops between stations 14 and 16. The bedrock is fractured beneath stations 6 to 8 and indicates anomalous resistivity low zones suspected to be contamination plume of mature biodegraded hydrocarbons.

The 2D inverted resistivity section beneath Traverse 4 depicts clayey overburden with resistivity ranging from 11.0 Ωm to 105 Ωm (Fig. 7). The resistivity lows (4.33 Ωm – 7.48 Ωm) beneath stations 10 – 12 may be due to buried pieces of uncontrollably disposed waste metallic substances. Resistivity of the bedrock varies from 149 Ωm to 5031 Ωm representing weathered /fresh bedrock. The bedrock is fractured beneath stations 6-8 and 13-14 while the resistivity lows (1.53 Ωm – 4.02 Ωm) occurring in the depth interval 2.5 m – 5.0 m possibly delineate contamination plumes of mature biodegraded hydrocarbons.

The resistivity of the overburden beneath Traverse 5 ranges from 11.1 Ωm to 77.3 Ωm characteristic of clay (Fig. 8). The bedrock has resistivity varying from 149 Ωm to 3454 Ωm representing weathered/fresh bedrock. Its outcrop occurs between station 5 and station 8 while it is fractured from station 7 to station 11. The resistivity lows (2.98 Ωm - 4.24 Ωm) below 3 m depth within the fracture suggest contamination plume of mature, biodegraded hydrocarbons.

3.2. Geochemical analysis of soil samples for Polycyclic Aromatic Hydrocarbons

The concentrations (in $\mu\text{g}/\text{kg}$) of the 17 PAHs extracted from the soils studied are presented in Table 1. The total concentration of PAHs ranges from 1390.4 $\mu\text{g}/\text{kg}$ in Sample 4 to 16140.03 $\mu\text{g}/\text{kg}$ in Sample 2. The high molecular weight PAHs (HPAHs) are the main contributors accounting for about 86.28% to 95.79% of the total PAHs in the soils. This indicates that the PAHs are of combustion origin. HPAH/LPAH ratio greater than 1 typically indicates pyrogenic (combustion) origin while HPAH/LPAH ratio less than 1 indicates petrogenic (fresh liquid fuels) source [28, 29, 30]. This claim is also supported by the diagnostic ratios Phe/Ant less than 10 and Flu/Pyr greater than 1 obtained for the study area [31, 32]. Composition of the low molecular weight PAH(LPAH) ranges from 4.21% in Sample 2 to 13.72% in Sample 4. HPAHs are generally hydrophobic and partition more readily into organic matter than LPAHs [33].

Traverse 4 (2-D Resistivity Structure)

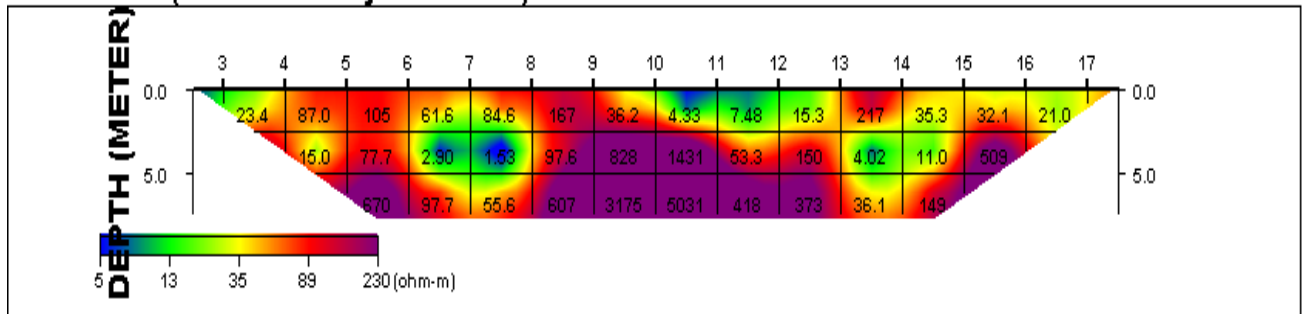


Fig. 7: 2D inverted resistivity section beneath Traverse 4

Traverse 5 (2-D Resistivity Structure)

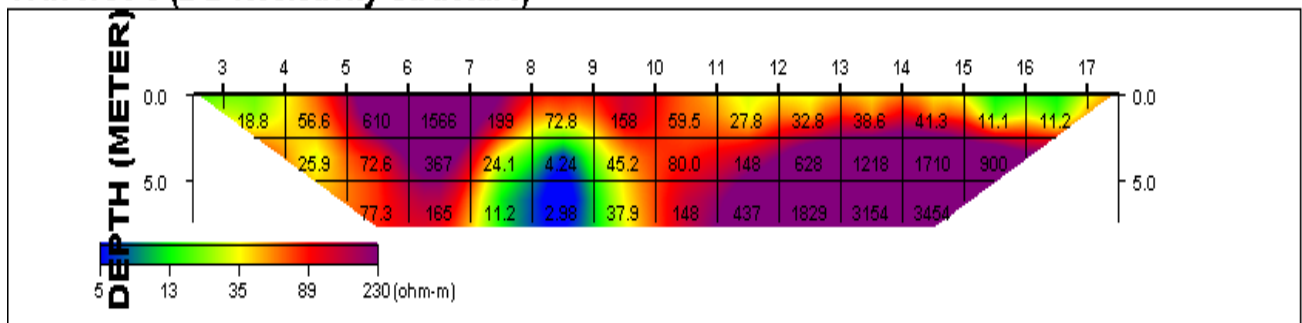


Fig. 8: 2D inverted resistivity section beneath Traverse 5

Name of PAHs	No. of Rings	Sample 1(μg/kg)	Sample 2(μg/kg)	Sample 3(μg/kg)	Sample 4(μg/kg)	Sample 5(μg/kg)
Naphthalene Nap	2	-	12.95	20.76	26.97	32.08
AcenaphthyleneAcy	3	2.74	53.38	28.42	44.44	8.56
AcenaphtheneAcp	3	21.17	33.00	24.27	15.17	14.49
Fluorene, Flr	3	6.03	334.80	177.92	80.78	152.31
Phenanthrene, Phe	3	45.43	173.72	69.04	1091.60	63.55
Anthracene, Ant	3	7.59	70.82	3.29	52.51	7.30
Fluoranthene Flt	4	9.63	1546.10	594.43	9.79	39.51
Pyrene, Pyr	4	4.61	333.11	21.96	38.26	26.04
Benzo[c]phenanthreneBcPh	4	3.33	792.53	347.18	349.29	14.45
Benzo[a]anthraceneBaA	4	202.54	4038.12	1667.10	172.81	141.45
ChryseneChr	4	3.48	1134.77	435.57	553.73	15.10
Benzo[j+k+b]fluoranthene	5	17.16	438.94	152.28	197.42	154.67
Benzo[e]pyrene	5	200.54	148.96	140.82	1745.81	257.05
Benzo[a]pyreneBaP	5	32.02	83.18	217.19	26.28	465.82
Benzo[g,h,i]peryleneBghiP	6	97.04	189.16	77.18	626.34	884.03
Indeno[1,2,3,-cd]pyreneIcP	6	546.06	6083.86	199.49	1071.93	582.95

Dibenz[a,e]pyrene DeP	6	191.03	672.63	226.45	3453.42	16.04
%LPAHs		5.97	4.21	7.35	13.72	9.68
%HPAHs		94.03	95.79	92.65	86.28	90.32
Carcinogenic PAHs		801.26	11778.87	2671.63	2022.17	1359.99
Total PAHs Conc.(Σ 17PAHs)		1390.40	16140.03	4403.35	9556.55	2875.40

Table 1: PAH Concentrations in soil samples from the study area

Typical GC-FID Total Ion Chromatogram which shows the concentrations of the different PAHs in the soil samples is presented in Fig. 9. The PAHs are distinguished by the different hydrocarbon fingerprints that they exhibit in the chromatograms. In accordance with the European Classification System of Soil Contamination in which total concentration of PAHs, Σ PAHs < 200 $\mu\text{g}/\text{kg}$ indicates no contamination, 200–600 $\mu\text{g}/\text{kg}$ corresponds to weak contamination, 600–1000 $\mu\text{g}/\text{kg}$ represents moderate contamination, and >1000 $\mu\text{g}/\text{kg}$ suggests heavy contamination [34], the study area is highly contaminated (Table 2).

The total PAHs concentrations for Sample 1 to Sample 5 are respectively 1.39, 16.14, 4.403, 9.557 and 2.875 times higher than the heavily contaminated level of 1000 $\mu\text{g}/\text{kg}$. The dominant PAH in Sample 1 and Sample 2 is Indeno[1,2,3-cd] pyrene with concentrations of 546.06 $\mu\text{g}/\text{kg}$ and 6083.86 $\mu\text{g}/\text{kg}$ representing 39.27% and 37.69% of the total concentration respectively. Benzo[a] anthracene is the predominant PAH in Sample 3 at 1667.1 $\mu\text{g}/\text{kg}$, and is notably present next to Indeno[1,2,3-cd] pyrene in Sample 1 at 202.54 $\mu\text{g}/\text{kg}$ and Sample 2 at 4038.12 $\mu\text{g}/\text{kg}$. The most abundant PAH in Sample 4 is Dibenz[a,c]pyrene at 3453.42 $\mu\text{g}/\text{kg}$ while the highest concentration in Sample 5 is Benzo[g,h,i] perylene at 884.03 $\mu\text{g}/\text{kg}$ followed by Indeno[1,2,3,-cd] pyrene (582.95 $\mu\text{g}/\text{kg}$) and Benz [a] pyrene (465.82 $\mu\text{g}/\text{kg}$).

The International Agency for Research on Cancer (IARC) and the United State Environment Programme, (USEPA) listed chrysenene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthrene, benzo(k)fluoranthrene and indeo(1,2,3-cd)pyrene as the topmost potential human carcinogens. Dibenzo(a,h)anthracene was not detected in the soils from the study area. The total concentration of carcinogenic PAHs ranges from 801.26 $\mu\text{g}/\text{kg}$ in

Sample 1 to 11778.87 $\mu\text{g}/\text{kg}$ in Sample 2. These carcinogens and the others detected in the study area constitute potential health risk to all forms of life by contact via breathing and ingestion.

This study has shown that the subsoils have been impacted by large amounts of PAHs. The PAHs resulted mostly from pyrogenic sources. Remedial measures are necessary to clean the area prevent further spread into neighbouring soil and groundwater systems. The results are expected to serve as useful guide in planning remediation programme for the area and its vicinity.

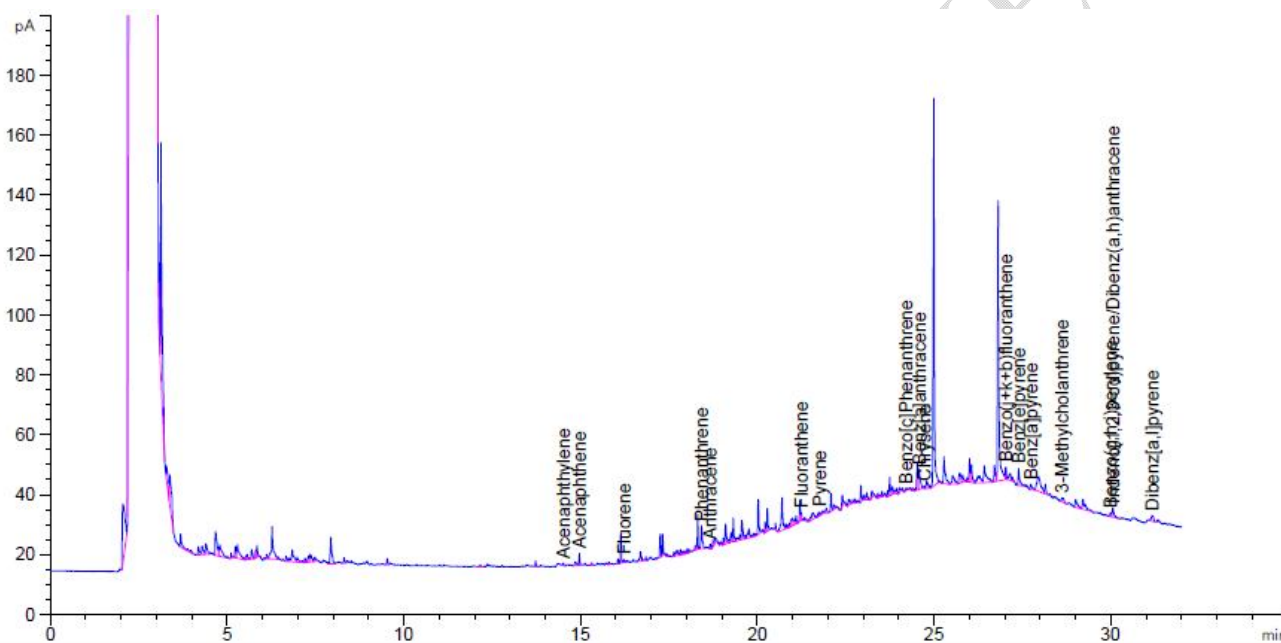


Fig. 9: Typical GC-FID Chromatogram of PAH concentrations in soil samples from the study area

Table 2: Classification of contamination level of soil samples from the study area based on [34]

Sample No.	Total Concentration ($\mu\text{g}/\text{kg}$)	Contamination level
Sample 1	1390.4	Heavily contaminated
Sample 2	16140.03	Heavily contaminated
Sample 3	4403.35	Heavily contaminated

Sample 4	9556.55	Heavily contaminated
Sample 5	2875.4	Heavily contaminated

4. CONCLUSIONS

The study has demonstrated the effectiveness of combining 2D electrical resistivity imaging with geochemical analysis in characterizing hydrocarbon-contaminated sites. The low resistivity anomalies delineated on the 2D resistivity sections revealed mature biodegraded hydrocarbon contamination. The results of geochemical analysis indicated that the study area is highly contaminated by the used motor oil and may constitute potential health risk to the soil and groundwater systems in its vicinity.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

There are no competing interests

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