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Research Article

Spatial Distribution of Physicochemical and Electrical Properties in Soils around Abandon illegal Refineries Sites

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Abstract

This study assessed how residual petroleum hydrocarbons influence both the physicochemical and electrical properties of soil. Soil samples were collected from five spatial locations near clusters of abandoned artisanal refineries. The concentrations of total hydrocarbons content (THC), copper (Cu), lead (Pb), nickel (Ni), cadmium (Cd), as well as the electrical resistivity (ρ) and dielectric constant (ε') values of the soil samples presumed to be contaminated and those from the reference point, were determined following approved standard guidelines. The findings indicated the presence of residual petroleum hydrocarbons in the sites of the old refineries, as evidenced by significantly higher THC values in the soil samples collected from the abandoned refinery sites compared to the control soil ($p \leq 0.05$). It was observed that the THC levels ranged from 1052 to 4024 mg/kg, significantly exceeding the result (71 mg/kg) recorded at the control point. The concentrations of Cu, Ni, Pb, and Cd ranged from 3.63 to 8.10 mg/kg, 5.73 to 9.10 ppm, 5.13 to 8.30 ppm, and 0.90 to 1.53 mg/kg, respectively. Conversely, at the reference location, concentrations of Cu, Ni, Pb, and Cd were recorded as 2.27, 2.67, 3.70, and 0.08 mg/kg, respectively. The results revealed that ρ across the five sampled points varied from 451.00 to 836.00 Ωm, while ε' values ranged between 3.16 and 3.73. As evidenced by the results, proper remediation of areas where illegal refineries were once located is crucial to mitigate the risks associated with petroleum toxicity.

Keywords	*Spatial Distribution; Dielectric Constant; Heavy Metals; Residual Petroleum Hydrocarbons; Illegal Refineries*
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Introduction

Artisanal refining of petroleum has emerged as a significant socioeconomic and environmental challenge in Nigeria, particularly in the Niger Delta region of the country (Obenade and Amangabara, 2014; Igben, 2021; Richard *et al.,* 2022). Discharged of untreated waste from artisan (illegal) refineries in Nigeria into the ecosystems, is one of the major causes of environmental degradation of the Niger Delta region of Nigeria (Idisi and Uguru, 2020). Waste generated by these refineries contains significant amount of toxic metals, volatile aromatic compounds and other hazardous chemicals, which presence create avenue for air, water and soil contamination. This poses serious hazards to both the biotic and abiotic communities of the environment. Volatile organic compounds (VOC), particulate matter (PM) and other lethal gasses emitted during petroleum refining contribute immensely to air pollution, resulting in respiratory related health problems and interference in plants growth and performance (Manisalidis *et al*., 2020). Bashir *et al*. (2020 reported that effluent from petroleum products can reduce the dissolve oxygen (DO) content and light penetration level of water bodies, and these pose severe risks to the aquatic ecosystems. Furthermore, most of the compounds present in petroleum residues have persistence attribute, leading to accumulation in the soil and sediments (Ambaye *et al*., 2022). These challenges have serious consequences on the performance of the primary producers; therefore, resulting to the disrupting of the food chain.

Petroleum hydrocarbons have significant effect on the soil electrical properties, by causing serious alteration in its electrical conductivity (EC), electrical resistivity, dielectric constant (ε'), and dielectric loss (Ahmadian et al., 2013; Yodrot *et al*., 2023). This alteration may impede the soil ability to transmit electronic and electrical charges effectively. Soil EC and ε' varies inversely with the volume of petroleum contamination in the soil. Soils with lower the oil contamination level tend to have smaller EC but more stable ε'. Furthermore, the fluctuation in soil electrical properties induced by hydrocarbon contamination can interfere with the performance of sensors and electronic equipment used in various industrial monitoring applications. The consequences of this challenge can lead to machines/equipment failures, operational inefficiencies, and exposing the workers to operational hazards.

Several researches have been conducted to evaluate the impact of illegal refineries activities on the environment. Sayed et al. (2021) reported that effluent discharged from their (illegal refinery) wastes which are indiscriminately discarded into the swamps, caused significant accumulation of total petroleum hydrocarbon (TPH) in the soil and water bodies. According to Chinedu and Chukwuemeka, (2018) research, seepage from the locations of illegal refineries can lead to the bioaccumulation of trace metals and hydrocarbons in plant bodies, resulting in heavy metal (HMs) poisoning and retarded growth. Plants, fishes and animals whining the vicinity of abandon illegal refineries locations were observed to have doses of HMs and TPH, which have detrimental effect on human beings and the ecosystems (Akpomrere and Uguru, 2020). Flourizel et al. (2024) stated anthropogenic activities associated with illegal refinery operations are a major contributor to the high concentration of petroleum hydrocarbons recorded in vegetation, sediments, and water sampled from areas surrounding abandoned artisan refineries. Though numerous studies have been done to ascertain the pollution level of these petroleum products on the environment, there's a noticeable gap in understanding how this pollution affects the electrical properties of soils in the vicinity. Therefore, it is paramount to establish the current pollution status of the abandon illegal refineries environment. This study will assess the TPH and HMs contamination degree of the soils, and the soil conductivity, dielectric constant, and dielectric loss factor of the soils.

Materials and Methods

Description of the Study Area

This research was carried out in Delta State, Nigeria, focusing on areas with presence of non-functioning (abandon) illegal refineries. The region is characterized by thick forest, swampy wetlands and high annual rainfall of about 1800 mm volume per year, which supports numerous plant and animal species (Akpomrere and Uguru, 2020b). Streams located with the study region have seasonal flow characteristics, while most of the rivers emptied their waters into the Atlantic Ocean through the River Nigeria. The region has several clusters of illegal crude oil refining centers hidden in the creeks, and some of them have been destroyed by the Nigeria law enforcement agencies (Figure 1). These artisans only refine petrol, diesel and kerosene from the crude oil, and discard the remaining residues as wastes into the adjacent environment. This has significant ecological and public health menaces. Destruction of these illegal petroleum refining centers contributes to the environmental pollution at times, because the petrol products are allowed to spill into the environment untreated.

Figure 1: A scene of abandon refinery

Sample Collections and Preparation

Soil samples were collected from five locations with proximity to destroy/old refinery. The soil was sampled at a depth of 0.3 m by using the soil auger. Soil samples were also taken from another location with no history of oil contamination (about 10 km away from the contaminated points), to serve as the control (reference) point. The "refineries" were destroyed about two years ago by the Nigeria military. All the sampling locations have been overgrown with shrubs. The specimens were air-dried at a temperature of 30±5°C.

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Laboratory Analyses

Digestion of the Samples

The dried soil samples were grind and sifted 1 mm sieve. Approximately 10 g of the filtrate was digested with 20 mL of HNO_3, HCl, and H_2SO_4 mixture (combined in a ratio of 5:1:1), at a temperature of 85ºC in a water bath until a clear solution was attained. This solution was cool at room temperature (28±2°C), sieved into calibrated bottle with a filter paper and diluted to 100 mL volume using distilled water. The diluted digested solution was placed in a dark cabinet waiting further laboratory testing.

Total Hydrocarbon Content (THC) Determination

The THC of the digested soil samples was done by using the Soxhlet Extraction Method recommended by ASTM D 9071B – 7 (Akpomrere and Uguru, 2020b).

Heavy Metals Determination

The Cu, Ni, Pb and Cd levels in the digested solutions were measured by using the atomic absorption spectrophotometer, in accordance with ASTM approved procedures.

Soil Electrical Resistivity

The electrical resistivity (ρ) of the dried undigested soil was done in agreement with ASTM G187 (2018) guidelines. The resistivity (ρ) was computed by using expressions shown in Equations 1 and 2 (Obukoeroro and Uguru, 2021).

$$R = \frac{V}{I} \quad (1)$$

$$\rho = \frac{RA}{L} \quad (2)$$

Where: A is the soil column area and L is the column length of sample

Soil Dielectric Properties

The dielectric constant of the undigested soil samples was measured following the guidelines outlined in ASTM D150 (2018), employing a microwave frequency of 7.0 GHz at a temperature of 25±2ºC.

Statistical Analysis

The one-way analysis of variance (ANOVA) was employed to analyze the influence of the spatial location on the residual THC, HMs and electrical properties distribution in the soil.

Results and Discussion

Physicochemical Properties

Total Hydrocarbon Content (THC)

The one-way ANOVA results presented in Table 1 show that there is significant difference in the THC level among the five spatial points investigated (p ≤0.05). The mean results of the soil THC are plotted in Figure 2. It was noted the THC ranged from 1052 to 4024 mg/kg, which was significantly higher than the result (71 mg/kg) recorded at the control point. This portrayed that the effluent discharged from the waste products still have significant on the soil hydrocarbons concentration. Aljerf and AlMasri (2018) reported that petroleum hydrocarbons have low solubility characteristics; therefore they can persist in the ecosystems for extended periods. Aigberua *et al*. (2016) reported similar circumstances in crude oil contaminated soils. The THC level in the soil is directly proportional to the volume and concentration of oil in the soil; but THC distribution within the soil is affected by the soil physical characteristics and moisture content (Ejairu and Okiotor, 2022).

Table 1: ANOVA Result of the effect of Spatial Location on THC

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	14245494.93	4	3561373.73	1287.65	1.64E-13*	3.4780
Within Groups	27658	10	2765.80			
Total	14273152.93	14				

* = significant at p ≤ 0.05

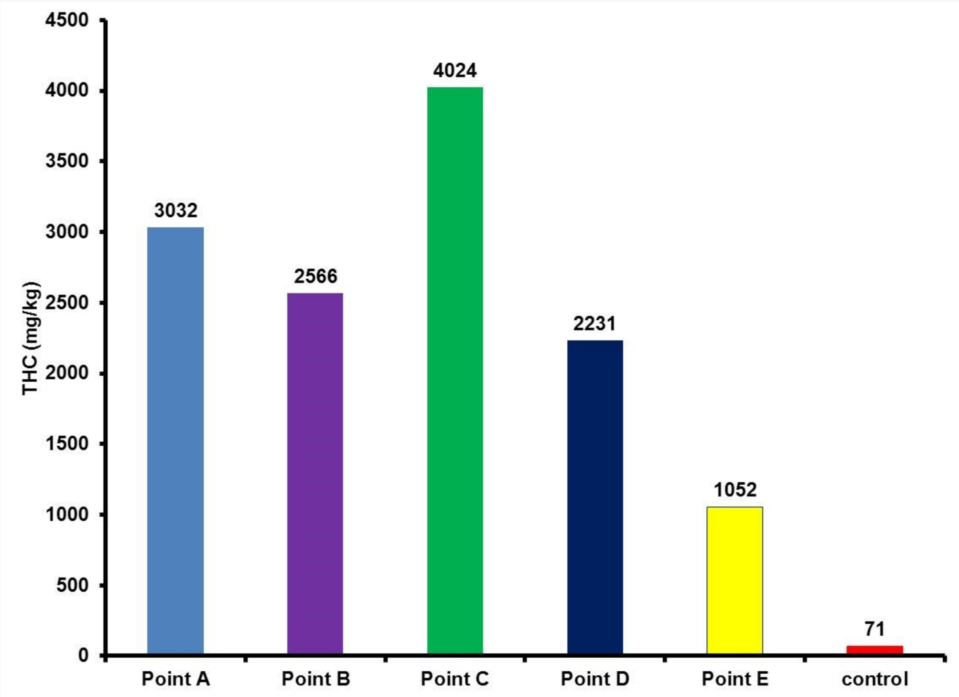

Figure 2: The THC levels in the soil samples

Heavy Metals

The ANOVA results indicate the effect of spatial location on the level of heavy metals (HMs) in the soil is presented in Table 2. It was noted from the one-way ANOVA findings that the spatial points of samples collection had significant effect of the specimens HMs concentration ($p \leq 0.05$). The mean separation results of the various HMs are presented in Table 3. It can be observed in Table 3 that HMs level in the soil samples, regardless of the sampling location were significantly higher than the concentration recorded at the reference point ($p \leq 0.05$). The Cu, Ni, Pb and Ni concentrations ranged from 3.63 to 8.10 mg/kg, 5.73 to 9.10 ppm, 5.13 to 8.30 ppm and 0.90 to 1.53 mg/kg, respectively within the study region. At the reference location, concentrations of Cu, Ni, Pb, and Ni were recorded as 2.27, 2.67, 3.70, and 0.08 mg/kg, respectively. Similar spatial variation in HMs content in soil samples randomly sampled from various oil spill sites in the Niger Delta region was reported by Ejairu and Okiotor (2022).

These results portrayed that the residual crude oil waste products still have significant impact on the environment, despite natural remediation efforts over time carried out by the vegetation and organic materials. Uguru *et al*. (2020) stated that plants and organic materials have the ability of degrading the harmful effects of petroleum products in the environment, through the process of phytoremediation and bioremediation, which are powerful natural processes for alleviating the hazardous impacts of toxic substances in the ecosystems. According to Bolan *et al*. (2011), incorporating organic matter into the soil enhances phytoremediation capacity by improving soil structure, microbial activities, and immobilizing the pollutants.

Table 2: ANOVA Result of the Influence of Location on the HMs Level

HM		Sum of Squares	df	Mean Square	F	p-value
Cu	Between Groups	74.176	5	14.835	186.74	6.02E-11*
	Within Groups	0.953	12	0.079		
	Total	75.129	17			
Ni	Between Groups	79.252	5	15.850	88.33	4.85E-09*
	Within Groups	2.153	12	0.179		
	Total	81.405	17			
Pb	Between Groups	36.513	5	7.303	58.95	4.99E-08*
	Within Groups	1.487	12	0.124		
	Total	38.000	17			
Cd	Between Groups	3.776	5	0.755	96.209	2.95E-09*
	Within Groups	.094	12	0.008		
	Total	3.870	17			

* = significant at $p \leq 0.05$

Table 3: Heavy Metals Concentration

Spatial point	Heavy metals (mg/kg)			
	Cu	Ni	Pb	Cd
Spatial point A	$6.43^{c}\pm0.25$	$8.47^{d}\pm0.60$	$5.87^{c}\pm0.35$	$1.19^{cd}\pm0.09$
Spatial point B	$8.10^{e}\pm0.20$	$5.73^{b}\pm0.38$	$6.83^{d}\pm0.31$	$0.90^{b}\pm0.10$
Spatial point C	$3.63^{b}\pm0.42$	$9.10^{d}\pm0.53$	$8.30^{e}\pm0.44$	$1.28^{d}\pm0.09$
Spatial point D	$5.97^{c}\pm0.31$	$6.47^{b}\pm0.45$	$5.57^{bc}\pm0.38$	$1.53^{e}\pm0.08$
Spatial point E	$7.23^{d}\pm0.25$	$7.27^{c}\pm0.21$	$5.13^{b}\pm0.35$	$1.11^{c}\pm0.12$
Control	$2.27^{a}\pm0.21$	$2.67^{a}\pm0.21$	$3.70^{a}\pm0.26$	$0.08^{a}\pm0.02$

Means sharing the same common letter (superscript) within the same column for each metal are not significantly different ($p > 0.05$); ±= standard deviation

Electrical Properties

Table 4 presents the ANOVA results demonstrating the impact of spatial location on the soil's electrical properties. The one-way ANOVA findings revealed a significant effect of the spatial points of sample collection on the ρ and ε′ levels in the specimens ($p \leq 0.05$). The separated mean results of the specimens' ρ and ε′ are presented in Table 5. The findings depicted that the electrical resistivity across the five sampled points varied from 451.00 to 836.00 Ωm, while the dielectric constant values varied between 3.16 and 3.73. This affirms that the soils around the localities of the abandon illegal refineries still contains significant amount of petroleum hydrocarbons. According to Igboama and Ugwu (2016), oils are generally poor conductors of electrical current, hindering the flow of electrical current through the soil, which can lead to an increase in soil electrical resistivity when they are present. Similarly, Yodrot et al. (2023) during their investigation into the impact of oils on soil dielectric properties reported that, since oils have relatively high ε′, their presence in the soil may cause an increment the soil's dielectric constant.

Table 4: One way ANOVA Result of the Spatial Point on the Soil Electrical Behaviors

Parameter		Sum of Squares	Df	Mean Square	F	p-value
P	Between Groups	660048.000	5	132009.60	290.34	4.41E-12*
	Within Groups	5456.000	12	454.67		
	Total	665504.000	17			
ε′	Between Groups	1.572	5	0.314	84.99	6.07E-09*
	Within Groups	.044	12	0.004		
	Total	1.617	17			

* = significant at $p \leq 0.05$

Table 5: Electrical Properties of the Specimens

	Electrical resistivity (Ωm)	Dielectric constant
Spatial point A	$451.00^{b}\pm4.36$	$3.16^{b}\pm0.04$
Spatial point B	$576.67^{c}\pm3.51$	$3.51^{d}\pm0.07$
Spatial point C	$836.00^{e}\pm49.43$	$3.73^{e}\pm0.04$
Spatial point D	$596.67^{c}\pm5.86$	$3.38^{c}\pm0.04$
Spatial point E	$675.67^{d}\pm5.51$	$3.44^{cd}\pm0.11$
Control	$218.00^{a}\pm13.75$	$2.80^{a}\pm0.01$

For each metal, if means share the same common letter (superscript) within the same column, they are not significantly different ($p > 0.05$); ±= standard deviation

The findings indicate a clear presence of residual petroleum byproducts in the soils, particularly in the vicinity of the refineries. The higher concentrations of the parameters investigated in the refinery neighborhood compared to the reference point strongly suggest contamination by petroleum-related substances (Zhuang *et al*., 2023). Furthermore, the results clearly showed that soil sampled from spatial point C generally recorded the highest values for all the physicochemical and electrical properties investigated. This could be attributed to the volume of waste materials this point received, and the remediation process it has undergone (Igboama and Ugwu, 2016; Ejairu and Okiotor, 2022). The elevated ρ and ε′ will pose some challenges to electrical installations. High soil ρ can impede the dissipation of electrical currents through grounding systems (Zhao et al., 2024). Similarly, the high ε′ in soil around the refineries locations will affects the capacitance of grounding systems. This will affect their integrity and expose human beings to the risk of electrocution (Odoh *et al*., 2024). Additionally, the high HMs recorded in the locality formally occupied by these refineries can lead to heavy metals toxicity, which have serious consequences on human beings and the environment. Lead, cadmium, and nickel can lead to body organs and systems malfunctioning even at minute concentrations (Tchounwou *et al*., 2012). As seen in the results, proper remediation of areas where illegal refineries were located is paramount to mitigate the risks associated with petroleum toxicity.

Conclusion

This research evaluated the effect of residual petroleum hydrocarbons on the physiochemical and electrical properties on the soil. Soil samples were taken from five spatial locations with proximity to clusters of abandon artisan refineries. The THC, Cu, Pb, Ni, Cd, electrical resistivity and dialectical constant values of the presumed contaminated soil samples and from the reference point, were determined in accordance with standard approved guidelines. Outcomes of this research revealed the presences of residual petroleum hydrocarbons in the old refineries sites. The laboratory results depicted that the THC, Cu, Pb, Ni, Cd, electrical resistivity and dialectical constant values recorded at the old refineries sites were higher than the values recorded at the control position. This correlation suggests the presence of a significant amount of petroleum in the soil at the old refinery sites. These findings highlight the urgent need for remediation efforts to protect both human health and the environment from the harmful effects of petroleum contamination.

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