Geochemical Screening of Oil Spill Impacted Agricultural Soil in Okpari-Olomu Niger Delta, Nigeria.

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Abstract

Nigeria's Niger Delta, oil exploration have been hampered by oil spills. The study's goals were to identify the origins of polycyclic aromatic hydrocarbons (PAHs) in Okpari-Olomu, Niger Delta, Nigeria, as well as the physiochemical features of the soil, concentration, pollution, and risk assessment level of heavy metals. Fifteen soil samples were gathered in three clusters. Prior to laboratory analysis, samples were dried, powdered, and sieved to the necessary particle size. The Geoaccumulation Index (Igeo), Enrichment Factor (EF), and Pollution Load Index (PLI) were the three geochemical indices that were used. We measured the sample's pH, EC, temperature, oil and grease (O & G), TOC and concentrations of the sixteen priority PAHs. Site 12 had the lowest Oil and Grease value (63.2 mg/kg) which was greater than the control site's O and G value (58.92 mg/kg). *According to the Vanadium (V) EF values of clusters one, two, and three, which are 538.63, 148.98, and 57.30, respectively, the soil is highly contaminated (extremely enriched) by V.* Significant vanadium and lead pollution was noted by Geoaccumulation Index. Pollution Load Index values classified cluster one as highly polluted, clusters two/three as significantly contaminated. Since concentration values were greater than threshold of 1.0 mg/kg for heavy pollution, the mean values (3.53, 1.51, and 1.51) mg/kg for ∑16PAHs of the three clusters indicated heavy pollution. PAHs in these soils were from pyrogenic or petroleum emissions, oil, and oil burning. Therefore, rehabilitation of the soil is urgently needed.

Keywords: Spilt oil, Agricultural soil, Geochemical screening, Soil pollution, Okpari-Olomu, Niger Delta

1. Introduction

Crude oil is made up of hydrocarbons and other organic compounds and is found naturally. Drilling is the common method of obtaining crude oil, which is frequently found in conjunction with other resources like saline water and natural gas. Petrol, diesel, and other petrochemicals are among the useful products made from refined crude oil, a form of fossil fuel. Nigeria's primary economic resource at the moment is petroleum. Nonetheless, according to [1], it is among the most common organic contaminants in the Niger Delta.

Natural catastrophes, intentional releases, mistakes made by people, or technical malfunctions can all result in oil spills. An estimated 30–50% of oil spills are directly or indirectly related to human mistake, while 20–40% are attributed to equipment failure or malfunction [2]. Oil well blowouts, seepages, tanker accidents, and deliberate damage to operational facilities are possible additional causes of oil spills in the area [3]. A number of figures indicate that Nigeria experiences more oil spills than any other country in the world, with an estimated 400,000 barrels occurring per day, according to an Agency Report published by Premium Times on July 6, 2021. Mexico follows with approximately 5,000 to 10,000 barrels per day. According to Ahiamadu *et al.* [4], the National Oil Spill Detection and Response Agency (NOSDRA) reported that there were 4,919 oil spills between 2015 and March 2021, and the Nigeria Natural Resource Charter stated that Nigeria lost an estimated $4.75 trillion due to illicit oil activities between 2015 and 2018 [5].

Over time, the Niger Delta region has seen significant environmental degradation caused by oil, which has resulted in a decline in agricultural output, a loss of soil fertility, and a depletion of biomass [6]. Chemicals such as saturated hydrocarbons, naphthenes, alkenes, aromatics, and certain heavy metals like chromium, lead, zinc, mercury, and cadmium may be present in this polluted soil [7].

Frequent exposure to high concentrations of PAHs and trace metals is one of the biggest problems related to oil pollution. One of the main ways that these pollutants and toxins enter the food chain is through plants. These pollutants are consumed by organisms that get their nourishment from plants, which can result in illnesses like cancer, liver and kidney damage, and anemia [8].

The effects of crude oil pollution on Nigeria's surface water and aquatic ecosystems have been studied in connection with the country's agriculture, biological variety, human health, and groundwater sources [9, 10]. Little attention was paid to the effects on groundwater contamination; most of the research was devoted to understanding the advection and dispersion mechanisms of crude oil pollution on surface water [11]. Nevertheless, dissolved sources of contamination from surface water eventually affect the groundwater system. Most research on subsurface crude oil contamination employ a point sample technique to measure the total amount of crude oil in soil and water samples.

One method for analyzing and evaluating petroleum pollution is geochemical or oil fingerprinting. It entails measuring the amount of hydrocarbon compounds in the leaked oil and analyzing it using gas chromatography (GC) [12]. The qualitative approach (visual comparison of chromatograms) and quantitative assessment of the diagnostic ratio of PAHs, n-

alkane distribution, and statistical analysis of the data acquired are used to identify the source and interpret chemical data from oil spills. Therefore, it is necessary to measure and evaluate hydrocarbon contamination to lessen the region's accelerating pace of environmental degradation and its impacts on the social, economic, and health domains. This research covers the origins, properties, distribution, and fate of organic contaminants, including aliphatic hydrocarbons (AHs) and PAHs, in the Niger Delta.

There is currently little information on the geochemical screening of oil-impacted agricultural soil in Nigeria's Niger Delta, according to a review of the literature. Consequently, the purpose of this study is to identify certain chemical components in an oil-impacted soil and investigate how these components affect soil fertility in Okpari-Olomu, Niger Delta, Nigeria.

2. Materials and Methods

2.1 Study Area

The Okpari-Olomu study area is situated in Delta State's Ughelli South Local Government Area and is a community in Nigeria's Niger Delta geopolitical zone. It is located in the Nigerian Niger Delta at latitude 050 25' 43' N and longitude 50 56' 48' E. passing through several settlements, such as Okwagbe and Otu-Jeremi, before joining the Forcados River. Due to illegal refining and crude oil bunkering, the region has seen years of environmental contamination and a number of crude oil pollution incidents [13]. The sampling sites are depicted in figure 1. The primary occupations of the residents are fishing, periwinkle picking, boating, and local sand dredging. During refining, residues are disposed of into the nearby water body, affecting the quality of the water that is frequently used for domestic, fishing, and recreational purposes like swimming by indigenous members of the community. River monitoring is necessary to prevent public health implications, which is why this study is necessary.

Sampling Sites

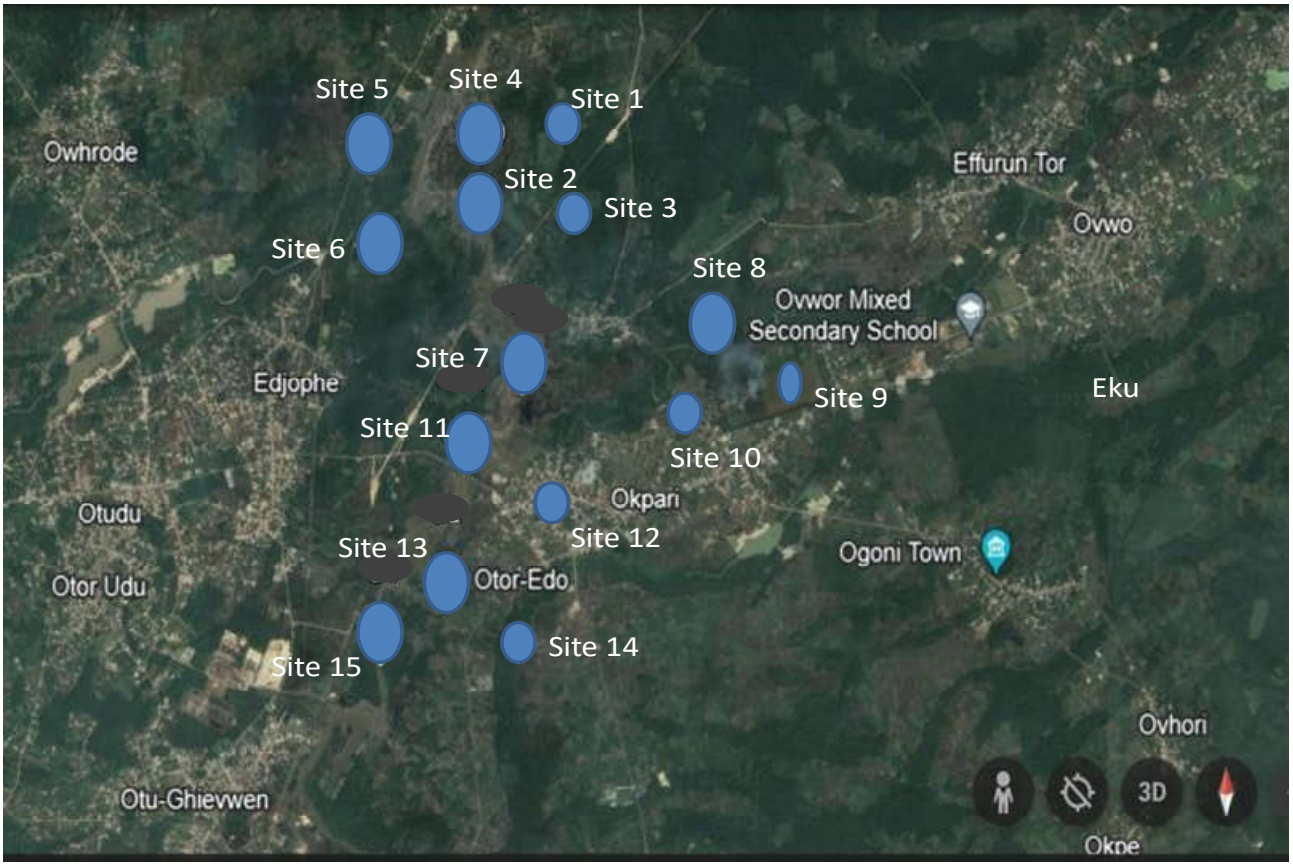

Figure 1: Geographic location of three clusters sampling sites and control (Eku).

2.2 Sampling

Fifteen soil samples were collected from oil spill sites in Delta State's Okpare Community, located in the Ughelli South Local Government Area, using a Dutch hand auger. Soil samples were collected in 60mL clean bottles with labels for hydrocarbon analysis; samples were collected in Ziploc bags for physiochemical analysis; and samples were collected in a dust-free, clean environment using certified metal-free collection containers (powder-free gloves) to minimize specimen contamination for metal analysis. The samples were then kept in an ice chest until they were brought to the laboratory to be examined.

2.3 Sample Preparation for Chemical Analyses

To prevent gas adsorption in the lab before chemical analysis, soil samples for physicochemical and heavy metal analyses were air dried, pounded with a sterile ceramic pestle and mortar, sieved through a 2 mm sieve, and promptly placed in an airtight, clean plastic bag.

2.4 Determination of pH of Soil Samples

In accordance with the Standard Test Method (ASTM D4972) for pH of Soils, the pH of soil samples was electronically measured using a Sharp glass electrode pH meter model pH-98108. Before measuring the pH of the sample, the pH meter, which has a sensitivity of ±0.01, was calibrated with buffer pH 4.0, 7.0, and 10.0 solutions.

2.5 Determination of Electrical Conductivity (EC) of Soil Samples

A Horiba D-70 Series glass electrode conductivity meter was used to electronically measure the EC of the soil samples using a standard procedure in accordance with the US Environmental Protection Agency's (USEPA 9050A) Method for measuring Specific Conductance. Before measuring the sample, the conductivity meter, which has a sensitivity of ±0.01, was calibrated using a standard conductivity solution of 1413 µs/cm.

2.6 Determination of Temperature in Soil Samples

A mercury-in-glass thermometer was used to measure the temperature of soil samples using a standard procedure in accordance with the American Public Health Association Method (APHA 2550B). A NIST-certified thermometer, which is utilized with its certificate and correction chart, was regularly used to calibrate the thermometer.

2.7 Total Organic Carbon (TOC)

TOC was evaluated using finely separated 0.42mm sieved soil sample by the chromic acid wet oxidation method [14]. 0.5 grams of soil samples was weighed into 500mL conical flask. To evenly distribute the soil, 10 mL of 1.0 M analyte grade potassium dichromate ($K_2Cr_2O_7$) was precisely measured, added to each flask, and gently stirred. The identical procedure was used for the blank sample, but soil was not used to standardize the dichromate. Within a fume cabinet, 20 mL of concentrated sulfuric acid (H_2SO_4) was quickly poured to the flask, stirred, and left to stand for half an hour. After adding 100 mL of distilled water, the flask was let to stand for half an hour. 10mL of O-phosphoric acid was added to the flask. 3 to 4 drops of ferroin was added to the solution contained in the 500 mL conical flask. The end point was reached when the solution's color transitioned from green to blue and then to red (maroon) after being titrated against 0.5M ferrous ammonium sulphate. Total Organic Carbon (TOC) was computed using the following formula as it was expressed as a percentage:

$$TOC(\%) = \frac{mL\ Fe^{2+} for\ blank\ - mLFe^{2+}\ for\ sample}{Weight\ of\ soil\ in\ gram} \times Normality\ of\ Fe^{2+} \times 0.390$$

Where:

0.390 =Milli equivalent weight of Carbon/Correlation factor

2.8 Oil and Grease

They used the Soxhlet-Gravimetry method as outlined in USEPA9071B. The fume cupboard was equipped with a heating mantle that was set to 60°C. After filling the thimble with Pyrex glass wool and adding 10g of soil sample and 10g of anhydrous sodium sulphate (Na_2SO_4), the thimble was carefully lowered into the Soxhlet extractor. Five to six anti-bumping granules were introduced to a 500 mL round-bottom flask that was clean and dry and contained 100 mL of acetone and 100 mL of hexane. After 16 to 24 hours of refluxing the mixture in the round-bottom flask in a Soxhlet system, it was allowed to cool.

Oil & Grease in soil samples is calculated thus:

$$O\ \&\ G\ (\frac{mg}{kg}) = \frac{Weight\ of\ Flask + Dried\ Residue\ - Weight\ of\ Empty\ Flask}{Weight\ of\ sample} \times 1000$$

The concentration of O&G obtained was expressed as mg/kg, dried weight.

2.9 Determination of Heavy Metals

Heavy metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer according to the method of APHA [15] (American public health association). 1g of each sample was digested with aqua-regia for 5 days. The extract was centrifuged 30,000 for 15 mins and the heavy metal was determined using appropriate calibration curves prepared in the same acid matrix with standard metal solutions for atomic absorption spectrophotometer Heavy metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer according to the method of APHA (American public health association). 1g of each sample was digested with aqua-regia for 5 days. The extract was centrifuged 30,000 for 15 mins and the heavy metal was determined using appropriate calibration curves prepared in the same acid matrix with standard metal solutions for atomic absorption spectrophotometer Using an Atomic Absorption Spectrophotometer (Varian Spectra AA 880 model), heavy metal analysis was conducted in accordance with the American Public Health Association's 2017 methodology (APHA).

One gram of each sample was digested using ten milliliters of aqua-regia solution, which is a mixture of 70% HNO_3 and 37% HCl in a (1:3) v/v) ratio. The sample solution was then heated to 240°C for two hours until all of the samples had completely dissolved and a clear, colorless solution was produced. 30 mL of distilled water was added to the sample solution after it had finished digesting and had been let to cool in the air. The mixture was then diluted with 50.0 mL of distilled water after being filtered through Whatman filter paper. The heavy metal was identified using suitable calibration curves made in the same acid matrix with reference metal solutions using atomic absorption spectrophotometry after the extract was centrifuged for 15 minutes at 30,000 rpm. For accuracy and precision, all experiments were conducted in triplicate. The same process used to prepare the samples was also used to prepare blank solutions, which contained only the mixture of HNO_3 and HCl.

2.10 Extraction and Fractionation.

Using a ceramic mortar and pestle, soil samples were mashed and thoroughly homogenized in order to eliminate stones and other foreign elements. As instructed by the USEPA 8270E2021 technique, the extraction was performed using ultrasonography. After weighing and homogenizing 10g of well-mixed samples separately with 20g of anhydrous sodium sulphate (Na_2SO_4), additional Na_2SO_4 was added and thoroughly mixed to create a free-flowing, finely divided slurry if the homogenate still included a significant amount of moisture. To enhance the surface area and aid in the rapid removal of moisture, the sample homogenate was spread out on foil paper. Before extraction, a well-mixed sample was obtained by crushing the sample homogenate in a sterile laboratory ceramic mortar. 20mL (1:1 v/v) of dichloromethane-acetone mix was added to a 250mL glass Soxhlet extraction flask containing the crushed sample homogenate. The flask was then firmly sealed and left for 11 hours at a rate of 5 cycles per hour.

A motorized shaker was used to shake the flask for sixty minutes. The material was then further agitated ultrasonically for 30 minutes at roughly 70°C in a Sonicator after the flask had been moved there. After that, a 250 ml Erlenmeyer flask that had been securely corked to stop solvent extract evaporation was carefully filled with the solvent extract. In a temperature-

controlled hot water bath that was already set to 50°C, the combined extracts were moved to a rotary evaporator that included a 500 ml round-bottomed flask, condenser, and extractor tube. The extract's volume was decreased to about 1-2 milliliters by evaporating it.

Glass fractionating columns were filled with chromatograph glass wool and kept in a fume cupboard before extraction. Overnight oven drying at 105°C activated 10 grams of silica gel. The silica gel was combined with dichloromethane (DCM) (1:1 w/v) (HPLC grade; 99% reagent grade Fisher Scientific, Loughborough, UK) to create a slurry that was then moved to the column. Before the cleanup procedure, 10 mL of DCM was poured to the fractionating glass column to condition it after 5 g of anhydrous sodium sulphate (Na_2SO_4) was added to absorb water. Following the cleanup process, the Agilent 8890 Gas Chromatograph-Flame Ionization Detector (GC-FID) and Agilent 8860 Mass Selective Detector (GCMSD), thermal conductivity detectors (GCTCD), chemiluminescence detectors (GCXCD), instruments were used to separate and detect the analyte in the sample.

2.11 Assessment of Contamination in Sediment

The levels of contamination in the sediment samples were assessed using three popular indices: the Geo-accumulation Index (I_{geo}), the Enrichment Factor (EF), and the Pollution Load Index (PLI). Their descriptions and particular applications in the study are as follows.

2.11.1 Geo-Accumulation Index

Müller [16] states that the geo-accumulation index (I_{geo}) is a quantitative metric commonly used to assess the level of heavy metal pollution in sediments found in lakes and rivers [17]. To calculate I_{geo}, use the following formula:

$$I_{geo} = \log_2[C_i/(k \times B_i)] \quad - - - - - - \quad (1)$$

where Ci is the measured element I concentration in the sediment, Bi is the element I geochemical background value, and k = 1.5 is added to lessen the effect of any background value fluctuations that could be brought on by lithological variations.

3. Results

3.1 Physiochemical Parameters

To examine the level of tainting in both polluted as well as pure samples, a soil chemical analysis was conducted. When the pH readings of each site were contrasted with those of the control (Eku), it was found that all 16 sites, including the control site, had acidic soil. The physiochemical parameters, pH, temperature, electrical conductivity (EC), oil and grease (O & G), and total organic carbon (TOC) outcome are shown in Table 1.

Table 1: Physiochemical Parameters

Parameters	Test Method	Soil Sample sites															Total	Soil Site Control
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
pH	ASTM	4.25	4.02	4.14	4.61	4.64	4.37	4.7	4.32	4.44	4.09	4.2	4.3	4.64	4.54	4.48	65.74	4.19
EC (µS/cm)	USEPA 9050A	37	27	25	19	21	28	34	13	22	20	57	41	77	36	45	502	46
Temperature (^{0}C)	APHA 2550B	26.1	26.3	26.1	26.2	27.3	26	27.1	26.2	26.2	26.1	26.2	26.3	26.1	25.9	25.9	394	26
O&G (mg/kg)	USEPA 9071B	$1.55x10^3$	$8.30x10^3$	$10.04x10^3$	$7.34x10^3$	$5.11x10^3$	$4.16x10^3$	$98.9x10^1$	$2.848x10^3$	$3.262x10^3$	$1.86x10^3$	$121.4x10^1$	$63.25x10^2$	$4.585x10^3$	$7.182x10^3$	$1.97x10^2$	$5.6736x10^4$	$4.28x10^2$
TOC(%)	Walkley-Black 1974	5.89	5.17	4.88	5.38	6.01	5.23	5.62	4.97	5.11	5.19	5.34	2.96	4.78	4.39	5.15	76.07	5.07

Table 2: Concentration of Heavy metals (mg/kg).

Sites		Pb	Fe	V	Cr	Cd	Ni	Cu
Cluster 1	Mean ± SD	20.62±6.79	3334.2±1446.3	0.47±0.21	8.03±2.75	7.07±1.63	24.32±3.53	68.37±19.2
Cluster 2	Mean ± SD	11.57±2.14	279.43±151.63	0.13±0.06	6.42±2.50	5.43±1.87	22.27±12.2	106.93±67.7
Cluster 3	Mean ± SD	8.31±2.95	2568.72±1776.7	0.05±0.11	5.36±1.81	4.50±2.20	26.18±3.97	71.93±39.25
Soil Site Control		2.14	3821.00	0.001	2.19	1.90	11.30	80.70
WHO, [18] (Target value)		85.00	N/A	N/A	100.00	0.80	35.00	36.00
Intervention Value		530.00	N/A	N/A	360.00	12.00	210.00	190.00
DPR, [19] (Target Value)		85.00	N/A	N/A	100.00	0.80	35.00	36.00
Intervention value		530.00	N/A	N/A	380.00	17.00	210.00	190.00
Regulatory standards of heavy metals concentration in agricultural soil [20]								
Australia		300.00	N/A	N/A	50.00	3.00	60.00	100.00
Canada		200.00	N/A	N/A	250.00	3.00	100.00	150.00
China		80.00	N/A	N/A	150-300	0.3-0.6	40-60	50-200
Germany		1000.00	N/A	N/A	500.00	5.00	200.00	200.00
Tanzania		200.00	N/A	N/A	100.00	1.00	100.00	200.00
Netherland		530.00	N/A	N/A	180.00	13.00	100.00	190.00
New Zeeland		160.00	N/A	N/A	290.00	3.00	N/A	>104
UK		N/A	N/A	N/A	N/A	1.80	230.00	N/A
USA		200.00	N/A	N/A	11.00	0.48	72.00	270.00

Table 3: I_{geo} values for heavy metals from the oil spill impacted sites for this study.

Sites	Pb	Fe	V	Cr	Cd	Ni	Cu
Cluster 1	2.68	-0.78	8.29	1.29	1.31	0.52	-0.82
Cluster 2	1.85	-4.36	6.44	0.97	0.93	0.39	-0.18
Cluster 3	1.37	-1.16	5.06	0.71	0.66	0.63	-0.75

The I_{geo} is categorized into seven classes, as shown in Table 4 (Supplementary Material).

The contamination categories are recognized on the basis of the enrichment factor (EF) [21].

Table 6: Enrichment factor (EF) of heavy metals present in the oil spill impacted site

Metals	**Cluster One**	**Cluster Two**	**Cluster Three**
Pb	11.04	6.20	4.45
Fe	1.00	0.08	0.77
V	538.63	148.98	57.30

Cr	4.20	3.36	2.80
Cd	4.26	3.28	2.71
Ni	2.47	2.26	2.66
Cu	0.97	1.52	1.02

The PLI value of soil sample were discovered to be above 3 for cluster 1 showing enormous defilement and between 2 and 3 for stations 2 and 3 indicating a considerable degree of pollution.

Table 7: PLI Values

Sites	PLI values
Cluster 1	5.17
Cluster 2	2.73
Cluster 3	2.86

According to Table 7's Pollution Load Index (PLI) amount for the metals found in the three cluster sites of this study, cluster one's PLI value of 5.17 indicates firmly tainted, while clusters two and three's PLI values of 2.73 and 2.83, respectively, indicate considerably tainted. The pollution grading standard is shown in Table 8.

Table 9**:**Concentrations of PAHs in (mg/kg) of components from Oil spill sites and the control site

		Soil Sample sites																
Parameters	Test Method																	
16 PAHs		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Total	CTRL Soil
NAP		0.29	2.01	0.3	0.86	0.54	0.31	0.27	1.17	0.37	0.88	0.29	0.17	0.67	0.38	0.27	8.78	0.03
ACY		2.06	4.41	17.41	9.25	13.53	0.47	N.D	1.85	0.65	0.54	N.D.	0.11	10.99	6.93	N.D.	68.2	0.02
ACE		2.93	3.6	4.67	3.15	2.44	4.36	N.D	0.65	0.44	2.36	N.D.	N.D.	2.82	3.42	N.D.	30.84	0.04
FLU		4.61	3.53	10.14	0.4	4	0.62	N.D.	1.23	1.56	1	N.D.	N.D.	2.19	3.84	N.D.	33.12	N.D.
ANT		1.3	2.85	4.9	3.09	2.82	0.56	0.23	1.84	1.85	4.73	0.27	0.12	4.68	4.51	0.29	34.04	0.04
PHE		1.42	5.82	12.09	7.61	10.27	5.25	0.18	0.68	0.88	0.26	0.21	0.1	7.9	8.3	0.23	61.2	0.03
FLA		0.2	10.05	20.85	2.24	1.57	0.88	0.21	3.13	4	0.75	0.19	0.14	1.13	1.54	0.37	47.25	0.02
PYR		0.73	1.32	26.39	0.82	1.49	2.16	0.19	0.38	1.21	0.63	0.18	0.33	0.82	10.09	0.33	47.07	0.02
BaA		4.78	6.87	7.97	6.58	3.29	4.5	0.28	6.11	2.25	1.46	0.32	0.14	11.2	3.34	0.3	59.39	0.03
CHR		1.59	2.03	2.15	5.14	1.23	2.35	0.15	2.43	2.78	0.11	0.17	0.07	4.12	13.05	0.16	37.53	0.02
BbF		1.6	5.3	5.4	0.84	3.54	2.46	0.28	1.14	0.43	1.86	0.43	0.6	6.46	7.42	0.28	38.04	0.03
BkF		1.02	0.7	2.76	0.42	0.6	3.75	0.14	0.45	0.21	0.9	0.21	0.1	1.16	1.35	0.14	13.91	0.03
BaP		1.4	1.44	1.93	2.49	2.24	3.21	0.21	1.28	3.65	1.26	0.2	0.21	3.19	5.42	0.21	28.34	0.06
InP		1.59	1.71	1.83	0.33	0.34	0.56	N.D.	0.75	2.78	1.83	N.D.	0.16	0.87	0.54	N.D.	13.29	N.D.
DBA	USEPA 8100	2.18	1.33	0.2	1.81	1.95	2.32	N.D.	1.01	2.43	2.45	N.D.	0.2	4.54	0.35	N.D.	20.77	0.03
BgP		0.48	3.74	1.5	1.19	1.58	2.56	N.D.	0.21	1.21	0.68	N.D.	N.D.	0.37	1.25	N.D.	14.77	0.02

∑ PAHs	28.18	56.71	120.49	46.22	51.43	36.32	2.14	24.31	26.7	21.7	2.47	2.45	63.11	71.73	2.58	556.54	0.42

Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Anthracene (ANT), Phenanthrene (PHE), Fluoranthene (FLA), Pyrene (PYR), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)perylene (InP), Dibenz[a,h]anthracene (DBA), Benzo[ghi]perylene (BgP). PAH- Polycyclic Aromatic Hydrocarbons, AHF- Aliphatic Hydrocarbon Fraction, TPH- Total Petroleum Hydrocarbon

According to Table 9, the range of ∑16PAHs for 15 affected sites is 2.14–120.49 mg/kg. Concerns have been raised about the existence of PAHs in the surrounding because many of them are mutagenic and others are carcinogenic [22]. US Environmental Protection Agency has designated 16 PAHs as primacy contaminants due to their possible toxicity [23]. BaA, CHR, BbF, BkF, BaP, InP, and DBA are among them.

Table 10: Concentrations of PAHs

PAHs	Sites in Clusters		
	Cluster One	Cluster Two	Cluster Three
	(1,2,3,4,5,6)	*(8,9,10)*	*(7,11,12,13,14,15)*
NAP	0.72	0.81	0.34
ACY	7.86	1.01	3.01
ACE	3.53	1.15	1.04
FLU	3.88	1.26	1.01
ANT	2.59	2.81	1.68
PHE	7.08	0.61	2.82
FLA	5.97	2.63	0.60
PYR	5.49	0.74	1.99
BaA	5.67	3.27	2.60
CHR	2.42	1.77	2.95
BbF	3.19	1.14	2.58
BkF	1.54	0.52	0.52
BaP	2.12	2.06	1.57
InP	1.06	1.79	0.26
DBA	1.63	1.96	0.85
BgP	1.84	0.70	0.27
∑16PAHs	56.56	24.24	24.08
Mean	3.53	1.51	1.51
∑7PAHs	17.62	12.52	11.33
Mean	2.52	1.79	1.62

Table 10 lists the mean concentrations of the seven carcinogenic PAHs (~7PAHs) and the sixteen priority PAHs (~16PAHs) for the fifteen affected sites in three clusters (Clusters One, Two, and Three). While the total summations of the 16PAHs in each cluster and their mean values are (56.56 and 3.53) mg/kg respectively for cluster one, (24.24 and 1.51) mg/kg respectively for cluster two, and (24.08 and 1.51) mg/kg apart for cluster three, the average concentrations of the 16PAHs in Clusters 1, 2, and 3 range from 0.72-7.86), (0.52-3.27), and (0.27-3.01) mg/kg respectively. Each cluster's mean 16PAH levels are higher than the 0.03 mg/kg found at the control location, which is unaffected.

Table 11: Mean concentrations of Σ16 PAHs in soils from different cities around the world

District	Soil Types	Depth (cm)	Number of PAHs	Mean (µg/kg)	Mean (mg/kg)	References
Loess Plateau, China	Petroleum-contaminated soil	0–10	16	5502.44	5.50	Wang *et al.* [24]
Delhi, India	Urban/rural soil	0–20	16	550	0.55	Kumar *et al.* [25]
Ma'an, Jordan	Urban soil	0–10	13	917.4	0.92	Alsbou *et al.* [26]
Chongqing, China	Urban soil	0–30	16	1780	1.78	Zhang *et al.* [27]
New York, USA	Garden soil	0–10	16	14,200	14.20	Marquez-Bravo *et al.* [28]
Pearl River, China	Urban soil	0–10	16	219	0.22	Cai *et al.* [29]
Taiyuan, China	Urban soil	0–10	21	1,444.7	1.44	Liu *et al.* [30]
Banja Luka, Bosnia	Industrial soil	0–30	16	1,716	1.72	Bjelic *et al.* [31]

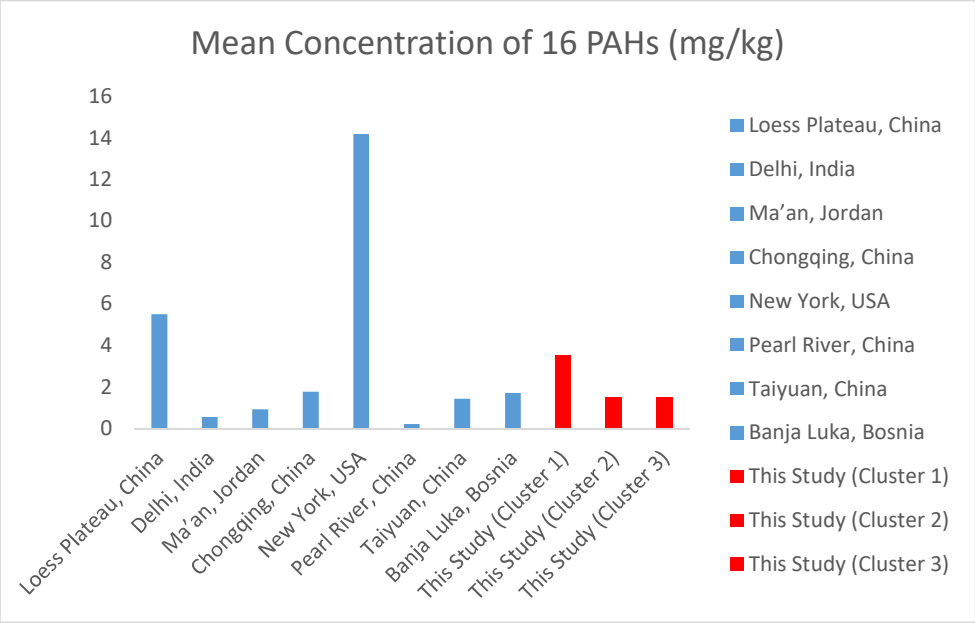

Figure 2: The mean concentrations of Σ16 PAHs in mg/kg of this study and those of other studies

The average concentrations of ~16PAHs at the three cluster sites of this investigation are displayed in Figure 2, along with the summary concentrations of ~16PAHs in a few cities

worldwide. Only the ~16PAHs concentrations derived from comparable investigations conducted in Loess Plateau, China, and New York, USA, surpass cluster one, which is the highest of the three clusters for this study, as the bar chart makes evident. Therefore, rehabilitation of the soil is urgently needed.

Table 13. Diagnostic ratios of PAHs in the oil spill sites

Diagnostic ratios	Fla/(Fla+Pyr)	BaA/(BaA+Chr)		Fla/(Fla+Pyr)	BaA/(BaA+Chr)		Fla/(Fla+Pyr)	BaA/(BaA+Chr)
Cluster1 (1,2,3,4,5,6)			Cluster 2 (8,9,10)			Cluster 3 (7,11,12,13,14, 15)		
MIN	0.21	0.73	MIN	0.66	0.93	MIN	0.44	0.67
MAX	0.44	0.61	MAX	0.77	0.69	MAX	0.13	0.20
MEAN ± SD	0.32±0.11	0.67±0.06	MEAN ±SD	0.71±0.05	0.81±0.17	MEAN ±SD	0.28±0.22	0.43±0.47

Table 14: Ringwise distribution of the three cluster sites.

Rings	**Cluster 1**	**Cluster 2**	**Cluster 3**
2	1	1	ND
3	25	7	10
4	19	8	8
5	8	6	5
6	3	3	1
LMW/HMW	0.87	0.47	0.71

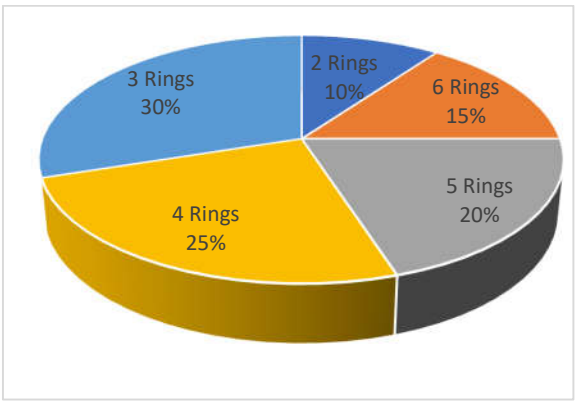

Fig. 3: *Spatial distribution of the PAH rings in soil samples.*

4 Discussion

4.1 Physicochemical Characteristics

The low pH range of the soil's crude oil defilement suggests that as the concentration of raw oil increases, the soil tends to become more acidic. The acidic quality of the soil is caused by

hydrocarbons found in crude oil, which can react with salts and soil minerals to make alkaline minerals acidic. Devatha *et al*.[32], who investigated. The physiochemical qualities of soil resulting from crude oil defilement and its regeneration, came to similar conclusions. They found that the pH range was significantly lowered when raw oil pollution was present, indicating that the soil tended to become more acidic as the raw oil concentration rose.

The metric that correlates with soil features that impact crop productivity—such as soil texture, cation exchange capacity, drainage conditions, organic content, salinity, and subsurface features—is soil electrical conductivity. Because crude oil is made up of petroleum hydrocarbons, it has a large number of ions that can form bonds with the ions in the soil. Because of the snowballed tainting, the contaminated soil becomes more electrically conductive. Sites 11 and 13 displayed higher Electrical Conductivity (EC) values (57 and 77 µS/cm, respectively) than the control, which had an EC value of 46 µS/cm. This suggested that the most polluted areas were 11 and 13.

The lowest Oil and Grease (O & G) value from site 12, 63.2 mg/kg, indicates the presence of petroleum hydro-carbons from an oil spill close to the sample site. Contrasted with the control site's O & G value of 58.92 mg/kg, this result was higher. Outstanding detection limits at every analytical wavelength. Goal value: This objective is intended to prevent, lessen, or mitigate adverse effects on human well being and/or the surrounding in general, and it should be accomplished whenever possible within a given time frame. Intervention value: These natural soil quality parameters are used to determine which areas are highly tainted. It alerts us when the soil's capacity to sustain human, animal, and plant life is seriously threatened. Additionally, it shows the level of pollution at which a significant case of soil defilement takes place.

4.2 Concentration of Heavy Metals

4.2.1 Lead (Pb)

According to Table 2, the mean Pb concentrations for the oil spill-impacted areas for clusters 1, 2, and 3 are 20.62, 11.57, and 8.31 mg/kg, respectively. This is within the WHO [18] and DPR [19] target and intervention values' tolerable limit concentrations and is more than the control site's 2.14 mg/kg. Additionally, it falls below the allowable limit when contrasted with the countries' farm soil weighty metal content regulatory standards listed in Table 2.

4.2.2 Chromium (Cr)

Each sample cluster has a medium chromium (Cr) content of 8.03, 6.24, and 5.36 mg/kg, which is bigger than the 2.19 mg/kg medium concentration of Cr in the control site (non-impacted). Nonetheless, it falls short of the legal grades for the degree of weighty metals in farm soil of the nations included in Table 2, as well as the WHO and DPR goal and intervention ranges.

4.2.3 Cadmium (Cd)

Clusters 1, 2, and 3 of the oil spill-impacted sites have greater mean concentrations of Cd than the control site, which has a mean concentration of 1.90 mg/kg. They are all above the WHO and DPR goal limits of 0.08 mg/kg, despite being below their intervention values of 12 mg/kg and 17 mg/kg, apart. When contrasted with the regulatory grades of weighty metals concentration in farm soil of

the nations listed in Table 2, the majority of the Cd average concentrations in the three clusters of this research are bigger than the allowable limit for nations like Australia, Canada, China, Tanzania, New Zealand, the United Kingdom, and the United States.

4.2.4 Nickel (Ni)

The medium concentration of nickel is higher in each of the three clusters of places affected by the oil spill than it is at the control site. All of them are within the DPR [19] and WHO [18] target value range. When contrasted with the regulatory grades for heavy metal concentration in farm soil of the nations listed in Table 2, it likewise falls below the allowable level.

4.2.5 Copper (Cu)

With the exception of cluster 2, which has a higher average concentration of Cu (106.93 mg/kg), the mean concentration of Cu at the cluster locations impacted by the oil spill is lower than the mean concentration at the control site, which is 80.70 mg/kg. The medium concentrations of Cu at the three cluster sites and the control site were higher than the WHO and DPR target, but they were within the range of the intervention values when contrasted with the target and intervention values. With the exception of cluster 2, whose mean concentration is higher than the range of acceptable concentrations of Cu in Australian farm soil, which is 100 mg/kg, the mean concentrations of Cu in all three clusters fall within their acceptable concentration range when compared to the regulatory grades of weighty metals concentration in farm soil of the nations listed in Table 2.

4.3 Pollution and Risk Assessment of Heavy Metals in the Sediments

4.3.1 Geo-accumulation index

This indicator is used to determine the degree of defilement in a sample. The level of tainting is likewise determined by it [16]. Tables 3 and 4 show the average I_{geo} and contamination degree of many metals in soil samples. Due to the absence of defilement sources such illegal refining, oil supply, and human activity, the results demonstrated that there was especially minimal pollution from Fe, Ni, and Cu in the studied area. The biological and geochemical interactions and fluctuations of the metals may also have resulted to the low I_{geo} degrees. However, the soil samples ranged from fully pure to highly tainted in terms of Cr, Mn, Ni, and Fe pollution. Raw oil procurement and long-term illegal refining may have abetted this defilement. The current outcomei support those of the previous research conducted by Jimoh [21]. Table 3 displays the geo-accumulation index level distribution for seven weighty metals identified in Okpari-Olomu's three cluster soil areas.

Table 3 shows the I_{geo} amount of the weighty metals concentration found in the soil specimen obtained in three cluster areas from the oil spill afflicted sites. Contrasting the amount with the congruent link amid metal I_{geo} and defilement level index by Muller [16], as given in Table 4, the I_{geo} amounts for the metals in cluster one suggests very tainted and fairly to heavily tainted for both V and Pb correspondingly. The I_{geo} amount for Cr and Cd showed moderate pollution, the Ni I_{geo} value showed unpolluted to fairly tainted, while the Fe and Cu I_{geo} values showed unpolluted. The I_{geo} values for V and Pb for Clusters two and three, respectively, showed highly and moderately polluted conditions. I_{geo} values for Cr, Cd, and Ni showed unpolluted to fairly tainted, whereas

those for Cu and Fe showed unpolluted. Ahmed et al. [33] discovered fair to severe levels of Cd metal pollution in 2024.

According to Table 6, the concentrations of Pb, Fe, V, Cr, Cd, Ni, and Cu in the soil have the following Enrichment Factors (EF): 11.04, 1.00, 538.63, 4.20, 4.26, 2.47, and 0.97 for cluster one, 6.20, 0.08, 148.98, 3.36, 3.28, 2.26, and 1.52 for cluster two, and 4.45, 0.77, 57.30, 2.80, 2.71, 2.66, and 1.02 for cluster three. All clusters had reported EFs of Fe and Cu (1.00, 0.08, and 0.77), and 0.99, 1.52, and 1.02, apart. This suggests that the soil is free of Fe and Cu metal contamination (deficiency to low enrichment). The soil samples from clusters one and two were extremely tainted (severe enrichment) by Pb metal, whereas the soil samples from cluster three were fairly tainted (moderate enrichment), as indicated by the EF values for Pb in clusters one and two, which were 11.04 and 6.20, respectively, and cluster three, which was 4.45. The soil is highly tainted (extremely enriched) by vanadium metal, as indicated by the EF values of clusters one, two, and three for V, which are 538.63, 148.98, and 57.30, respectively. For Cr, Cd, and Ni, the EF amount for all clusters range from 2.26 to 4.26, denoting that the soil is fairly tainted (moderately enriched) by the metals.

Cluster one's mean concentration values (3.53 mg/kg) surpass those of studies conducted in Delhi, India; Ma'an, Jordan; Chongquing, China; Pearl River, China; Taiyuan, China; and Banja Luka, Bosnia (0.55, 0.92, 1.78, 0.22, 1.44, 1.72) (mg/kg), respectively, when compared to the mean concentration values from similar studies displayed in Table 11. Cluster two and three's mean concentration values of 1.51 mg/kg each outperformed Delhi, Ma'an, Pearl River, and Taiyuan. The mean concentrations of 16PAHs in all three clusters of this investigation [34] are lower than the mean concentrations of 16PAHs for comparable studies conducted in Loess Plateau, China and New York, USA (5.50 and 14.20 mg/kg, respectively).

Four classes were established for PAH pollution in soils based on Maliszewska-Kordybach's [34] European categorization system of soil contamination.

It is pertinent to remember that the levels of ∑16PAHs in the soils affected by the oil spill in this research were 0.51 to 2.53 times greater than the typical range of 1.0 mg/kg for serious pollution. BaP is a common PAH that is of greatest interest in terms of potential cancer hazard [35], and its concentration for this study varied in a range of 1.57 – 2.12) mg/kg. This suggests that the oil spill affected soils stored a significant amount of PAHs, including the seven carcinogenic PAHs.

4.4 PAHs Source Identification

Identification of sources using isomer ratios In order to control soil PAH pollution in the surrounding, it is crucial to evaluate the transit and destiny of PAHs by performing a PAH source apportionment. Methods for determining the sources of PAHs have been the subject of several investigations to date. To identify the sources of PAHs, the isomer ratio characteristic is typically employed among the various available approaches [36].

Numerous studies have shown that the diagnostic ratios of Fla/(Fla + Pyr) and BaA/(BaA + Chr) can frequently be used to identify potential sources of PAHs in the surrounding. Ratios <0.4, 0.4–0.5, and >0.5 for Fla/(Fla + Pyr) denote oil sources, oil burning, and coal and biomass combustion,

respectively. Oil supplies, oil combustion, and coal and biomass combustion are indicated by BaA/(BaA + Chr) ratios less than 0.2, 0.2–0.35, and larger than 0.35, respectively [37, 38].

Furthermore, LMW/HMW has been employed as an indication to determine PAH sources. LMW PAHs predominate in soil samples when LMW/HMW>1, and they are also the predominant source of petrogenic PAHs, such as those produced during biomass combustion [39]. HMW PAHs predominate in soil samples when LMW/HMW<1, and their primary anthropogenic sources include thermal alteration [40, 41].

The mean Fla/(Fla + Pyr) and BaA/(BaA + Chr) ratios for cluster one, cluster two, and cluster three were, respectively, 0.32 and 0.67, 0.71 and 0.81, and 0.28 and 0.43, as indicated in Table 13. These findings imply that pyrogenic or petroleum and diesel emissions [42], as well as oil, oil burning, and coal combustion [36], were the primary sources of PAHs in the soils studied in Okpari-Olomu.

High temperature burning of coal and petroleum, as occurs in factories, power plants, automobile engines, and gas-fired cooking utensils, produces high molecular weight (HMW, 4-6 rings) PAHs [43]. LMW/HMW ratios for all clusters were less than 1, as indicated in Table 14 and Figure 3. This suggests that 4-6 ring HMW PAHs predominated over LMW PAHs and further suggests that the PAHs were thermally produced, particularly through oil combustion. This supports previous research and raises the possibility that their strong resistance to microbial degradation is the cause [44].

Conclusions

The concentration of ∑16PAHs and ∑7PAHs for the three clusters impacted sites indicated the presence of heavy pollution within the oil spill impacted area, while the values of the Enrichment Factors, Pollution Load, and Geo-accumulation Indices values demonstrated a high level of heavy metal pollution. As a result, there is evidence that the residents of Okpari Community in Delta State, Nigeria's Ughelli South Local Government Area may be at ecological danger.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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