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ARTISANAL REFINING AND ITS IMPACT ON PHYSICOCHEMICAL PROPERTIES OF SOILS IN OKPOROWO, AHOADA EAST LOCAL GOVERNMENT AREA, RIVERS STATE

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Abstract

The research gauged the consequences of the activities of artisanal refineries on topsoil physicochemical properties. Three topsoil samples were taken from geo-referenced stations in the Okporowo community and a control station from Ahoada main town. The different physicochemical properties were examined using basic operating techniques. Mean values of the physical and chemical properties in the topsoil were as follows: Cation exchange capacity (CEC) 6.99±0.003 (meq(+)/g), electrical conductivity 563.75±11.30 µS/cm, pH 4.54±0.24, total organic carbon (TOC) 0.81±0.046%, total nitrogen (TN) 0.069±0.008%, phosphate 0.022±0.91mg/kg, nitrate 0.319±0.148mg/kg and moisture content 21±0.61%. The concentration of the metallic elements evaluated was; Mn 2.00±0.041mg/kg, Cd 0.254±0.008mg/kg, Fe 83.201±0.309mg/kg, Pb 2.93±0.008mg/kg and Cr 4.30±0.005mg/kg. The resultant values of physicochemical properties from Ahoada main town were; cation exchange capacity (CEC) 7.81±0.07 (meq(+)/g), electrical conductivity 280.24±2.00 µS/cm, pH 6.07±0.08, total organic carbon (TOC) 0.75±0.14%, total nitrogen (TN) 0.072±0.002%, phosphate 0.022±0.002 mg/kg, nitrate was 0.332±0.005 mg/kg and moisture content 33±1.19% while the concentrations of the heavy metals were; Cd 1.355±0.005 mg/kg, Mn 2.337±0.03 mg/kg, Fe 67.82±0.003 mg/kg, Pb 4.43±0.007 mg/kg and Cr 3.39±0.006mg/kg. The resultant values of the physical and chemical properties of topsoil from contaminated stations displayed a departure from the values of local and international regulatory bodies due to the anthropogenic inputs from the activities of the artisanal refineries. This implies that samples of topsoil analyzed in this study were slightly contaminated. Thus, the government should checkmate the activities of the artisanal refineries to mitigate the deleterious effect on the environment.

Keywords: Artisanal Refineries, Physicochemical Properties, Heavy Metals, Contamination Factor

Introduction

Soil is crucial to human existence for various reasons. It is also one of the sustainable development goals (SDG 3) for healthiness and wellness. Wellness and wholesomeness are closely connected with soil because good soils yield good crops that in turn sustain humans and animals, allowing for their healthiness and productiveness. Unfortunately, the soil has been exposed to diverse forms of abuses including crude oil spills. The discharge of crude oil into the surroundings introduces pollutants which impact and change soil biochemical properties (Ewetola,2013). In addition, hazardous substances from soil and water can infiltrate the human food chain as a result of petroleum pollution, upsetting biochemical processes and eventually having detrimental effects on living things. Pollution adversely affects the ability of soils to play important roles in ecological units (Smith et al., 2021). Soil is a living resource, but should be considered functionally dead if contaminated.

Artisanal petroleum refining (aka kpo-fire) became well-known in the Niger Delta region of Nigeria (Rivers State included) several years ago. The illicit refining of crude oil produces highly sub-standard products; its accompanied activities have also brought about serious pollution of the environment and deterioration in the Niger Delta habitat (Isa, 2012). According to Isa (2012), Jafarinejad (2015) and Jafarinejad (2016), some of the grim environmental effects associated with the oil-producing industry in general (and artisanal refineries in particular) include a dearth

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of forests, soil, water and atmospheric pollution, deposition of amorphous carbon due to incomplete combustion of organic matter, environmental degradation, heating up of Earth's surface and acid deposition.

The danger of heavy metal poisoning to all living forms brought attention to the soil contamination near the artisanal refineries. Humans, animals and ecosystems are vulnerable to dangerous chemicals such as metallic elements via intake of agricultural products cultivated on polluted land, direct consumption as well as through drinking of water that seeps into affected soil (McLaughlin et al., 2000). Petroleum products produced by illegal refineries are substantially below the internationally accepted standards. As a result, when fuels are not burned completely, they emit a variety of harmful pollutants into the atmosphere, which endangers not only living things but also automobiles and other machinery that use them (Isa, 2012).

Materials and Methods

Study Area: Okporowo is a community in Ekpeye ethnic nationality of Ahoada-East local government area of Rivers State. It is situated in the Orashi region and comprises five sub-communities. It is one of the 80 towns and villages in Ekpeye nation. The spoken dialect is Ekpeye, which has tropical rainforest vegetation and borders the riverine community of Okoma 1, the people residing in the community are mostly farmers who depend on the land for their survival. The geographical coordinates of the Okporowo community are $4^0$57`56" and $6^0$38` North, $6^0$38` and $6^0$64` East respectively. Sample collection and preparation: Topsoil (0-30cm) samples were collected within three farmlands around artisanal refineries in Elekena, Umuakpu and Unakala sub-communities in Okporowo. The sampling depths were confirmed using a tape measure. The sample which served as Control was taken from an active farm in Ahoada main town. A representative sample of each station was acquired by pooling topsoil samples, coning and quartering repeatedly. Topsoil samples were deposited in clean polythene bags and transported to the school laboratory for assessment. Extraneous materials were removed from topsoil samples before air drying at prevailing room temperature for a couple of weeks. Air-dried samples were ground using porcelain mortar and pestle, mixed thoroughly before being passed through a sieve (2 mm) and preserved in labelled polythene bags until analysis (Wonodi & Ekpete, 2021).

Determination of soil pH: The method of Adebiyi and Adeyemi (2010) was employed. 20g of prepared soil was transferred into a 200 ml glass beaker, 40 ml of deionized H_2O was added and mixed with a glass rod and left to stand with intermittent stirring for proper dissolution of salts for 30 minutes. A HANNA pH meter (Model H12209) was then placed in the solution and the pH level was recorded.

Determination of Electrical Conductivity (EC): The method of Anegbe and Okuo (2013) was used. 20g of prepared soil sample was weighed, then mixed with 40ml deionized water in a 100ml beaker. The mixture was stirred periodically for 30 minutes. The conductivity cell of an Equiptronics digital electrical conductivity bridge was inserted in the solution, the soil was allowed to settle down and the EC value of the topsoil was noted.

Determination of Cation Exchange Capacity (CEC): Determination of Ca^{2+}, Na^+, and K^+ was conducted as described by Eze et al. (2022). 5g of individual topsoil sample was placed on filter paper (Whatman No. 1) which was properly fitted into a glass-funnel on a leaching support with 100ml measuring flask to collect the filtrate. The sample was leached with 1.0N NH_4OAc (ammonium acetate) solution and a 100ml volume was collected. For the determination of Ca (Calcium) and Mg (Magnesium), 10ml of the leachate was transferred into a 100ml conical flask which was followed by the addition of 10ml NH_4Cl (ammonium chloride) solution to the flask. The resulting solution was mixed thoroughly and 0.01g of Eriochrome Black-T indicator was added and titrated at once with 1.0N ethylene diamine tetra-acetic acid (EDTA). Calculation:

$$T \text{ x } N \text{ x Volume. x } 100 = \text{Meq. } Ca^{2+} /100\text{g of soil Aliq. wt} \quad (1)$$

Where; T = Titre of sample; N = Normality of EDTA; Vol = Initial volume of leachate collected; Meq. = Milliequivalent; Aliq = Aliquot of leachate titrated; Wt = Weight of soil sample.

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Colourimetric determinations of Sodium (Na) and potassium (K) were done using a flame photometer (Jenway PEP7 Flame Photometer, Germany) from the left-over leachate.

Determination of Total Organic Carbon: The analytical method reported by Eze et al. (2022) was followed. 1g of prepared topsoil sample was transferred into a 250ml Erlenmeyer flask. 10ml N K_2CrO_7 solution was accurately measured into each flask with the aid of a pipette, the flask was softly agitated to distribute the soil. Thereafter, 20 ml of 0.05M sulfuric acid was added. The contents of the flask were agitated until soil and reagents were mixed and allowed to stand on a ceramic surface for approximately 30 minutes. 100ml of distilled H_2O was then added to the flask. 3 drops of ortho-phenanthroline indicator (6.9 g of $FeSO_4.7H_2O$ and 14.8 g of 0-phenanthroline monohydrate dissolved in 1L of distilled water) was also added. This was titrated with acidified 0.5N $FeSO_4$ solution (14g/L of water containing 15ml 0.05M sulfuric acid). The $FeSO_4$ was added dropwise until there was a colour change (from blue to maroon colour) in reflected light on a white surface.

Calculation:

$$\% \text{ Organic carbon in soil} = \frac{(MeK_2CrO_7 - MeFeSO_4) \times 0.003 \times 100 \times F}{\text{wt in of prepared soil}} \qquad (2)$$

The correction factor, F = 1.33; Me = Normality of solution x volume of solution used.

Total Nitrogen: This was determined according to the method of Keeney and Nelson (1982). 5g of already prepared topsoil sample was placed in a 500 Kjeldahl flask. A catalyst mixture of 0.20g selenium powder, 5.0g Li_2SO_4 and 100 ml of 30% H_2O_2 was prepared. 200 ml of conc. H_2SO_4 was also added to the catalyst mixture. 100 ml of the freshly made digestion mixture was steadily added to the topsoil sample in the Kjeldahl flask. The digestion of the mixture was done with the aid of a heating mantle in a fume cupboard until the digest was clear and allowed to cool. 50ml of the digest was poured into a 1000ml Kjeldahl flask and 400ml distilled H_2O was added. The content of the flask was stirred and left to stand until a clear solution was formed. 100ml of 45% NaOH was added to the solution in the flask and the flask was connected instantly to the distillation apparatus. NH_3 was collected over 50ml of 2.5% H_3BO_3 solution contained in 250ml Erlenmeyer flask with 5 drops of mixed indicator (bromocresol green and methyl red mixed in ethanol). Titration was performed using 200ml of the distillate against standard 0.05N HCl.

Calculation of % Nitrogen:

$$\%N = \frac{T \times N \times 14.01 \times 100}{1000 \times \text{wt of soil sample}} \qquad (3)$$

Where: T = sample titre; N = normality of HCl; wt = Weight of topsoil sample used.

Phosphate: The Bray No. 1 Method as described by Aigberua et al. (2016) was used in the determination of Phosphate in the topsoil samples. 1g of prepared topsoil sample was transferred into a 15ml centrifuge cylinder and 7ml of extracting solution (made up of 15ml 1.0N NH_4F + 25ml, 0.5N HCl + 460ml deionized H_2O) was added. The mixture was shaken on a mechanical shaker for 1 minute and then centrifuged for 15 minutes at 2,000 revolutions per minute. 2sml of transparent filtrate was poured into a 20ml test tube and 5ml of deionized H_2O and 2ml of $(NH_4)_2MoO_4$ was added. The content was stirred thoroughly, followed by the addition of $SnCl_2$ dilute solution (1ml $SnCl_2$ stock solution prepared by dissolving 10g $SnCl_2.2H_2O$ in 25ml of conc. HCl + 333 ml deionized H_2O). The solution was allowed to stand for 10 minutes until a bluish colour confirming the presence of phosphate ion was seen and read at a wavelength of 840 nm using a HACH DR 890 colourimeter. A blank, consisting of deionized H_2O and every other reagent as used in the test sample filtrate was mixed and used to calibrate the equipment. The level of PO_4^{3-} available in the topsoil sample was read as ppm PO_4^{3-}.

Determination of Nitrate (NO_3^-): Analysis of topsoil nitrate was done using the Na-acetate extraction method. 5.0g of prepared soil sample was weighed into a shaking bottle and approximately 0.25g of activated carbon and 20ml of extracting solution (consisting of 100g CH_3COONa + 30ml of 99.58% CH_3COOH, diluted to 1L with deionized H_2O) were also added; the mixture was shaken for 1 minute then separated by filtration. 1ml of the filtrate was measured into a sample bottle and mixed with 0.5ml $C_{23}H_{23}N_2O_8S$ reagent (2.5g $C_{23}H_{23}N_2O_8S$ in 100ml anhydrous CH_3COOH) and 2ml H_2SO_4. The solution was stirred steadily for 30 seconds and left to stand for 5 minutes, after which it was stirred again before 2ml deionized H_2O was added with steady stirring for almost 30 seconds. More deionized H_2O was added to make the solution up to the 10ml mark of the sample bottle. Sample bottles were allowed to stand for 15 minutes (until the test solution turned brownish). The concentration of NO_3^- in ppm was determined using the HACH DR 890 colourimeter at an absorbance of 400nm (Aigberua et al., 2016).

Determination of Moisture Content: Determination of the topsoil moisture content was done using the mass loss procedure as reported by Adeodu et al. (2013). Moist samples were wrapped in an empty foil paper of a known mass (M1). The mass of foil paper and moist soil (M2) was noted after which the wrapped moist sample was oven-dried at 25°C for 1 hour. The mass of the oven-dried sample and the foil paper (M3) was noted. Then, the moisture content of the soil was calculated in percentage following the relationship given in equation 4;

$$\% \text{ moisture content} = (M2 - M3)\ X\ 100 / (M3 - M1) \quad (4)$$

Where M1 = Mass of empty foil paper (g); M2 = Mass of foil paper + Moist soil (g); M3 = Mass of foil paper + oven-dried soil (g).

Element Determination: Soil samples were digested according to the method described by Adebiyi and Ayeni (2010). Prepared topsoil samples (5g) were carefully measured and mixed with 20 ml aqua regia (HNO_3 and HCl acids, 1:3 ratio). The soil and acid mixture was heated using a heating mantle at 70^0C (in a fume cupboard) until it was almost dry, stood and left to cool. 5 mL of hydrofluoric acid was added to the mixture and reheated. The digested samples were filtered, then transferred into graduated flasks and made up to 50ml mark with double-distilled H_2O and stored in plastic containers until analysis. The digests were examined for metallic elements (Cd, Mn, Pb, Cr and Fe) using AAS, (Perkin Elmer Analyst 200).

Contamination factor (Cf): The extent of topsoil contamination by metallic elements was evaluated using the contamination factor. The standard for the interpretation of contamination factor values was adopted from Edori and Kpee (2017) and Adebiyi and Ayeni (2022). The contamination factor is the ratio of the level of the metallic element in the soil sample to the background value. They are graded in categories of 1-6 (Cf <1= Low contamination, 1–3 = Moderate contamination,3-6 = Considerable contamination, CF > 6 = Very high contamination).

Calculation of the Contamination factor is as shown in Equation 5;

$$\text{Contamination factor (Cf)} = Cm/Cb \quad (5)$$

Where; Cm is the concentration of the metallic element in the soil sample, and Cb is the background value. The background values adopted in this study were derived from DPR target values for metallic elements in topsoil: Cd 0.80; Cr 100; Fe 47,000; Mn 850; Pb 85.

Pollution Load Index (PLi): The Pollution load index is a powerful instrument applied in heavy metal pollution assessment. It estimates the level of total contamination in a study site. The calculation of PLi for individual stations was performed using Tomlinson et al. (1980) equation:

$$PLi = \sqrt[n]{(Cf\,1 \times Cf\,2 \times Cf\,3 \times ....Cf\,n)} \quad (6)$$

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Where; n is the total number of metallic elements; Cf1-Cfn = contamination factors of the individual metals. PLi is graded in categories from <1 to >1 (PLi <1: No pollution, PLi = 1: Baseline pollution, PLi> 1: Degradation of soil properties).

Enrichment factor (EF): The levels of metallic elements in the soils of the study area attributed to human influence were assessed using (Hakanson, 1980; Barbieri, 2016). Ef is calculated by normalizing each metallic element in the topsoil about the concentration of a geochemical reference element. Iron was used as a reference metal due to its natural abundance in the earth's crust in this study.

$$Ef = \frac{C_n / C_{Fe}}{B_n / B_{Fe}} \qquad (7)$$

Where; C_n = amount of the metallic element (n) in soil samples; C_{Fe} = amount of Iron in topsoil sample; B_n = geochemical baseline concentration of metal (n); B_{Fe} = geochemical background value of Iron. Categories of gradings of Ef values are as follows; Ef less than 2 = deficiency to minimal enrichment; Ef greater than 2 but less than 5 = moderate enrichment; Ef greater than 5 but less than 20 = significant enrichment; Ef greater than 20 but less than 40 = very high enrichment and Ef greater than 40 is extremely highly enriched.

Results

Table 1: **Mean Values of Physicochemical Properties of Soil and Standard Reference Values**

	STATIONS				
Soil Properties	**Ahoada**	**Elekena**	**Umuakpu**	**Unakala**	**WHO / NESREA**
Ph	6.07±0.08	4.86±0.160	4.50±0.030	4.27±0.520	6.5-8.5/6.5-8.5
EC	280.24±2.00	553.90±9.79	629.18±15.31	508.17±8.81	110 – 500/300-500
CEC	7.81±0.07	6.48±0.003	7.82±0.005	6.68±0.002	-
TOC	0.75±0.14	0.90±0.087	0.86±0.040	0.66±0.012	0.03/0.03
TN	0.07±0.002	0.10±0.005	0.04±0.002	0.07±0.017	0.20/0.20
PO_4^{3-}	0.02±0.002	0.03±0.002	0.01±0.002	0.02±0.002	0.4/0.5
NO_3^-	0.33±0.005	0.45±0.004	0.20±0.001	0.30±0.003	10-50/50
MC (%)	33.00±1.190	21.00±0.680	20.00±0.560	22.00±0.590	10-20/10-20
Cd	1.36±0.005	0.05±0.0004	0.01±0.001	0.70±0.020	0.3-1.0/0.5
Cr	3.79±0.006	5.35±0.001	3.18±0.002	4.37±0.013	0.1/0.4
Fe	67.82±0.003	83.77±0.660	77.90±0.190	87.92±0.076	50/50
Mn	2.34±0.030	1.76±0.044	2.64±0.020	1.60±0.060	0.48
Pb	4.43±0.007	3.83±0.004	1.93±0.002	3.03±0.018	0.3/0.50

Std. D. = Standard deviation

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Table 2: Computed result for Contamination Factor (Cf) & Pollution Load Index (PLI)

Heavy Metals	Sampling Stations			
	Ahoada	Elekena-Okporowo	Umuakpu-Okporowo	Unakala – Okporowo
Cadmium	1.694	0.065	0.010	0.878
Chromium	0.038	0.054	0.032	0.044
Iron	0.001	0.002	0.002	0.002
Lead	0.052	0.045	0.023	0.036
Manganese	0.003	0.002	0.003	0.002
PLi	0.025	0.014	0.008	0.022

Indices of Pollution: To estimate the contamination level of the crude oil on the impacted soils, the following indices of pollution were employed and the results of the estimations are presented in Table 2 and Figure 1.

Contamination Factor: The results from Table 2 showed that there was generally minimal difference in the computed contamination factor of all studied metals. The test soil samples of the study locations exhibited low/slight contamination (Cf<1) for Cr, Fe, Pb and Mn and moderate contamination by Cadmium in Unakala-Okporowo and the Control station (Table 2). The computed result of the pollution load index (PLI) indicated that no pollution was observed in the control and study areas.

Enrichment Factor: In the computation of the enrichment factor for this study, Fe was selected as the background reference metal. Fe and Mn enrichment factor laid in the range of deficiency to minimal enrichment for all stations (in essence, EF<2), Pb and Cr registered very high enrichment across board (20>EF<40), while Cd enrichment factor computation registered extremely high enrichment (EF>50) in Unakala-Okporowo and Control stations. Enrichment factors for all analyzed metals followed the decreasing trend: Cd> Cr>Pb>Mn>Fe (Figure 1).

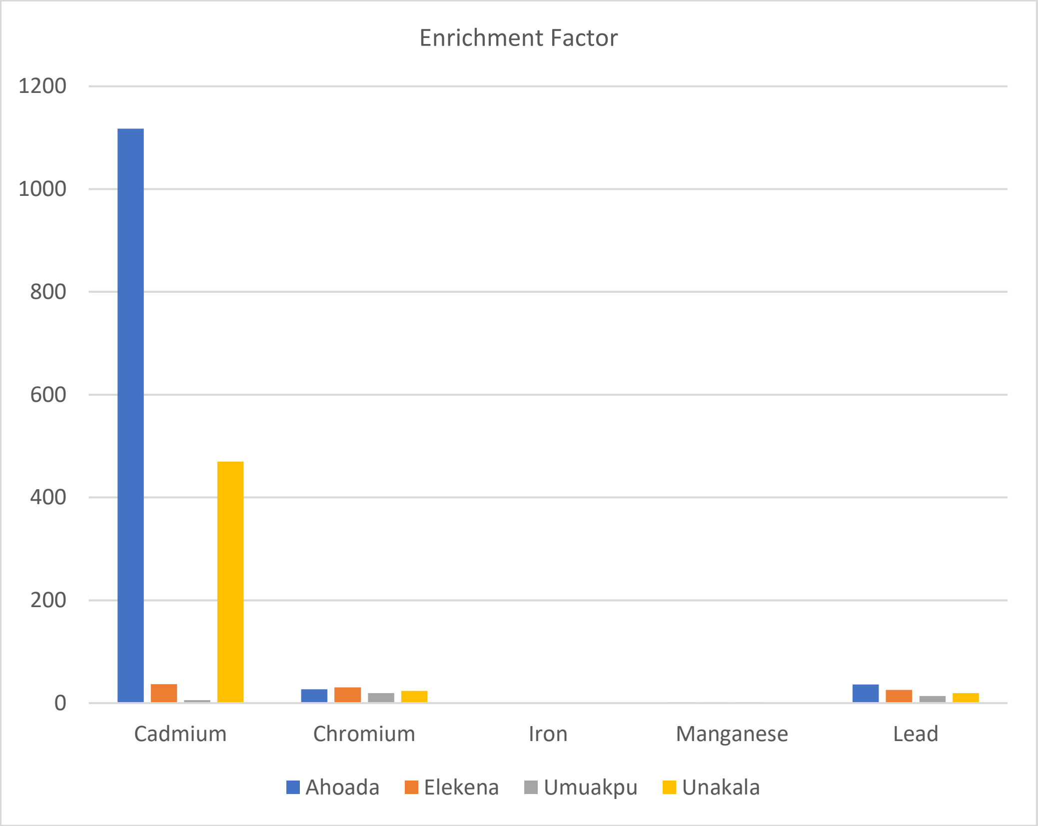

Figure 1: **Enrichment factor for all metals in the control and study stations**

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Table 3: **Principal Component Analysis (PCA) Result**

PHYSICOCHEMICAL PROPERTIES	PC1	PC2	PC3
Moisture Content	1.00	-0.017	-0.225
Electrical Conductivity	-0.977	-0.119	0.176
pH	0.936	0.122	0.331
Cadmium	0.907	-0.066	-0.415
Iron	-0.829	0.300	-0.472
Lead	0.751	0.661	-0.010
Phosphate (PO_4^{3-})	0.111	0.991	-0.707
Total Nitrogen (TN)	0.140	0.990	0.027
Nitrate (NO_3^-)	0.145	0.986	0.083
Chromium	-0.180	0.975	-0.129
Cation Exchange Capacity (CEC)	0.438	-0.796	0.419
Total Organic Carbon (TOC)	-0.344	0.196	0.918
Manganese (Mn)	0.264	0.409	0.874
Eigen Value	5.368	5.284	2.348
% Variance	41.292	40.645	18.063
Cumulative Variance	41.292	81.937	100.00

PC1 = Principal Component 1; PC2 = Principal Component 2; PC3 = Principal Component 3

Principal components with Eigenvalue >1 (Kaiser Criterion) were selected using varimax rotation. Three-factor loadings were extracted which explains about 100% of the total variance (Table 3). The first-factor loading (F1 also called PC1), which explained 41.292% of the total variance, was positively associated with pH, moisture content, cadmium and lead. The first factor (F1) could be linked to human activities owing to the crude oil refining activities and atmospheric deposition of pollutants from transport emissions. The second factor loading (F2), explained 40.645% of the total variance and described high–positive loadings in Phosphate, total Nitrogen, Nitrate and Chromium. F2 could be linked to both natural and human activities relating to parent rock weathering and organic waste from agricultural activities. Total organic carbon and Manganese showed greater cooperation in the third factor (F3) which described 18.063% of the total variance. This association in F3 could be a result of the combustion of fossil fuel and domestic waste disposal generated in the locations of this study, all traceable to the activities of artisanal refineries in the Okporowo community.

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Discussion

Physicochemical parameters from the studied area are shown in Table 1.

Soil pH: The pH of the soil greatly influences elements and nutrient availability in the soil (Igwe et al., 2005). Studies have proven that metal concentrations in soil solution and consequently leaching can be much enhanced in soils with low pH and/or redox potential (Adie & Osibanjo, 2009). The result of pH of the test soil samples in the study locations varied from 3.62 to 5.08 with an average of 4.54±0.24 for all sites while the control station's pH result ranged from 5.9 to 6.2 with a mean value of 6.07±0.08. One-way ANOVA results at $p<0.05$ revealed a statistical difference in the study area and the control. The study area pH values were highly acidic whereas that of the control station was moderately acidic. The pH result of the study area were below the standard set by WHO, (2003) and NESREA, (2021) (6.5-8.5). The results obtained agreed with the position of Birma et al. (2022) and Obianefo et al. (2017) with pH values ranging from 4.1 to 5.7 in hydrocarbon-impacted soil and selected dumpsite soils respectively but varied with the findings of Adebiyi and Ayeni (2022) in soils around refined petroleum depot in Ibadan, Nigeria with values ranging from 7.07 to 7.33 with a mean value of 7.24. The acidic state of topsoil samples from the study locations may be attributed to the impact of the oil as well as the production of organic acid by microbial metabolism (Okoro et al., 2011).

Soil Conductivity: The EC of the three stations investigated in this study were 553.90±9.79µS/cm, 629.18±15.31 µS/cm and 508.17±8.81µS/cm for Elekena, Umuakpu and Unakala respectively, with a mean value of 563.75±11.30µS/cm, these values were high when compared with the EC of the control station (280.24±2.00µS/cm) and also higher than the WHO (2003) and NESREA (2021) permissible limits (110-500&300-500µS/cm) for soil. The one-way ANOVA result at $p<0.05$ indicated a statistical difference between the result of the oil-impacted stations and the control. This result was higher than the observations of Igwe et al. (2021) on soils samples obtained from oil-producing communities in the Afam area of Port Harcourt, Niger Delta, Nigeria, with a value range of 58.80 to 138.40µS/cm. However, it did not agree with the report by Moses and Uwah (2015) on crude oil-impacted soil with EC values between 0.03 to 0.08 µS/cm. Marcus and Edori (2020) revealed higher EC values for soil samples from a leachate-contaminated dumpsite within the Port Harcourt metropolis, ranging from 11,556 to 32,142µS/cm. The comparatively high conductivity values recorded in this study suggest the existence of ionizable minerals, which may be caused by soluble metal salts that were released into the soil by wasted hydrocarbon products.

Soil Cation Exchange Capacity (CEC): The result of the cation exchange capacity of the test soils of the study sites ranged from 6.47 to 7.83 meq(+)/g with an average of 6.99+0.003 meq(+)/g for all stations, similar to the CEC value of the control area with a mean value of 7.81+0.07 meq(+)/g. CEC was obtained in the present study. One-way ANOVA result carried out at $p<0.05$ revealed no statistical difference in CEC levels of the study area and control. The observed CEC values of this current research exceeded the results of Ololade et al. (2010), with values ranging from 2.6 to 15.8 meq(+)/g with an average of 4.6 meq(+)/g in farmland soils in Ondo, Southwestern. However, it is in agreement with the report of Wonodi and Ekpete (2021) for soils of the control area within Port Harcourt City with a CEC mean value of 7.277±1.522 meq(+)/g. Similar CEC values were obtained by Moses and Uwah (2015) on crude oil-impacted soil with ranges between 6.47 and 7.83. Soils with high CEC values have greater water retention abilities (which is supported by the high moisture content of the studied soils) and are less susceptible to leaching the cations present (Nnaji & Egwu, 2020).

Soil Total Organic Carbon (TOC): Table 1 showed mean total organic carbon values in the soils of the study area and control which were 0.81±0.05 and 0.75±0.14% respectively. There was no statistical difference in the result of one-way ANOVA at $p<0.05$ in all the stations under investigation. In this present study, the TOC was found to be above the permissible limit of 0.03% stipulated by the World Health Organization (2003). Nonetheless, the results obtained were lower than the results of Ekanem et al. (2019) which ranged from 1.29 to 8.40% for soil samples around an oil-producing community and also lower than 6.87% reported by Igwe et al. (2021). The TOC values observed though exceeded the recommended limit by WHO (2003), there is an indication that the crude oil in the oil-impacted soil has not undergone a significant decomposition process. It is expected that the organic carbon content of the soil should increase owing to the deposition of carbonaceous materials and hydrocarbon materials in the soil (Okoro et al., 2015).

Total Nitrogen (TN): The level of total nitrogen in the soils of the study locations were 0.099±0.005%, 0.042±0.03% and 0.067±0.002% for Elekena, Umuakpu and Unakala respectively with an average of 0.069% for all stations while that of the control station ranged from 0.06 to 0.07% with an average of 0.0702±0.002%. These values showed no significant difference in TN levels for the three stations analyzed and the control according to the one-way ANOVA result at $p<0.05$, they were also lower than the WHO (2003) maximum limit of 0.20%. The results obtained aligned with the findings of Moses and Uwah (2015) and Odoh et al. (2014) whose values ranged between 0.05 to 0.18% and 0.05 to 0.09% respectively. However, higher values of 2.00±0.05% were reported by Wonodi and Ekpete (2021) for the soil around the Ibeto cement factory in Port Harcourt. The reason for the observed drop in TN with rising oil levels could be attributed to the temporary immobilization of this nutrient by bacteria, which may have multiplied in number. Previous research revealed that land-based oil spills caused an imbalance in the carbon-nitrogen ratio, which, if it was higher than 17:1, caused microorganisms to immobilize nutrients in soils, resulting in a loss of soil productivity (Agbogidi et al., 2007).

Phosphate ($PO4^{3-}$): Phosphate levels in the study area varied from 0.008 to 0.040mg/kg and 0.0023 to 0.032 mg/kg in the control. The test of significance result using one-way ANOVA at $p<0.05$ revealed no statistical difference in the phosphate levels for the control and study area. In addition, the overall phosphate concentrations in this study did not meet the standard recommended by WHO (2003) (0.4mg/kg) and NESREA (2021) (0.5mg/kg). The decrease in phosphate levels in the study stations may be associated with the level of crude oil in the contaminated soil that resulted in acidification of the soil whereas the low concentration observed at the control may be due to depletion of soil nutrients by plants and excessive cultivation on farm soil. The findings of this study on the level of phosphate in the test soil samples showed that the values are lower than those reported by Aigberua et al. (2016) with values ranging from 0.68-1.87 mg/kg from soil samples collected from oil-spill impacted sites.

The Nitrate (NO_3^-) levels are similar to the phosphate results as the concentration levels for the control and study stations were low with corresponding average values of 0.332±0.005mg/kg and 0.319±0.148mg/kg respectively. Furthermore, the results in the current study were below the WHO (2003) acceptable limit of 10-50mg/kg. The results agreed with the finding of Obianefo et al. (2017) whose mean value was 0.04±0.01mg/kg but were lower than the values observed by Wonodi and Ekpete (2021) in soils around cement factories in Port Harcourt, Rivers State which ranged from 2.10±0.06mg/kg to 2.40±0.19mg/kg.

The moisture content results in the study area varied from 21±0.61%- 33±1.19%. Statistical difference was observed from the result of one-way ANOVA at $p<0.05$ in the moisture content result of the control and study area. Ijah and Antai (2003) attributed it to the blockage of the soil pores which prevented the infiltration of water into the soil. This idea was supported by Osuji and Opiah (2007) and Adeyemo and Aliu (2021).

Heavy metals concentration in Soil: The levels of Cadmium, Chromium, Iron, Manganese and Lead were analyzed. The results followed the trend Cadmium 0.0077- 0.702mg/kg, Chromium 3.18 – 5.36mg/kg, Iron 77.90 – 87.92mg/kg, Manganese 1.58– 2.66mg/kg and Lead 1.93 – 3.83mg/kg. Higher concentrations of Iron, Chromium, Lead and Manganese were observed and the least was Cadmium.

In all the heavy metals analyzed, we did not observe any significant difference at $p<0.05$ ANOVA except for Cadmium and Iron where a significant difference was observed. The results of the heavy metals analysis observed in this study agree with the findings of Edori and Kpee (2017) and Ekpete and Owhoeke (2019) but contrasted with the results obtained by Ekpete and Festus (2013), Nwosu et al. (2021); Kpee et al. (2009) and Uzamere et al. (2023).

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Conclusion

Artisanal crude oil refining activities which resulted in the contamination of farmland soils in the Okporowo community have limited soil fertility thus negatively affecting crop yield and the livelihood of the people. The results of the analysis of the test soil samples from the study of the crude oil-impacted soils owing to the artisanal refining activities showed statistical differences in levels of pH, EC, MC, Cd and Fe levels of the study area and control stations. In addition, pH, TN, PO_4^{3-} and NO_3^- were all below the WHO (2003) standards while EC, TOC, MC, Mn, Pb, Cr and Fe were all above the permissible limits of WHO (2003) and NESREA (2021). Furthermore, indices of pollution revealed a severe degree of contamination of Cr at Unakala - Okporowo and the control station, Pb and Cr were highly enriched in all stations studied and Cd showed extremely high enrichment at Unakala and Control stations. This present study has clearly shown that spillage of the uncontrolled volume of crude oil on soils in the Okporowo community, Ahoada East LGA, Rivers State, has affected the soil's physicochemical properties negatively. It is therefore recommended that a synergy between governments at all levels, regulatory agencies and international oil companies be put in place to nip the menace in the bud (to reduce further degrading of the soil) and work out modalities of remediating the impacted sites using an eco-friendly approach of phytoremediation. There is also a need for further investigations on the soil quality of Ahoada town based on the position of this research despite being used as the control station.

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