

Research Article

Evaluation of Simulated Petroleum Hydrocarbon on the Physicochemical Properties of Soil

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Abstract: Petroleum hydrocarbon contamination of soils has become a global concern, which is often caused by anthropogenic activities, posing serious threat to all living beings. The study for evaluation of the variability of crude oil on the physicochemical characteristics of sandy loam soil was conducted at demonstration farm, Rivers state university, Port-Harcourt, Nigeria. The Bonny light crude oil was obtained from an oil and gas production company. Uncontaminated soil was mixed with crude oil. Standard procedures were adopted for the laboratory analysis, the parameters analyzed include bulk density, total porosity, pH, available phosphorus (P), Total hydrocarbon content (THC), organic carbon, organic matter, exchangeable cation (Mg, K, Na, Ca), effective cation exchange capacity (ECEC), total exchangeable acidity (TEA), and base saturation were monitored for a period of 21 days. 10 kg of sandy loam soils were mixed with 100, 300, 500, and 700ml of crude oil while no crude oil serves as the control using plastic reactors. The reactor with 700ml of crude oil recorded the highest THC of 1734.33 mg/kg, followed by 500ml with a THC of 1601mg/kg while the control with no contamination recorded the least THC of 534.33mg/kg. However, the values of all concentrations did not meet 5000 mg/kg of Department of Petroleum Resources (2018) intervention value but exceeded the target value of 50 mg/kg. Other parameters followed same trend except porosity which decreased with increase in crude oil volume. There were significant differences at $P < 0.05$ except for pH, available P, and base saturation. Therefore, this study calls for the utilization of its findings for adoption of remediation on crude oil contaminated soils.

Keywords: Contamination; Petroleum hydrocarbon; Physicochemical characteristics; Sandy loam soil.

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1. Introduction

Soil is the foundation of food security, global economy, and environmental quality [1]. Due to urbanization and industrialization, soils have become increasingly polluted by heavy metals and organic pollutants, which threaten ecosystems, surface and ground waters, food safety and human health [2]. Hence, there is a great need to develop effective technologies for sustainable management and remediation of contaminated soils. The United Nations Food and Agriculture Organization (FAO) highlighted soil as a serious cause for concern. They stated that the current rate of soil degradation threatens the capacity to meet the needs of future generations [3]. Several studies on soils contaminated with petroleum hydrocarbon in so many parts of the world including Niger Delta region of Nigeria have received so much attention [4]. Pollution of agricultural soils is one of the

most prevalent problems associated with the exploration and processing of petroleum hydrocarbon [5].

In Nigeria especially in the Niger Delta region, it has been estimated that about 0.7-1.7 million tons per year of crude oil spilled into agricultural soils, oceans, and rivers. This oil is mainly infused into the environment through accidental discharge, leakages from ruptured pipeline or flow-line, hose failure, and perhaps sabotage [6, 7]. Though crude oil is otherwise known as “black gold” because it plays a pivotal role in the mainstay of Nigerian economy in revenue generation and development of the country [8]. Petroleum or crude is a complex mixture of hydrocarbons and other chemicals. The composition varies widely depending on where and how the petroleum was formed. Hydrocarbons found in crude oil are mainly of four types, namely; paraffin (15-60%), naphthene (30-60%), aromatics (3-30%), and asphaltic (remainder). The elemental composition of crude oil is carbon (83- 87%), Hydrogen (10 - 14%), Nitrogen (0.1- 2%), Oxygen (0.05-1.5%), Sulfur (0.05- 6.0%) and Metals (<0.1%), most common metals are iron, nickel, copper, and vanadium [9].

Petroleum hydrocarbons have immunotoxic and carcinogenic effects and alter soil physicochemical and microbiological properties, thereby posing severe harm to human health and the environment [10]. This subsequently affects the growth of plants [11, 12] by retarding seed germination and reducing plant height, stem girth, photosynthetic rate, and biomass [13]. The pore spaces of the contaminated soil might be clogged which reduces soil aeration, saturated hydraulic conductivity, infiltration and/or percolation of water in the soil, increased bulk density, and restrict permeability which will hinder optimum productivity of the soil [13]. Eneje and Ebomotei [14] stated that pollution of soils with crude oil increases soil organic carbon, bulk density and reduces soil water holding capacity, exchangeable cations, soil nitrate, and phosphorus.

Also, Ijah and Antai [15] and Osuji and Nwoye [16] observed a decrease in soil pH in crude oil-polluted soil. Oil polluted soil leads to build-up of heavy metals such as lead, zinc, Nickel, copper, manganese, cadmium, etc., in soils, and these elements are eventually translocated into plant tissues [17]. Although some of the heavy metals at low concentrations are essential micronutrients to plants, at high levels, they may cause metabolic disorders and growth inhibition for most plant species [18]. The interactive effects of crude oil pollution on some plant species with some of the physiochemical properties showed a significant reduction in exchangeable Calcium (Ca) in the soil that was impacted by crude oil concentration due to plant uptake and temporal immobilization of nutrients by soil microbes [19]. The incessant degradation of soil resulting from petroleum hydrocarbon pollution has greatly impacted the environment, economy, and social benefits to human beings. Therefore, there is a need for this study. The aim of this study is to investigate the variability of crude oil on the physicochemical characteristics of sandy loam soil.

2. Materials and Methods

2.1. Description of study area

The study was conducted at the crop/soil science greenhouse situated at the demonstration and research farm of Rivers State University, Port-Harcourt on a Global Positioning System coordinates with latitude of 4°81'N and longitude of 7°04'E and longitudes 6°55' – 7°56' N as shown in Figure 1. The area experiences two distinct seasons rainy and dry seasons. The rainy season starts from April and lasts till October with a brief period of dryness which is known as August break. The rainfall is heavy with an estimated annual range which may vary from 2000 to 2680 mm [5].

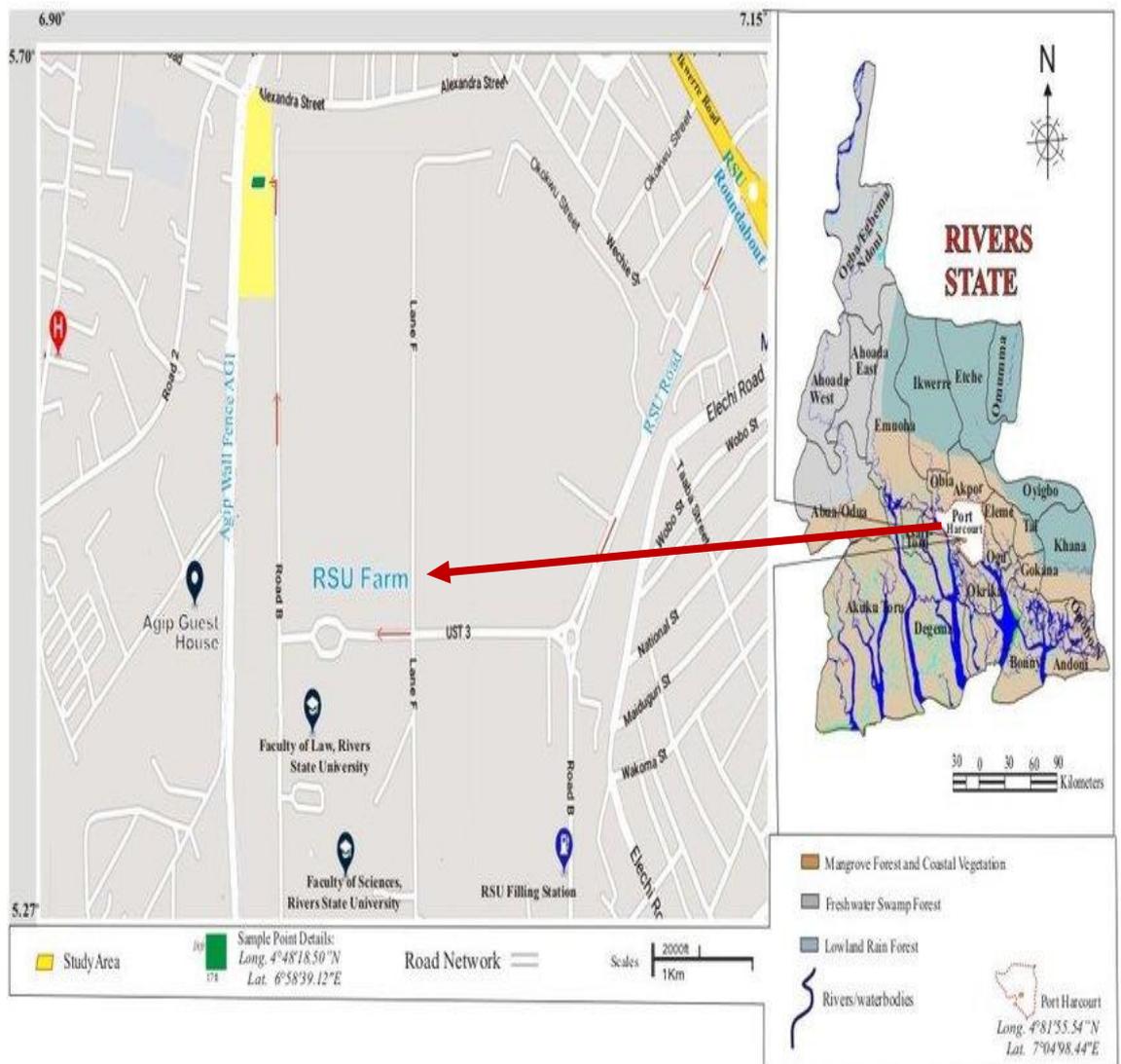


Figure 1. Map of Rivers State Showing Rivers State University Demonstration Farm (Red Arrow points towards the experimental site situated in the University)

2.2. Soil Sample Collection

Topsoil (0 – 15cm) was randomly collected from three points with the use of auger, bulked to form composite samples, and kept in sterile polyethylene bags. Placed in a covered cooler with ice and transported immediately to soil science laboratory, at Rivers State University, Port Harcourt for analysis in a refrigerated cooler to arrest microbial growth.

2.3. Determination of Physicochemical Properties of the Soil samples

2.3.1. Particle size analysis

Particle size distribution (PSD) was analyzed using the Bouyoucouos Hydrometer method as describe by Juo [20]. About 5g of sieved soil was weighed and transferred into a 250 ml beaker. The mixture was stirred and allowed to stand overnight. It was then transferred into a dispersion cup and distilled water was added to the 100 ml mark. Immediately, the hydrometer was placed into the slurry and the reading taken after 40 seconds. Blank was analyzed the same manner using 50 ml of 5% Calgon solution.

2.3.2. Bulk density

This was determined by using the core method, where undisturbed soil samples were collected with the use of cores. It was determined mathematically using equation 1:

$$\rho_b = \frac{M_s}{V_b} \quad (1)$$

Where:

ρ_b = bulk density (g/cm³)

M_s = Mass of oven dry soil (g)

V_b = bulk volume of soil (cm³)

2.3.3. Porosity

The porosity was calculated using equation 2:

$$\text{Total porosity} = 1 - (\text{bulk specific gravity}/\text{real specific gravity}) \times 100 \quad (2)$$

2.3.4. Soil pH Determination

The pH of the soil samples was determined with a glass electrode in a 1:2:5 soil water suspension [21]. Soil pH was determined by mixing 10g of homogenized soil in a beaker with 25 ml of distilled water, and stirring thoroughly, the mixture was kept to stand for 30 minutes to settle. The pH meter electrode was allowed to stabilize using a buffer solution (pH 4.0 or 7.0). Then the electrode was rinsed with the soil solution and readings were taken.

2.3.5. Total organic carbon

Total Organic Carbon (TOC) was determined by wet combustion method of Walkley and Black [22] as modified by Juo [20]. This was calculated using equation 3:

$$\%OC = N(T - b) \times 0.390/W \quad (3)$$

Where:

N = Normality (concentration of KMnO₄)

T- Titre value (samples)

N - Weight of soil used

B - Blank reading.

2.3.6. Organic matter

Organic matter was obtained by multiplying the organic carbon value by 1.724 (Van Bemmelen correlation factor).

2.3.7. Total nitrogen

This was determined by the macro-kjedahl digestion distillation method. About 1g of soil was disintegrated with concentration of H₂SO₄. The digest was then distilled with acid. The percentage nitrogen was calculated using equation 4.

$$N = T \times M \times 1.4 \times 100 \quad (4)$$

Where:

N = Total nitrogen (%)

T = Titre value,

M= Molarity of acid (HCl)

2.3.8. Total hydrocarbon Content

THC was estimated using the method of Odu *et al.* [23] 10 kg of the soil was shaken with 10 ml of Toluene. The hydrocarbon was extracted and determined by the absorbance of the extract at 420nm spectro-photometer. Standard curve of absorbance of different known concentrations of equal amount of crude oil in the extractant were drawn after reading from the spectrometer.

2.3.9. Available phosphorus

Available Phosphorus was determined by the Bray and Kurcz No. 1 (1945) method. This was done by agitating the soil with a solution containing 0.03M NH₄F and 0.25MHCl. phosphorus standards were prepared, absorbance of the samples containing the extracts were also measured using visible spectrophotometer, and concentration of P were determined from a standard curve graph.

This can be calculated using equation 5:

$$\text{Available Phosphorus in soil} = 50/10Y \times A/W \text{ (ppm)} \quad (5)$$

Where:

Y = Graph reading of samples

W = Weight of soil used (2.85) g

A = Amount of extracting solution (20).

2.3.10. Exchangeable cations (Ca, Mg, Na, and K)

Ca, Mg, Na, and K were extracted by 1N NH₄OAc buffered at pH 7. Ca and Mg were determined using Ethylene diamine tetra acetic acid (EDTA) titration method, while the concentration of Na and K were with the flame photometer method.

2.3.11. Effective Cation Exchange Capacity

This was determined using the summation of exchangeable bases and exchangeable acidity.

2.3.12. Base Saturation

Base saturation was computed as the sum of cations taken as percentage ratio of the ECEC.

2.4. Statistical Analysis

Data were statistically analyzed using data analysis tool pack of Microsoft Office Excel 2019 for Analysis of variance (ANOVA). Significance differences were evaluated at P <0.05 level using the appropriate degree of freedom for each source of variability.

3. Results

Table 1 shows the physical and chemical properties of the soil at different crude oil contamination levels. Also, Figures 2 and 3 show the graphical presentation of the physicochemical characteristics of the simulated soils with varying proportions of crude oil. Figure 2 and 3 illustrate the graphical representation of the physicochemical characteristics of the crude oil contaminated soils These include bulk density, total porosity, pH, available phosphorus (P), Total hydrocarbon content (THC), organic carbon, organic matter, exchangeable cation (Mg, K, Na, Ca), effective cation exchange capacity (ECEC), total exchangeable acidity (TEA), and base saturation.

Table 1. Physicochemical properties of the soil

Sample Parameters	Reactors				
	B ₀	B ₁	B ₂	B ₃	B ₄
Bulk Density (g/cm ³)	1.4	1.46	1.49	1.51	1.55
Total Porosity (%)	47	45	43	42	39
Textural Class	Sandy	Sandy	Sandy	Sandy	Sandy
	Loam	Loam	Loam	Loam	Loam
pH	5.7	5.8	6.1	6.4	6.6
Organic Carbon (%)	1.29	3.04	3.69	3.77	3.9
Organic Matter (%)	2.22	4.24	4.65	4.78	4.98
Available Phosphorus (mg/kg)	14	28.1	42.1	50	60
Total Hydrocarbon Content (mg/kg)	534.33	867.66	1334.33	1601	1734.33
Total Nitrogen (%)	0.002	0.003	0.004	0.006	0.009
Exchangeable Ca (cmol/kg)	2.2	2.4	3.2	3.4	3.8
Exchangeable Mg (cmol/kg)	0.006	0.008	0.009	0.01	0.013
Exchangeable K (cmol/kg)	0.92	0.97	0.99	1.03	1.05
Exchangeable Na (cmol/kg)	0.16	0.17	0.21	0.32	0.35
Total Exchangeable Acidity (TEA)	3.93	4.31	4.38	4.47	4.55
Effective Cation Exchangeable Capacity (ECEC)	0.64	0.67	0.68	0.71	0.72
Base Saturation	83.71	84.7	86.43	88.5	91.71

*B₀; 0 concentration of crude oil, B₁; 100 ml concentration of crude oil, B₂; 300 ml concentration of crude oil, B₃; 500 ml concentration of crude oil, B₄; 700ml concentration of crude oil

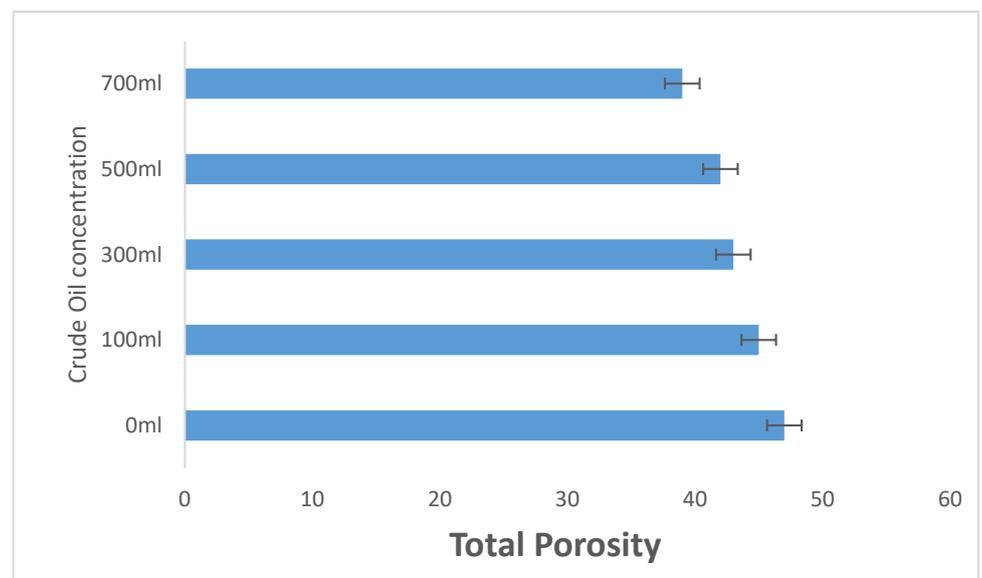


Figure 2a. Porosity at Different Contamination Levels (Error bar is standard error at 0.05)

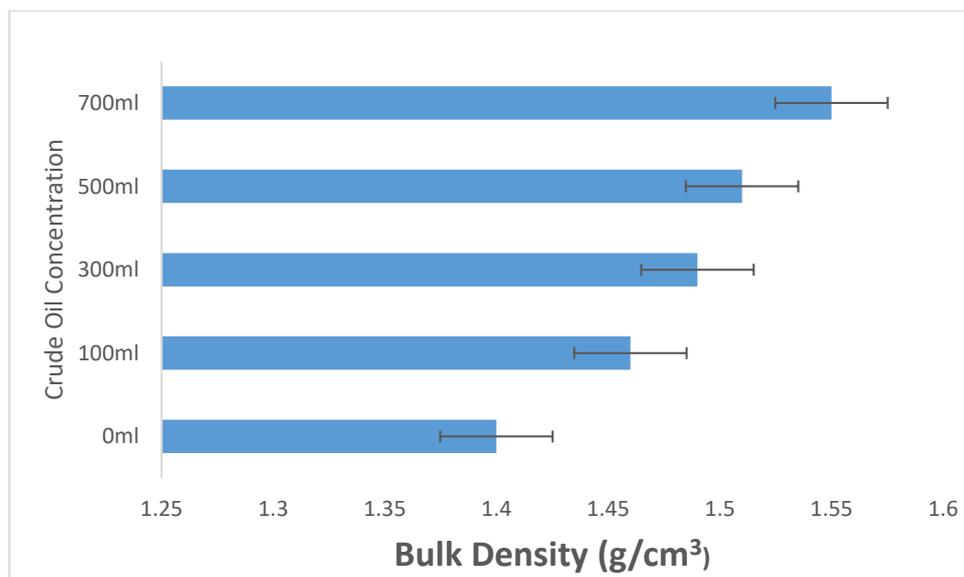


Figure 2b. Bulk Density at Different Contamination Levels

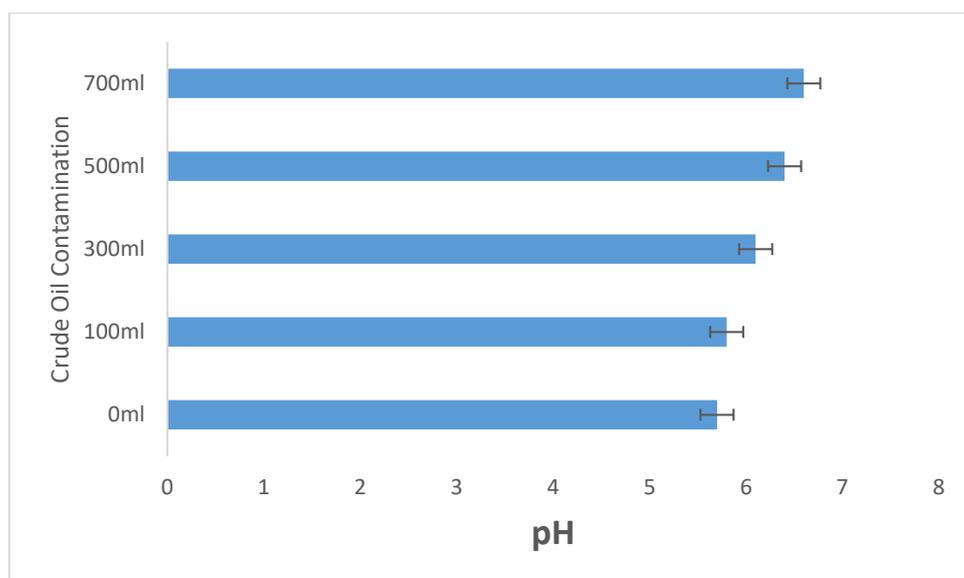


Figure 2c. pH at Different Contamination Levels

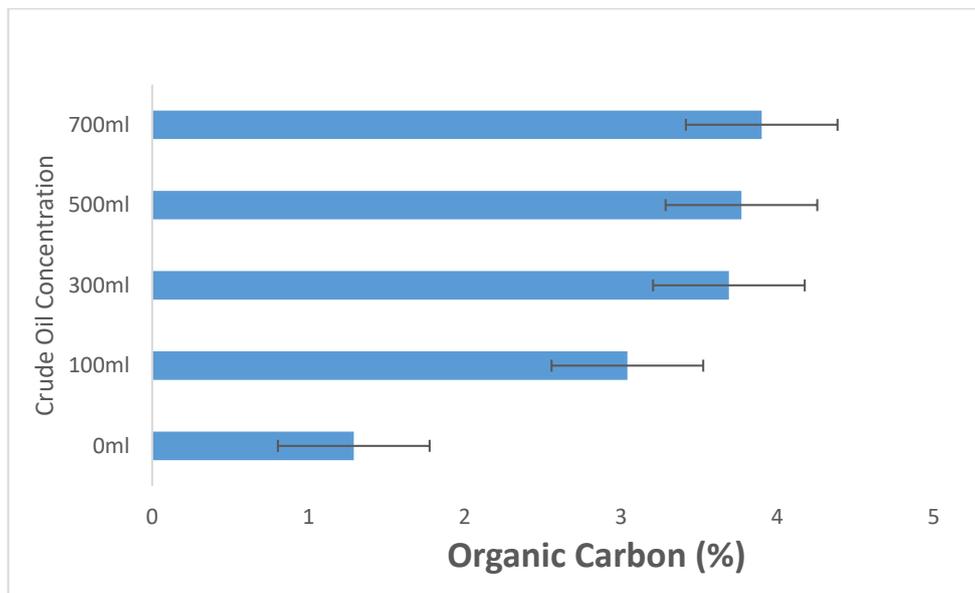


Figure 2d. Organic Carbon at Different Contamination Levels

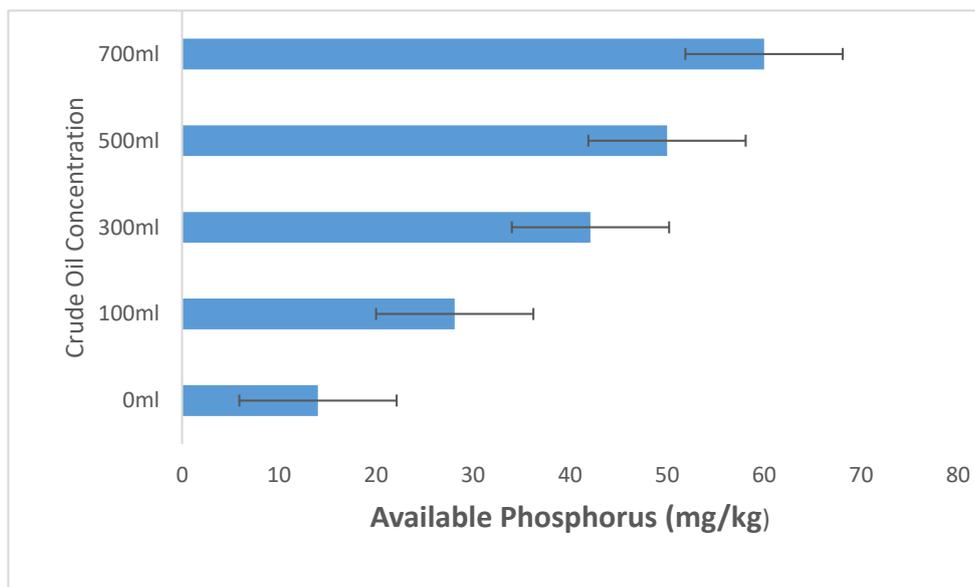


Figure 2e. Available P at Different Contamination Levels

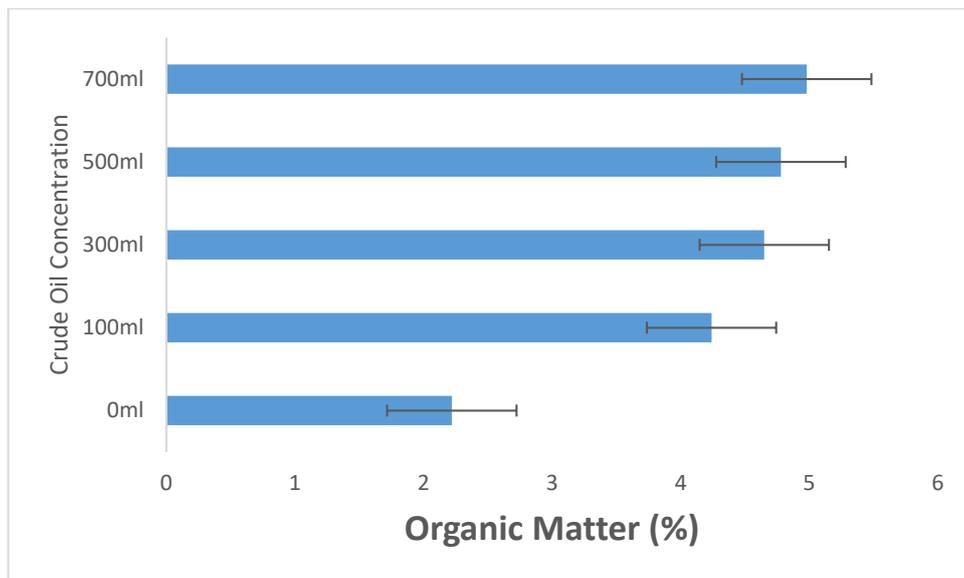


Figure 2f. Organic Matter at Different Contamination Levels

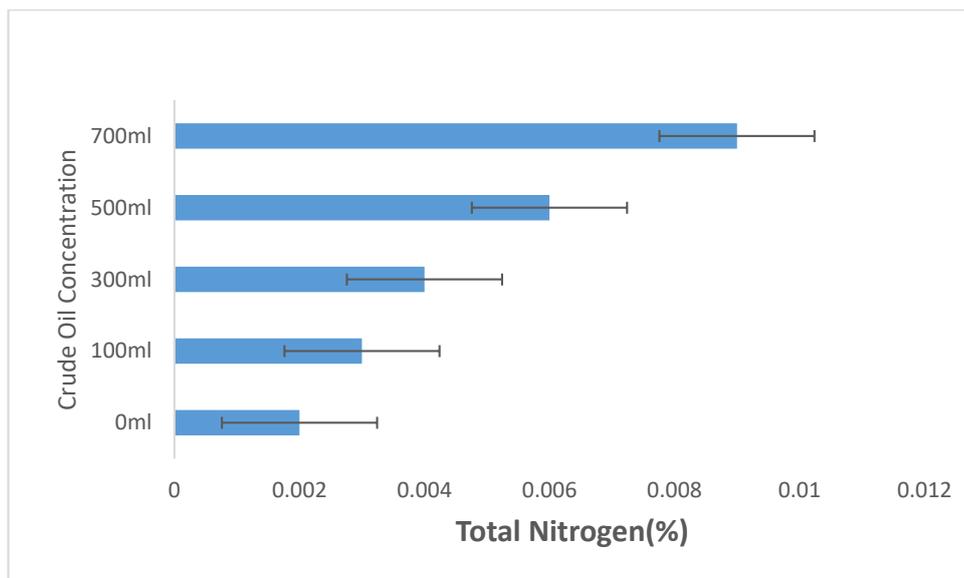


Figure 3a. Total Nitrogen at Different Contamination Levels

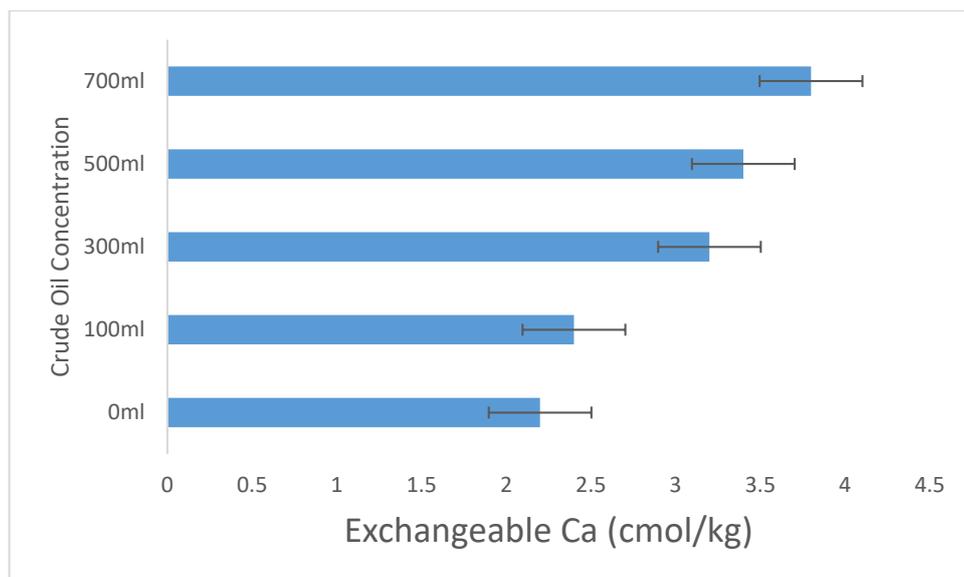


Figure 3b. Exchangeable Calcium at Different Contamination Levels

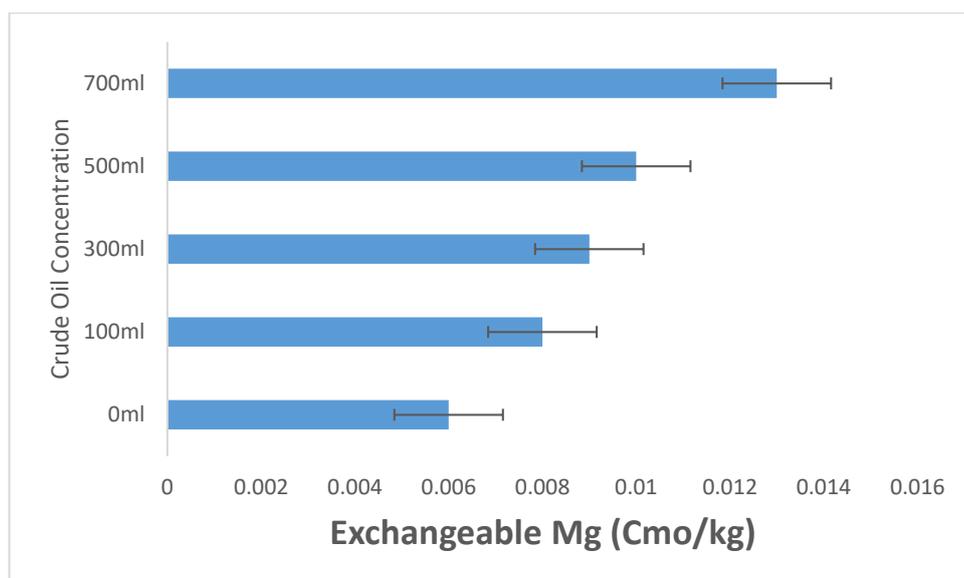


Figure 3c. Exchangeable Magnesium at Different Contamination Levels

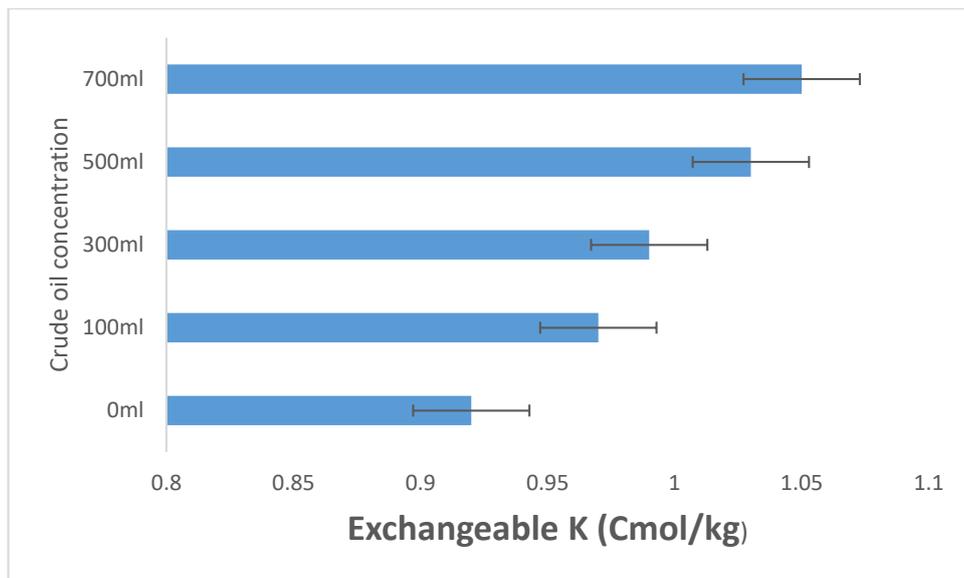


Figure 3d. Exchangeable Potassium at Different Contamination Levels

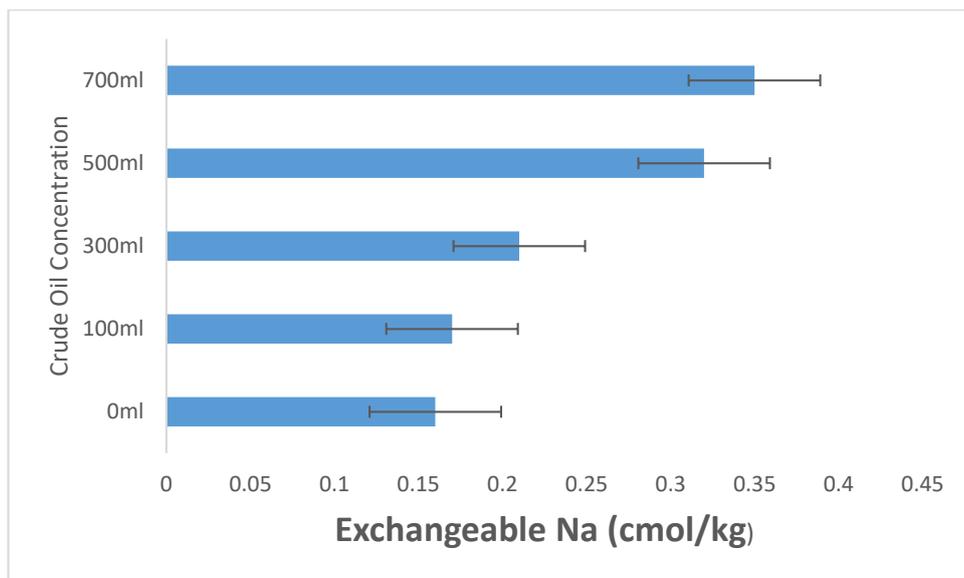


Figure 3e. Exchangeable Sodium at Different Contamination Levels

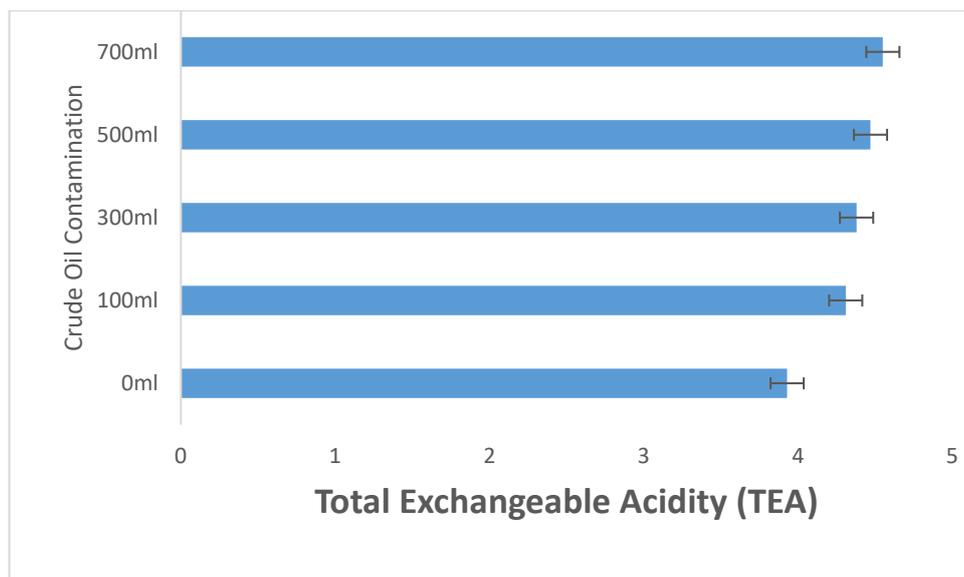


Figure 3f. Exchangeable Acidity at Different Contamination Levels

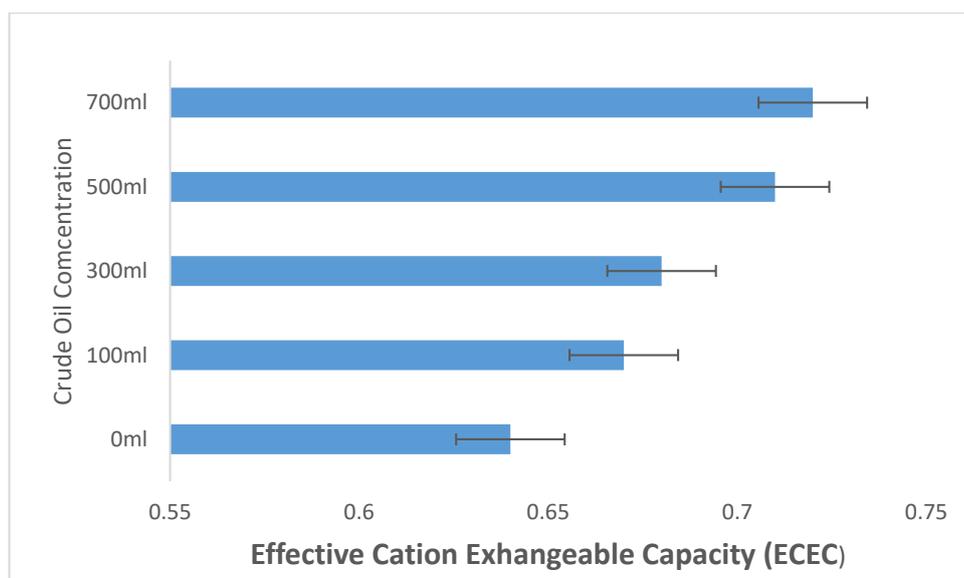


Figure 3g. ECEC at Different Contamination Levels

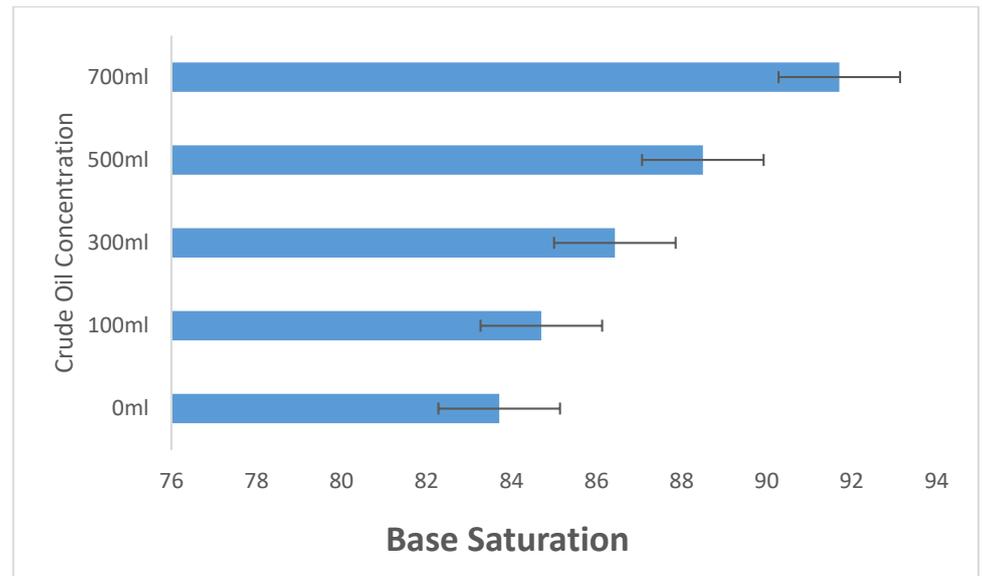


Figure 3h. Base Saturation at Different Contamination Levels

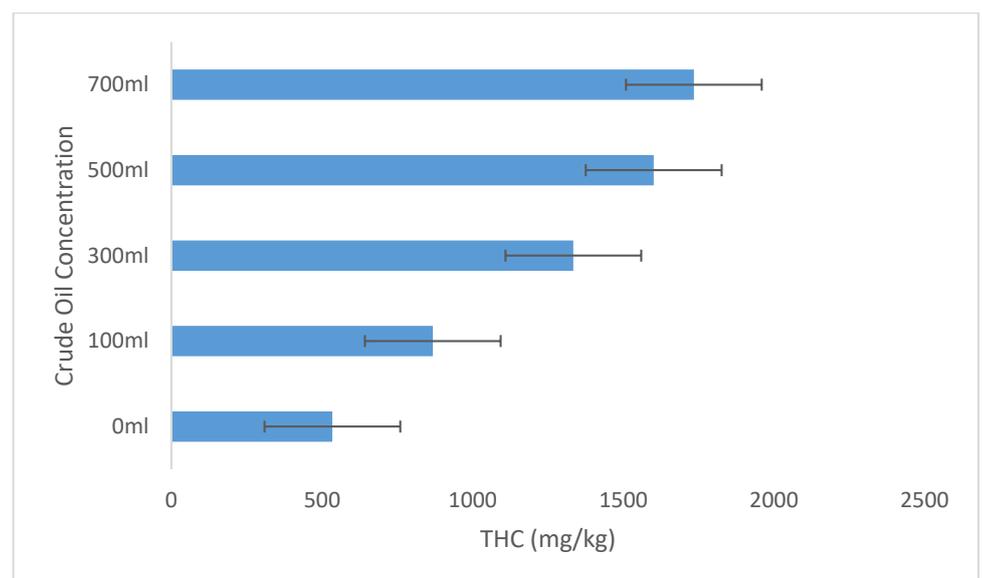


Figure 3i. THC at Different Contamination Levels

4. Discussion

Porosity as shown in [Figure 2a](#) decreases as crude oil volume increases in the soil, which is in conformity with the findings of Eneje and Ebommotei [14] who reported that population of soils with crude oil reduces soil water holding capacity. However, there were significant different at $P < 0.05$. From [Figure 2b](#), it was found that the increase in crude oil volume in soil increases the bulk density of the soil. The soil bulk density increased from the least polluted soil to the highly polluted soil. This can be on the crumping nature of the soil caused by excess crude oil which is in line with the study by Eneje and Ebommotei [14] stating that pollution of soils with crude oil increases soil bulk density. There was significant difference at $P < 0.05$ using ANOVA.

The highest value of soil pH was recorded in the 700 ml crude oil volume ([Figure 2c](#)). pH value increases in soil as crude oil concentration increases; however, most soil organisms can survive within the range. More so, most plants can tolerate pH values of about 5.0 to 8.0 [21]. Organic carbon is a major component of which it is attributed to

microbial mineralization of crude oil. The organic carbon at different concentrations of crude oil in the soil increases with increase in crude oil volume. The organic carbon values at 700 ml volume showed the highest value as shown in [Figure 2d](#). This agrees with the findings of Enije and Ebomotei [14], Ijah and Anitai [15], and Ogboghodo et al. [24] who reported that crude oil increases in percent organic carbon. However, there was significant difference at $P < 0.05$. Organic matter is a measure of the quality of any soil. The percentage organic matter was found to be high in 700 ml pollution level of crude oil, while the least was recorded in the control as shown in [Figure 2f](#). The increase of soil organic matter may be due to the significant presence of crude oil in the soil which blocks pore spaces and reduces the rate of air penetration in the soil. This is similar to the report of Pareteno-Clarke and Achuba [25] who stated that organic matter increases as the volume of oil increases. However, there was a significant difference at $P < 0.05$.

The available phosphorus values of the petroleum oil polluted soil were shown in [Table 1](#) and presented in [Figure 2e](#). It can be observed that the available phosphorus was relatively high among all impacted soil. However, the soil available phosphorus increases from the control level with an increase in polluted soil samples which agrees with the report of Enije and Ebomotei [14], and Ogboghodo et al. [24]. However, there were significant different at $P < 0.05$. From [Figure 2e](#), it may be due to the fact that crude oil contained some nutrient elements such as nitrogen or could also be that crude oil initiates soil reactions that result in the Availability of soil nutrients in the polluted soil. This result is similar to the result obtained by Eneje and Ebomotei [14], and Udo [26] in crude oil polluted soils ($P < 0.05$).

The exchangeable calcium was found to be the pollution level of 700 ml crude as illustrated in [Table 1](#) and [Figure 3b](#). Exchangeable Calcium has been increasing in soil on the basis that crude oil releases metals to soil environment. The variation in soil exchangeable calcium may be due to the presence of crude oil, which is in line with the findings of Shukry et al. [19] who reported decrease in Exchangeable calcium in crude oil polluted soils but also support the findings of Eneje and Ebomotei [14] who observed increase in Exchangeable calcium in polluted soils ($P < 0.05$). The values of exchangeable magnesium are shown in [Table 1](#). This increased with an increase in the volume of simulated crude oil in the soil ([Figure 3c](#)). The exchangeable Mg increased in the soil on the basis that crude oil releases metals to soil environment. Also, soil magnesium in the polluted and unpolluted soil samples may be attributed to leaching losses in the soil, which is in line with the findings of Eneje and Ebomotei [14] who reported a reduction in Exchangeable bases as a result of crude oil in the soil. In addition, ANOVA results showed that $P < 0.05$. The values of Exchangeable Potassium at various concentrations are displayed in [Table 1](#). Also, the results indicated that the potassium was high at 700 ml crude oil concentration ([Figure 3d](#)). There were significant different at $P < 0.05$. Generally, the values of Exchangeable Na were low. The values of Exchangeable sodium obtained from various samples as shown in [Table 1](#). Exchangeable Na was found to increase with increase in pollution level of crude oil. The increase of Na in crude oil-contaminated soil releases metals to soil environment ([Figure 3e](#)). Also, the values obtained as shown in [Table 1](#) revealed that the variation was due to the presence of crude oil., this study agrees with the findings of FAO [27] who reported decrease in Sodium content of the soil ($P < 0.05$).

The results indicated that the TEA increases with the volume of crude oil simulated into the soil. However, the values did not exceed the optimum level suitable for plant growth as reported by FAO [27]. The ANOVA results revealed that there were significant different at $P < 0.05$. The ECEC values at treatment samples showed the highest value at treatment 700 ml ([Figure 3f](#)). This reveals that the 300ml concentration had the highest number of ECEC ([Figure 3g](#)), the values were below critical values for optimum crop production as stated by FAO [27]. However, $P < 0.05$. The base saturation concentration in the soil showed the highest value at 700 ml concentration ([Figure 3h](#)). This revealed that

700 ml volume had the highest number of base saturations. From the result obtained, the values are higher than 50% recommended as being lower limit of base Saturation for crop production as reported by Udo et al. [28] However, there was no significant difference at $P < 0.05$.

From the results, it can be observed that the control which is zero 0 ml recorded the lowest THC of and the highest by 700 ml volume of crude oil. It can be observed that the increase in crude oil volume increases with THC (Figure 3i). The values of all concentration did not meet 5000 mg/kg of DPR [29] intervention value but exceeded the target value of 50 mg/kg. However, this is unfavorable to soil organisms, this report is in line with Eneje and Ebomotei [14] who observed that the higher the pollution, the more destructive it is to plants ($P < 0.05$).

5. Conclusions

This study investigated the effect of simulated petroleum hydrocarbon on the physicochemical characteristics of sandy loam soil. The study revealed that bulk density, total porosity, pH, available P, THC, organic matter, % organic carbon, Total Nitrogen, exchangeable Ca, Na, P, mg, ECEC, TEA, and base saturation were affected due to different volume of crude oil. In addition, all the characteristics studied including bulk density, pH, available P, THC, organic matter, % organic carbon, total Nitrogen, exchangeable cation (Ca, Na, P, Mg), ECEC, TEA, and base saturation increased with increase in volume of crude oil except porosity. Conclusively, crude oil alters the physicochemical characteristics of the soil. Hence the more crude oil in the soil the more physicochemical characteristics of soil change thereby causing imbalance in soil nature. Therefore, the study suggest that remediation should be adopted to regain the originality of the soil.

Author Contributions: For research articles with several authors, a short paragraph specifying their contributions must be provided. The following statements should be used “Conceptualization, R.A.E. methodology, R.A.E. and A.T.A.; formal analysis, C.E.; investigation, B.N.; resources, A.N.O.; data curation, C.E.; writing—original draft preparation, R.A.E.; writing—review and editing, A.T.A, A.N.O, B.N.

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Conflicts of Interest: Declare conflicts of interest or state “The authors declare no conflict of interest.”

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