#### Nigerian Journal of Science and Environment 2023 Vol. 21 (1) 397 - 410 PHYSICOCHEMICAL PROPERTIES OF CRUDE OIL POLLUTED SWAMP AT ORONI IN ENHWE COMMUNITY, DELTA STATE, NIGERIA. Judith O. Atonuje<sup>1</sup> and Christopher, C. Osubor<sup>2</sup> Corresponding author: atonujekome@gmail.com

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#### ABSTRACT

The study is aimed at investigating the physicochemical properties of crude oil polluted swamp soil at Oroni in Enhwe Community, Isoko South Local Government Area, Delta State, Nigeria. Soil samples were collected from sampling sites. Physicochemical parameters were determined using standard protocols. One way ANOVA (with statistical package SPSS version 22.0.) was used to analyze the mean values of the samples. The results showed that pH, Nitrogen (N), organic carbon, exchangeable acidity (EA), cation exchange capacity (CEC), silt, clay and sand in soil of polluted area varied when related to control. Electrical conductivity (EC), sulphate (SO<sub>4</sub>), phosphorus (P), nitrate (NO<sub>3</sub>), organic matter, calcium (Ca), magnesium (Mg) and potassium (K) levels of polluted soil were higher when compared to soil control. The study established that crude oil pollution affected the physiochemical properties of the soil since high concentrations of these parameters result in chemical composition of polluted soil, thus making it unsuitable for agricultural growth of crops. The study therefore recommends that possible actions be designed to prevent or reduce crude oil spillage in the area under study.

KEYWORDS: Physiochemical properties, soil, swamp, crude oil pollution, spillage

# INTRODUCTION

Crude oil is a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons of various weights and other liquid organic compounds that are found beneath the earth surface (Halanych et al., 2021). Crude oil varies in appearance and composition from one kind to another. A major component of crude oil is petroleum hydrocarbon. It is used as raw material for the production of goods and services in industries. These goods and services serve as symbols of our modern civilization. The fundamental compositions of petroleum hydrocarbon form the major sources of energy on which the development of humanity is based. It is worthy to note that although crude oil together with its products, are not artificial, they are manipulated by

man to satisfy his needs. Industries use its ingredients for the manufacture of a finite number of products that man uses every day. It is also noted that crude oil, though very useful has posed as a main source of environmental problems. Oil spills affect many species of plants and animals in the environment (Plohi et al., 2002; Jing et al., 2016).

Whenever crude oil is released from pipe lines on the land, which usually affects the soil ecosystem, then Land spill is said to have occurred. Crude oil enters the environment from natural seep (1%), atmospheric input (1%), offshore production (1%), coastal and estuarine effluents (3%), non-refinery industrial wastes (5%), Municipal waste (5%), urban runoff (5%), rivers (26%) and oil water discharge from industry (53%) (Cluster et al.1996; Stout and Wang, 2018; Halanych et al., 2021). Oil spillages along coastline cause immediate damage to the environment and have negative impact on economy of nations. It is also noted that though oil spillages result in harm to the immediate environment, their impact on oceans is minimal due to the largeness of those water bodies. The impact of crude oil pollution could be felt up to thousands of kilometers of land, sea and air. This results from the fact that wind and current serve as agents ocean of transportation of pollutants from gas and crude oil blowout sites. In many spills involving tankers or offshore oil wells, some of the oil spilled initially catches fires. When crude oil burns, the combustion results in atmospheric emission of gases, which contribute to warming and acid rain as well as large quantities of toxic ash (Ekperusi and Aigbodion, 2015; Al-Sayegh et al., 2016, Stout and Wang, 2018). In Africa, Nigeria ranks the topmost producer of crude and also occupies the 11<sup>th</sup> position in World records of crude oil production. It is also on record that Nigeria exports crude oil to Europe. Among the countries that supply crude oil to USA, Nigeria occupies the 5<sup>th</sup> position.

It is a known fact that crude oil exploration/exploitation has brought huge income to Nigeria as majority of the economy is financed from crude oil sales. The area where crude exploration and exploitation are predominant in Nigeria is the Niger Delta which covers Delta State, Bayelsa State, Rivers State, Cross River State, Akwa - Ibom State and Edo State. crude oil Exploitation of can be accompanied by accidents. This is usually in

the form blowouts from oil wells which occur during drilling of crude oil. Blowouts from oil wells also lead to loss of equipment and pose as danger by polluting surrounding environment. Blowouts are of two kinds. The first is gas blowouts which though appear to be explosive and also dangerous to site workers, have reduced environmental effect. The second are crude oil blowouts which are more hazardous than gas blowouts. It is assumed that coastline oil spillages cause more harm to both land and aquatic animals. The effects of crude oil pollutants from blowouts around drilling sites are so enormous that pollutants are conceived to be recalcitrant to natural biodegradation. The negative effects of blowout products usually persist over a long time in the affected ecosystems, as a result of low volatility and hydrophobicity of pollutants. These pollutants and any products of their degradation can be carcinogenic, mutagenic and they are potent immune-toxicants which affect the biological systems of living things 2000). Crude (Boonchan et al., oil exploration in Nigeria has resulted in a severely degraded environment, culminating in contamination of operation area due to oil spills. Toxic effects, of crude oil exposure have been reported (Kori- Siakpere, 1998). It is sad to note that crude oil exploration activities have equally brought numerous environmental hazards to the Niger Delta where these activities are predominant. In the Niger Delta Area alone, there have been over 550 reported cases of crude oil spillages since 1976, releasing over 2.8 million barrels of crude oil into the environment (Kori-Siakpere, 1998).

The impact of crude oil pollution on agricultural land is enormous. This has resulted in the inhibition of fruiting, flowering and general reduction in agricultural yields. This also has affected the production of the wild oil palm tree which flourishes in the environment. Enhwe is known as an oil producing community in Delta State. Enhwe town lies on the geographical coordinates of Latitude 5° 22' 31" North and Longitude 6° 6' 38" East. There are oil wells situated there by SPDC (Shell Petroleum Development Commission) and a part of the oil derived by Federal government comes from this community. However, there is no building of infrastructure in the area by government to show for it. With that, the community seems to be poor. Therefore, local youths in polluted region usually involve in illegal oil refining and theft, at least to have some fair share from the fabulous wealth coming from crude oil which God has deposited in their environment. This illegal activity gives rise to fire disaster. Fire disaster occurred in Enhwe Community (Urhobo Today, 2019). The source of the fire was linked to an oil bunkering camp within the Oroni area of the community where crude oil was refined into different petroleum products. This incident consequently may have adverse effects on humans, since the growth of food crops; green vegetation, trees and even the fertility of agricultural sustaining soil are reduced. In the area under study, it was found that soil

that soil and water are used for a number of activities. namely: agriculture and recreational use such as swimming. Other uses include fishing, domestic uses and drinking. The people of the Community are engaged in various occupations which include farming from where crops like cassava, yam, okra, coco yam, pepper and vegetables are produced. The people are also engaged in trading. Although, manv important researches have been carried out on the physical effects of crude oil spillages in the Niger Delta, (Abam (2001); Shaw, and Sutton (2021); Brumner and Mulvaney (1982); Olens et al (1954)), it appears that the works on the physiochemical properties, microbial and enzymes activities around crude oil spillage blowouts are quite few. Motivated by the works of some of the authors mentioned above, we focus our attention on the investigation of the physiochemical properties of the soil at Oroni crude oil spillage swamp in Enhwe Community, Delta State, Nigeria.

# MATERIALS AND METHODS

# **Sampling Stations**

This research work was carried out at Oroni swamp in Enhwe Community, Isoko South Local Government Area, Delta State, Nigeria. Below is a map showing the location of the study area:



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Figure 1: Location of Enhwe Community

The number of sampling sites selected for the study was five and they were labeled as sites (I, II, III, IV) and Control as shown in Figure 2 below.

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Figure 2: The Map of Enhwe Showing the Sampling Sites.

Site I (swamp A), Site II (swamp B), Site III (swamp C: control site), Site IV (crude oil polluted soil) and Site V (soil control), at Oroni in Enwhe Community, Isoko South Local Government Area, Delta State, Nigeria.

#### Soil Sampling

Soil sample collection from the three sampling sites (I, II and III) was done towards the end of 2022, precisely in October of that year. Before the collection of samples, all sampling containers were cleaned up thoroughly and dried up. The soil was kept in appropriate sample containers and there they were preserved as required. The collected samples were taken to the laboratory, in particular Quality Analytical Laboratory Service Limited, Benin City, Nigeria where the analysis was carried out.

#### Soil sample collection

Contaminated soil was collected from Oroni swamps in Enhwe Community, while the non-contaminated soil was collected from a swamp along Enhwe Olomoro road. Soil samples were collected according to method described by (Allamin et al.,2014) into sterilized foil papers in October 2021. The samples were transported within 24hrs in a tight bag to Quality analytical Laboratory Services Limited in Benin city, Edo State, and physiochemical properties analyzed.

#### Soil sample processing

300g of soil samples were air dried for 2days, grounded to fine dust and sieved with a 2mm-mesh sieve. The sieved soils were then analyzed in triplicate.

Determination of physiochemical Parameters

# pH in soil

Physicochemical parameters were determined by standard methods of APHA (2002).Soil pH was determined using a glass electrode in a 1:2:5 soil watersuspension. 10g of homogenized soil was mixed in a beaker with 25ml of distilled water, stirred thoroughly, the mixture and kept to stand for 30 minutes to settle. A pH meter electrode was allowed to stabilize using a buffer solution (pH 7.0) then the electrode was rinsed with the soil solution and readings were taken.

# Determination of sodium and potassium in Soil:

Determination of sodium and potassium is done using the Jenway flame photometry (model PFP7). It employs the principle of atomic excitation and emission. Standard known amount of solute of sodium and potassium in solution are aspirated. The emission is recorded to make a straight line graph and the concentrate of a solution which is not known can be roughly calculated from the resulting curve. The method is suitable for waters, waste-waters and soil/sediment extracts. The flame photometric method is an internationally accepted method with a detection limit Samples containing particles were filtered using filter paper and Calibration instrument using standard series. Aspirated unknown samples and record instrument respond with corresponding the Na. Κ filter. Concentration of analyte was estimated using equation of calibration curve or

reading directly from obtained calibration curve .The general equation of a straight is given by Where, y = instrument respond or reading (IR), m = slope of curve,

x = concentration of analyte (ppm) and c = constant of equation.

# Determination of calcium and magnesium

Determination of calcium and magnesium in soil was done using EDTA (versenate) titration method. Whenever a solution of certain metal cations is combined with EDTA as well as its sodium, a chelated complex is usually formed. Moreover, suppose a little quantity of dye like Eriochrome Black T is put in an aqueous solution which has Mg ions as well as Ca ions at pH 10.0 $\pm$  0.1, the solution is sure to turn wine red. Also, suppose that EDTA is again included as a titrant, the Mg and Ca will go complex. Again suppose that enough EDTA is continuously added so as to complex all the Mg and Ca, this will make the solution change in colour from red to blue. This change marks the terminating point of the titration. The computation is done as follows:

Where, is the volume of versenate used in titration and N is the normality of versenate. 1ml of 1M EDTA = 40.08mg Ca per aliquot, 1ml of 0.004M EDTA = 0.16032 mg Ca per 25ml aliquot and T titre of 0.004M EDTA = 0.16032T mg Ca per 25ml aliquot= 0.16032 T  $\times$  1000/25  $\times$  extraction ratio mg/kg as Ca Calculation if V<sub>2</sub>is the versenate used in the titration

Then

Ca2<sup>+</sup> + mg ( meq/l) = N ×  $V_2$  1000 / 25

The amount of  $mg^{2}is$  obtained by subtracting the value of calcium from the value obtained for (Ca<sub>2+</sub> =  $mg^{2+}$ )

# **Determination of nitrate**

The determination of nitrate present in the soil sample involves the application of the uv/visible approach of analysis. A polythene bottle of volume 250 ml was selected. Thereafter, dry soil samples of exactly ten(10) grams in weight were poured into the bottle, then 0.5g of activated carbon, 40ml of extracting solution were included into the bottle. These were shaken on a mechanical shaker for 45 minutes to one (1)

hour and then filtered thoroughly through Whatman filter paper. Calculation is as below: Nitrate concentration NO<sub>3</sub> mg/l =

Ac con  $\left(\frac{mg}{l}\right) \times DF \times EV(L) \times B$ Volume of water in (L)

where, DF is the Dilution factor, AC is the Concentration (mg/l), EV is the Final volume (L) and B is the Extraction ratio.

# **Determination of phosphorous**

A 250ml conical flask was selected and this was followed by weighing five (5) grams of soil which is now poured into the flask. 100ml of 0.5M Thereafter, sodium bicarbonate of ph 8.5 was included into the flask and shaken for a period of half an hour after which the solution was filtered. A pipette was collected and used to pipette 10 ml of the filtrate and poured into a 50ml volumetric flask after which a drop of pnitrophenol indicator and the ph adjusted to 3.0 with 4N HCl. 5 drops of 0.1N stannous chloride, was added and shaken without stopping.

It was observed that the color intensity read photometrically changed to red after aduring of five (5) minutes with a 660 light red filter in photoelectric calorimeter. Thereafter, the quantity of phosphorous was computed as mg/L. This process of obtaining phosphorus is called Olens method (Olens et al., 1954).

#### **Determination of total nitrogen**

To determine the total nitrogen present in the soil, a measure of one (1) gram of soil separated and sample was weighed. Thereafter, the sample was disintegrated so that it has the concentration of Acid was used to distilled the digest and the percentage nitrogen was computed. This method of determining nitrogen is called 'the Macro-kjedahl digestion distillation method'. The percentage of nitrogen is computed using the formula;

Where: N = Total nitrogen (%), T = Titrevalue and M = Molarity of acid (HCl)

### **Determination of sulphate content**

Barium chloride was added to sulphate after the sulphate was precipitated in hydrochloric acid medium as barium sulphate. It was ensured that precipitation was done when temperature was close to boiling point. Thereafter, the precipitate was filtered having gone through a period of digestion. It was then washed using water to ensure that it was free from chlorides and then ignited and weighed as barium sulphate.

A 25 ml volumetric flask was provided and ten (10) ml of sample was pipetted into it. So as to increase the volume to almost 20 ml, some distilled water was added.

Also added to the sample, was 1ml of the gelatin-BaCl<sub>2</sub> reagent together with set of working standard solutions in the volumetric flask and to obtain the volume needed, some distilled water was added and properly mixed. It was then made to settle for up to half an hour (30 minutes). Thereafter, the absorbance values were determined at 420nm with 30minutes on unicam 5625 spectrophotometer, with shaking of the content in the flask before measurement.

Concentration of sulphate content = concentration mg/kg

 $SO_4 - S = (AC \text{ con } (mg\l) \times DF \times EV (LZ) /$ 

(Vol of water in (l))

Where ,DF = Dilution factor, AC =Concentration (mg/l), EV = Final volume (L) and Z = Extraction ration.

# **Determination of Exchange acidity**

A weight of soil which is dried of air of which was five grams (5gms) was measured and poured into a 50 ml tube and then, 30 ml

of IM KCl was added. The tube was covered tightly with a rubber stopper and shook for 1 hour over a mechanical shaker. The content was separated by centrifugation at 2000 rpm within a period of 15 minutes, and then the supernatant which appeared very clearly was attentively decanted into a volumetric flask that is 100ml in size. Also added to the same soil sample, was an extra 30 ml of IMKCl. They were then shaken together for half an hour. Thereafter, the second step was repeated and the clear supernatant was transferred into that same volumetric flask. The third step was carried out for the very third time and once more, the clear supernatant was transferred into that same volumetric flask and the volume was completed to mark up with IMKCL.

# **Determination of CEC**

In this method, the CEC was taken as the total exchangeable bases (TEB) and theexchange acidity (EA)CEC = TEB + EA For acid tropical soils, the exchange acidity determined by 1M KCL is used. Theacidity determined with BaCl2-TEA is used by USDAEffective CEC (IITA) = TEB + EA (KCl)

CEC by summation of cations (USDA) = sum of exchange Ca, Mg, K and Na

These exchangeable bases are measured in the saturation extracts obtained bytreating the soils with 1M NH<sub>4</sub>O Ac as described above when determining theCEC either by leaching or by centrifuge procedure.

# Determination of organic carbon

The Walkley –Black Chrome acid wet oxidation method is applied to determine the soil organic compound. Whereas, the Oxidizable matter which can be found in the soil is oxidized by  $1N K_2Cr_2O_7$  solution. The reaction that follows from this oxidization is assisted by the heat generated whenever two volumes

of  $H_2SO_4$  are mixed with one volume of the dichromate. Ferrous sulphate is applied to titrate the extra dichromate and it was observed that the volume of C that is present in the soil sample varies inversely with the tire.

A representative sample was taken, and it was grounded then made to go through 0.5mm sieve. Thereafter, the weight of some soil samples were taken in duplicate and then poured into a 250ml Erlenmeyer flask (1.00g was used because the organic carbon content was between 1 and 3% or 2.00g if it is less than 1%).

An exact 10ml of  $K_2Cr_2O_7$  in solution was pipette and transferred into each flask which now swirled gently to disperse the soil. Using an automatic pipette, a 20ml concentrated H<sub>2</sub>SO<sub>4</sub> was included rapidly and also directing the stream into the suspension and this immediately then swirled the flask gently until soil and reagents are mixed. This then swirled more for one minute. The beaker was made to revolve all over so as to allow the flask to stand on a sheet of asbestos for almost half an hour. To the cold solution, 60ml of distilled water was poured into the mixture, shaken together and allowed to cool. This was done after 10ml of ortho phosphoric acid was added and 8-10 drops of 1% Diphenylamine solution, the solution assumes a dark violet color then titrated with 0.4N ferrous Ammonium sulphate solution continuously till a change of color to green is achieved.

The organic carbon content of the soil was calculated as %  $C = N \times V_1 - V_2 \times 0.39 \times mcf$ 

N = Normality of ferrous sulphate solution (from blank titration)

 $V_1 = ml$  ferrous sulphate solution used for blank.

# **Determination of Organic Matter in Soil**

The value of the organic carbon was multiplied by 1.724 to obtain the organic matter.

# **Determination of particle size**

What constitutes the analysis of the size of soil particles is the tendency to ascertain the percentage of clay, sand and silt fragments present in the soil. The relative abundance of these particles sizes is required for textural classification of soils. If accurate results are expected to be obtained, it is normal to treat the soil so as to remove all cementing agents and dissolved mineral matter. The major cementing agents are organic matter and calcium carbonate. Surface soils which usually contain high contents of organic matter require H2O2 treatment to destroy the organic matter. Subsoil samples which have negligible organic contents may not need the peroxide treatment.

# Procedure

Fifty grams (50g) oven dry or 51g (air dry) of fine textured soil (or 100g of coarse textured soil) was collected and its weight taken and then placed in the baffled cup. Thereafter, water was poured into the cup until it was filled up to half its volume and this was followed by the addition of 50ml hexametaphosphate reagent. The cut was stirred after being placed on top of a stirrer. The stirring enabled the soil aggregates to be broken down. The time interval for breaking the aggregates was in the following order: six (6) minutes for the sand, ten (10) minutes for light heavy sandy loams followed by fifteen (15) minutes for other soils. A bouyoucos cylinder was provided and the suspension was transferred into it. The cylinder was then filled with distilled water up to the lower mark whereas the hydrometer was in suspension. To determine the percentage of the sand present in the sample, the following steps were followed:

A) The hydrometer and stopper the cylinder were removed, after which the cylinder was inverted several times so as to carefully mix the content. Thereafter, the time was recorded after placing the cylinder on a desk. At the end 20 seconds, the hydrometer was thoroughly placed and readings were taken after about forty (40) second, and a data sheet was provided on which the reading was recorded.

B) The temperature of the suspension was recorded after the hydrometer was removed from it.

C) An extra 0.2°F was added for every degree over  $67^{0}$ F so as to obtain the corrected hydrometer reading. Moreover, to every reading for temperature less than 67oF, an extra  $0.2^{\circ}$ F was reduced or subtracted. In the centrifuge scale, 0.3 unit was added for every degree above 20oc, 0.3 was subtracted for every degree below 20oc. 2 units was also subtracted so as to compensate for the dispersing agent, which was added for each hydrometer reading. In order to obtain the grams of soil materials in suspension, the hydrometer is calibrated to get the correct reading. Since the sand moves to the base of the cylinder to settle within forty (40) seconds, it was observed that quantity of clay and silt present in the suspension is accurately given by the forty (40) seconds hydrometer reading. The difference between the corrected hydrometer reading and the total weight of the sample gives the weight of the sand in the sample. To obtain the percentage sand in the sample, a calculation is done by simply 'dividing the weight of sand by that of the sample. The result of this quotient is multiplied by 100. The case of obtaining the percentage of clay in the sample, the following procedure was maintained:

The suspension was mixed and reading taken by the end of 2 hours, preceding the actual reading hydrometer is usually inserted. The reading of the suspension temperature was done and then corrected according to 4c. Left for a period of two (2) hours one sees that the sand together with silt has settled out of the suspension. Here, what represents the grams of the clay found in the sample is the actually the corrected hydrometer reading. It is just easy to now compute the percentage clay present in the sample by dividing the weight of the sample by the total weight and then multiplying by 100.

1) The method of computing the percentage of silt in the sample is called 'calculation of percentage silt by difference'. This involves obtaining the percentage of sand and that of clay and then subtracting the sum from 100. This difference gives the percentage of silt present in the sample. 2) The texture of the soil which is also called class name of the soil was obtained from the textural triangle.

#### **Statistical Analysis**

The statistical tool used was one way analysis of variance (ANOVA) as well as post hoc test. Descriptive statistics was carried out on the data obtained and results were expressed as mean  $\pm$ SD. The significant differences between groups were analyzed using one way analysis of variance (ANOVA) and post hoc test. The SPSS programme package (version 22.0) was used analysis. A for statistical significant threshold of p < 0.05 was regarded statistically significance between the test and control group for the analysis.

#### **RESULTS AND DISCUSSION**

Parameters	Control soil	Polluted soil
рН	$4.10 \pm 0.10^{a}$	5.80± 0.10 <sup>a</sup>
EC (µS/cm)	$257.0 \pm 1.0$ <sup>a</sup>	$509.33 \pm 1.53$ <sup>b</sup>
SO <sub>4</sub> (mg/kg)	$272.47 \pm 3.7$ <sup>a</sup>	$152.70 \pm 4.07$ <sup>b</sup>
P (mg/kg)	$34.62\pm3.15^{\mathrm{a}}$	$79.07 \pm 2.82$ <sup>b</sup>
NO <sub>3</sub> (mg/kg)	$5.29\pm0.85^{\rm a}$	19.15 ±0.52 <sup>b</sup>
N (%)	$0.16 \pm 0.01^{a}0.$	$29\pm0.01^{a}$
Organic carbon (%)	$1.72 \pm 0.02$ <sup>a</sup>	$3.04\pm0.03^{a}$
Organic matter (%)	$2.97\pm0.03^{a}$	$5.26\pm0.55~^{b}$
Ca (mg/kg)	$448.89 \pm 111.07^{a}$	$769.54 \pm 0.00$ <sup>b</sup>
Mg (mg/kg)	$259.33 \pm 44.92^{a}$	$207.47 \pm 44.92$ <sup>b</sup>

 Table 1: Physicochemical properties of soil samples from Oroni Enhwe, Delta State Soil

 chemical characterization

	Nigerian Journal of Science and Environment 2023 Vol. 21 (1) 397 - 410		
Na (mg/kg)	$480.29 \pm 41.44$ <sup>a</sup>	772.40 ± 44.88 <sup>b</sup>	
K (mg/kg)	$580.09 \pm 39.72^{a}$	$863.14 \pm 38.07$ <sup>b</sup>	
EA (meq/100g)	$0.83\pm0.058^a$	$0.63\pm0.06$ a	
CEC (meq/100g)	$2.41\pm0.06~^a$	$2.67\pm0.07$ $^{\rm a}$	

Triplicates values are given in mean  $\pm$  SD. Mean values in same column differ significantly at p < 0.05 with different superscript letter.

 $EC = Electrical Conductivity, SO_4 = Sulphate, P = Phosphorus, NO_3 = Nitrate, N = Nitrogen ,Ca=Calcium, Mg=Magnesium, Na=Sodium, K=Potassium, EA = Exchange Acidity, CEC = Cation Exchange Capacity$ 

Parameters	control soil	polluted soil
CLAY (%)	$8.70 \pm 0.58$ <sup>a</sup>	$6.70\pm0.58^a$
SILT (%)	$6.59\pm0.58^{a}$	$4.93\pm0.58^{\text{a}}$
SAND (%)	$84.70\pm0.58^{\rm a}$	$88.37 \pm 0.00^{a}$

Triplicates values are given in mean  $\pm$  SD. Mean values in same column differ significantly at with different superscript letter.

The soil chemical analyses are presented in table 1 and the physical parameters results are presented in table 2.

There were no significant differences in pH and exchangeable acidity EA of crude oil polluted soil (pH 5.80 and EA, 0.83) when compared with the control (pH 4.10and EA, 0.53). However, slight increase in pH and EA was observed in the polluted site in comparison to the control. Exchangeable acidity is the measure of the H+ and  $Al_{3+}$  ions retained or fixed on soil colloid after the active acidity is measured (Nnaji and Egwu, 2020). Soil condition and a lot of other processes in the soil are usually affected whenever the EA of the soil is high followed by a resultant low pH. The findings

consistent with other research on are oilfields in China that found that crude oil pollution increased soil pH (Jia et al., 2009). The hydrophobic nature of crude oil may cause a potential drought in the surface and subsurface layers of polluted soil (Njoku et which could exacerbate al., 2009), salinization and raise the pH values compared to that in the control site. An important element concerning soil is the electric conductivity (EC) of soil solution. Electric conductivity usually points out low dissolved salt content and vice-versa. From the fact that the ability of crude oil to conduct electricity is quite low, one can easily conclude that the higher average value of electrical conductivity experienced in crude oil spillage sites soil cannot be tied to the presence of spilled crude oil.

Nevertheless, one can conclude that it is possible that the anoxic biodegradation mechanism which occurs by straight dehydrogenation enabled the anaerobic metabolism of hydrocarbons induced by electron acceptors and as such may result in the differences in electric conductivity. Average NO3, P were significantly raised at (p<0.05) in the control samples than in the spillage samples sites A and B. Nevertheless SO4 and Organic carbon (OC) and organic matter concentrations appeared to be significantly higher(p<0.05) in crude oil polluted soil (spillage sites A and B) than in control samples. The predominant inorganic forms of nitrogen in the soil are of course nitrate and ammonium.

Expectedly, TOC was higher in spillage samples compared to control samples and there was increase in TOC with increase in depth, indicating percolation of oil down the soil horizon (Nnaji and Egwu, 2020). Two forms in which phosphorus is discovered in the soil are organic and inorganic forms. When the amount of phosphorus in these forms is compared with total volume of phosphorus found in the soil, It was obvious that its solubility was lower. Nitrate and phosphorus were significantly higher in polluted soil when compared to the control; this may be attributed to the addition of NPK (Nitrogen, phosphorus and potassium) fertilizers to the soil. Also high nitrate concentration may be due to the high amount of organic matter present in the polluted soil. Sulphur is usually absorbed in the form of sulphate. Moreover, soil sulphate can also find its source from atmospheric deposition, fertilizer addition as well as mineralization of soil organic sulphur that constitute the major sulphur fraction. When the concentration of sulphur of soil in the control sites were compared with that of the spillage sites, it was found that the one from the spillage sites is by far higher. This is due to the amount of sulphur in crude oil which is oxidized to sulphate (Nnaji and Egwu, 2020).

The ability or state of the soil to hold exchangeable cations is called, Cation exchange capacity, (CEC). The cation exchangeable capacity is a very vital soil attribute. It influences the availability of nutrient, soil reaction to fertilizers as well as soil PH. Organic constituents and clay minerals of soil are found to have negatively charged crude oil sites on the surfaces. They are known to absorb and retain positively charged ions (cations) by means of electrostatic force. As a result of the fact that a lot of nutrients appear in the form of cation as calcium, potassium that is. and magnesium, the electrical charge is very important in the supply of nutrients to plants. Soil with large quantities of negative charges is more fertile because they retain more cations (Nnaji and Egwu, 2020). In this study, no significant difference was observed in EA and CEC of polluted soil when compared with the control. Nevertheless, when the soil has low CEC, productive crops as well as pastures can be raised on it. It is worthy to know that the values of CEC in the present research work were quite low. Whenever CEC in soils is high in the control, observation shows that such soils usually possess higher capacity to hold water. Soils with low CEC are more likely to develop deficiencies in potassium, magnesium and other cations while high CEC soils are less susceptible to leaching of these cations (Nnaji and Egwu, 2020). In this study a noticeable rise was observed in  $Ca_{2+}$ , Na, and K<sup>+</sup> in the sites where crude oil pollution has occurred as compared to

control (Table 1). Oil pollution in soil has been shown to be associated with the accumulation of exchangeable base (such as Ca2<sup>+</sup>, Na, and K<sup>+</sup>) (Jia et al., 2009; Nnaji and Egwu, 2020). These two factors may be the causes of increase in the values of pH around oil polluted sites. We also observed that the proportion of sand did not change because it remained the same for both polluted and unpolluted soil. Similarly, Marinescu et al., (2011) reported no significant result in crude oil pollution on granulometric fraction of the soil. Also observed was the fact that the silt content of the soil was not affected by the presence of crude oil (Table 2). A similar result was obtained by Marinescu et al. (2011) where they observed in a crude oil polluted area that granulometric fraction of the soil was not influenced by the presence of crude oil. The size of clay particles was not vitally affected by crude oil pollution (Table 2). Similar report was obtained by Marinescu et al. (2011) who observed no differences in fraction polluted clay between and unpolluted soils.

# CONCLUSION

The alterations in the physicochemical indices determined in the soil from sampling sites indicate that it is highly polluted and could affect terrestrial wellbeing of the flora and fauna as well as human activities. It was observed that the NO<sub>3</sub>, organic matter level of polluted soil in the swamp were far lower in the context of their value than the soil control. Also it was found that soils from the control which has a proportionally higher organic matter contents are thought to be more fertile than crude oil polluted soils with low organic matter contents. It was established that this level of concentration of physiochemical parameters results in the damage of polluted soil, thus making it to be unsuitable for agricultural growth of crops. This has resulted in the inhibition of fruiting, flowering and general reduction in agricultural yields and also affected the production of the wild oil palm tree which flourishes in the environment.

# REFERENCES

- Abam, T. K. S. (2001). Regional hydrological research perspectives in the Niger Delta. Hydrological Science,46,13-25.
- Al-Sayegh, Y.A., Sanket J., Saif, A.,
  Abdulkadir, E. and Ali, A. (2016).
  Bioremediation of Heavy Crude Oil Contamination. *The OpenBiotechnology Journal* 10(Suppl-2, M3):301-311
- Boonchan, S., Britz, M. L. and Stanley, G.
  A. (2000). Degradation and Mineralization of High Molecular Weight Polycyclic Aromatic
  Hydrocarbons by Defined Fungi Bacteria Cocultures. Applied
  Environmental Microbiol, 66 (3), 1007 – 1019.
- Brumner, J. M. and Mulvaney, C. S. (1982). Total Nitrogen Determination in; Methods of Monograph. No. 9, 2<sup>nd</sup> Edition, Pp 199 – 224.
- Ekperusi, O.A. and Aigbodion, F.I. (2015).Bioremediation of petroleum hydrocarbons from crude oilcontaminated soil with the earthworm: Hyperiodrilus africanus. *Biotechnology* 5: 957-965.
- Halanych, K.M., Ainsworth C.H., Cordes E.E., Dodge R.E., Huettel M.,

Mendelssohn I.A., Murawski S.A., Paris-Limouzy C.B., Schwing P.T., Shaw, R. F. and Sutton, T, (2021). Effects of Petroleum by Products and Dispersants on Ecosystems. Oceanograpy, 34 (1); 152 – 63.

- Jing, J., Tan, J., Hu, H. Sun, J. and Jing, P. (2016).Rheological and Emulsification Behavior of Xinjiang Heavy Oil and Model Oils. *Open Fuels and Energy Science Journal* 9: 1-10
- Kori-Siakpere, O. (1998). Petroleum induced attention in the African catfish (*Claries gariepinus*), Nig. J. Sci. Environ. 49:55-56.
- Olens, S. R; Cole, C. V; Watanabe, F. S. and Dean, L. A. (1954). Estimation of available Phosphorus in Soil by Extraction with Sodium Bicarbonate. Department Circular, U. S. Department of Agriculture, 939, P19.
- Plohl, K., Leskovsek, H. and Bricelj, M. (2002). Biological degradation of motor oil in water. *Acta Chim. Slov*. 49:279-289.
- Shaw, and Sutton, T. (2021). Effects of petroleum by-products and dispersants on ecosystems. Oceanography 34(1):152–163.
- Stout, S.A., and Wang Z. (2018). Oil Spill Environmental Forensics Case Studies. Butterworth-Heinemann, Elsevier, Oxford, UK, 860 pp,
- Urhobo Today (2019). Delta: 10 Burnt To Death, Scores Injured As Illegal Refinery Explodes In Isoko Community.https://urhobotoday.com

/delta-10- burnt-to-death-scoresinjured-as-illegal-refinery-explodesin-isokocommunity/