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Research Article

Assessment of the Impact of Artisanal Refinery on Soil Quality and Microbial Population at Obi-Ayagha Community, in the Niger Delta, Nigeria

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ABSTRACT

The impact of artisanal refinery on soil quality and microbial population of the soil at Obi-Ayagha Community, Delta State, Nigeria was studied. The model contamination rating Map of Obi-Ayagha Community indicated a total land mass of study area of 16,755.16Sq meters. Five (5) soil sampling points were selected within the abandoned Artisanal Refinery site using random sampling techniques. Uncontaminated soil served as control. Standard sampling and analytical analyses were carried out using standard methods of ASTM, APHA and API. Results of nitrate concentrations varied between 2.28 and 11.26mg/kg while phosphate concentration ranged from 3.02 - 17.36mg/kg. These values are below the recommended 10mg/kg for fertile soils. The pH values ranged from 3.80 – 5.10 (acidic) while Total Organic Carbon concentrations ranged from 0.37 – 2.96%. Total petroleum hydrocarbon concentration ranged from 1.28mg/kg to 152.58mg/kg and most values obtained were below the Nigeria Upstream Petroleum Regulatory Commission (NUPRC) target (50mg/kg) and intervention limit (5000mg/kg). However sampling point 1 was above NUPRC target value. Heterotrophic bacterial counts of the soils ranged from 1.15 x 10^5 CFU/g to 2.58 x 10^5 CFU/g, while fungal counts ranged from 1.00 x 10^4 CFU/g to 2.08 x 10^4 CFU/g. Control soil recorded higher counts. Heavy metals analyzed were in compliance with available NUPRC Target and Intervention limits, except Iron which was relatively higher ranging from 400mg/kg to 6645mg/kg. Most parameters analysed were below available regulatory limits which could be attributed to the prolonged abandonment of the artisanal refinery activities and natural attenuation that restored the contaminated site to some extent. However, the studied site would require remediation treatments to improve its nutrient status as to support revegetation which currently is scanty at the contaminated site.

Keywords: Artisanal refinery, crude oil, hydrocarbon contamination, soil quality, microbial density.

Introduction

Nigeria is the world's sixth largest exporter of crude oil and the Niger Delta is a particular hub for crude oil activities while also being one of the world's most bio-diverse ecosystems (Olumide and Ayodele, 2017). Exportation of petroleum is the mainstay for the nation's economy. The downstream sector of the Petroleum industry of Nigeria is key in the economy of the country, which is equipped with four refineries having a combined refining capacity of 445,000 (bpd) barrels per day (Ogbon *et al.*, 2018). Oil refineries are typically huge, expensive facilities where crude oil is converted to products like petrol, diesel.

However, Nigeria lacks effective domestic refining capacity and so relies on importation of refined products to meet local needs (Nkaginieme, 2005).

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There are over eight (8) major and more than three hundred and fifty (350) Independent Petroleum Product Marketers, all active in the marketing business that distribute and retail refined products in Nigeria (Onigbinde, 2014).

Presently, the country is faced with insufficient supply of useable energy due to poor development and management of the energy sector (Ohimain, 2012). In the year 2017, the consumption of refined products in Nigeria was put at about 24 billion litres per anuum and products utilized include: Dual Purpose Kerosene (DPK), Automotive Gas Oil (AGO), Premium Motor Spirit (PMS) and Aviation Turbine Kerosene (ATK). To the detriment of the nation's earnings, most of these products are imported from other sources and imports account for more than 80% of the products supply in the country, bringing about a huge potential for domestic refining (Olumide and Ayodele, 2017; Nathaniel, 2018). The effect of this shortage is severely felt in the country, especially in the Niger Delta region. Consequently, in quest to bridge the gap between production and consumption of refined petroleum products, some Nigerians have discovered an indigenous way of refining petroleum products using local technology (Social Action 2014; Akeredolu and Sonibare, 2015; Bebeteidoh *et al*., 2020).

Artisanal oil refining means small-scale crude oil processing or subsistent distillation of petroleum that is often outside the boundaries of the state law. This technology employs simple and local distillery process to achieve refined products by subjecting the distilleries with crude oil content to heat from open fire. The refining process yields Petrol, Kerosene and diesel. Materials deployed for the operation are indigenously constructed and acquired, including: crude oil, drilling machines, drums, Cotonou boats, pipes, fire woods, pumping machines, rubber hose, dried wood, storage facilities, among others (Onakpohor *et al*., 2019).

The operation is conveniently and effectively managed by a few personnel. It requires a low capital out lay to setup, depending on the choice of processing capacity adopted or entrepreneurial capability. The refinery is simple, efficient and cheap to set up. Its relatively low cost makes it an easy-going business for local private investors (Asuru and Amadi, 2016). This is the situation of the Niger Delta region where over 20,000 artisanal refineries have been setup by private investors who take advantage of the cheap labour and availability of raw materials in the area (Onakpohor *et al.,* 2019).

Artisanal oil refining is essentially siphoning off crude oil from pipelines and redirecting it into tanks, generally in bushes and forests, where the crude oil is boiled at high temperatures to convert it into different petroleum products. Over the last year alone, according to government estimates, more than $3 billion of crude oil has been stolen, also impacting funding for other needs like education and health care (Maclean and Steve, 2019).

The Niger Delta is home to the world's third largest mangrove forest, and a huge variety of plants and animal species live there (Bassey and Izah, 2017; Izah *et al.,* 2023). For decades, communities close to artisanal refineries have been severely affected by the business of crude oil, with people who rely on farms and fishing having lost their livelihoods, air and soil quality has been greatly affected as a result of pollution (Nwankwoala *et al.* 2017; Bebeteidoh *et al*., 2020). Artisanal oil refineries are also big consumers of limited energy resources and water, while also releasing harmful greenhouse gases into the atmosphere. The crude oil refining process also generates solid wastes that are difficult to clean and dispose of (Aiswaraya and William, 2017).

In fact, according to research published in 2020, the Niger Delta region is "one of the most environmentally impacted regions of the world caused by Artisanal oil refineries" — largely as a result of poor regulations, along with the practice of other illegal oil refineries **(**Bebeteidoh *et al*., 2020). The activities of the Artisanal oil refineries negatively affect soil quality. The set up at these illegal refineries is much less sophisticated and there are far fewer measures to protect people and the environment — making the process extremely dangerous and often sparking huge explosions, as well as causing land, water, and air pollution that impact the health, well-being and livelihoods of the people of the host community and in surrounding areas (Dean *et al.*, 2019; HEI, 2019). Plates of Artisanal Refining activities are shown in Plate 1 and Plate 2 below.

Artisanal Refining activities significantly impact nature, air, soil, plant regeneration, loss of biodiversity, natural

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wildlife habitats, disruption of water cycles, and loss of medicinal plant species (Raimi *et al*., 2022; Ogwu *et al*., 2022, Inatimi *et al*., 2022). Legally or illegally, oil refining still remains a very dangerous process because the extracts are highly flammable. Within minutes of a trigger, the fire can cause unprecedented damage to the air, soil, environment, properties, and loss of human life (Onakpohor *et al*., 2019; Ikezam *et al.*, 2021a).

The occurrences of artisanal refineries in the Niger Delta area are major environmental challenge that has led to adverse effects on the biotic and abiotic components of the Niger Delta environment (Raimi *et al*., 2022). Reports on the impact of artisanal refinery on microbial population and soil quality in Delta State are scanty which has necessitated this present study.

This study was therefore carried out to assess the impact of artisanal refinery on microbial population and soil quality at Obi-Ayagha Community, Obi-Ayagha in Delta State of Nigeria.

Plate 1: Artisanal Refinery Storage Drums of Crude Oil in the Niger Delta Areas (The Guardian, 2021)

Plate 2: A typical Artisanal Refinery site in the Niger Delta Areas (The Guardian, 2021)

Materials and Methods

Description of the Study Area

The study Area is at Obi – Ayagha community in Ughelli South Local Government Area of Delta State in Sounthern Nigeria. The area is made up of six (6) Urhobo kingdoms namely: Eghwu, Effurun Otor, Ughievwen, Arhavwarien, Okparabe and Olomu. Otu Jeremi is the headquarters of Ughelli South LGA. It is the fourth most populated local government in Delta State. Surface water (River body) within the study area (Obi – Ayagha) is fresh water environment while the type forest found within are mainly tropical rain forest and the trees around are mostly economic trees.

The major occupations of the inhabitants are farming, and civil servants jobs. The human population size is about 213,576 (Census 2006) and an area of 786 square kilometres (303 sq mi). The study location is an abandoned artisanal refinery site at Obi-Ayagha, with scanty and poor vegetation shown in Plate 3 below. The model contamination rating Map of Obi-Ayagha Community indicated a total land mass of study area of 16,755.16Sq meters.

Sampling and Sampling Techniques

The study methodology, field sampling techniques are consistent with established standard methodologies and also with Nigerian Upstream Petroleum Regulatory Commission (NUPRC) Environmental Guidelines and Standards for Petroleum Industries in Nigeria (EGASPIN, 2018) procedural Guideline. Top, middle and bottom soils were sampled from soil depths of 0-15cm, 15-30cm and 30cm-60cm respectively.

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Field sampling was carried out in accordance with procedures prescribed in the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN, 2018), Appendix II-4. Sample handling and lab methods were also in accordance with NUPRC (2018) and the other international reference methods such as those issued by the American Association for Testing and Materials (ASTM, 1999) and the American Public Health Association (21st Edition, 2017).

Plate 3: Abandoned artisanal refinery site at Obi-Ayagha, with scanty and poor vegetation

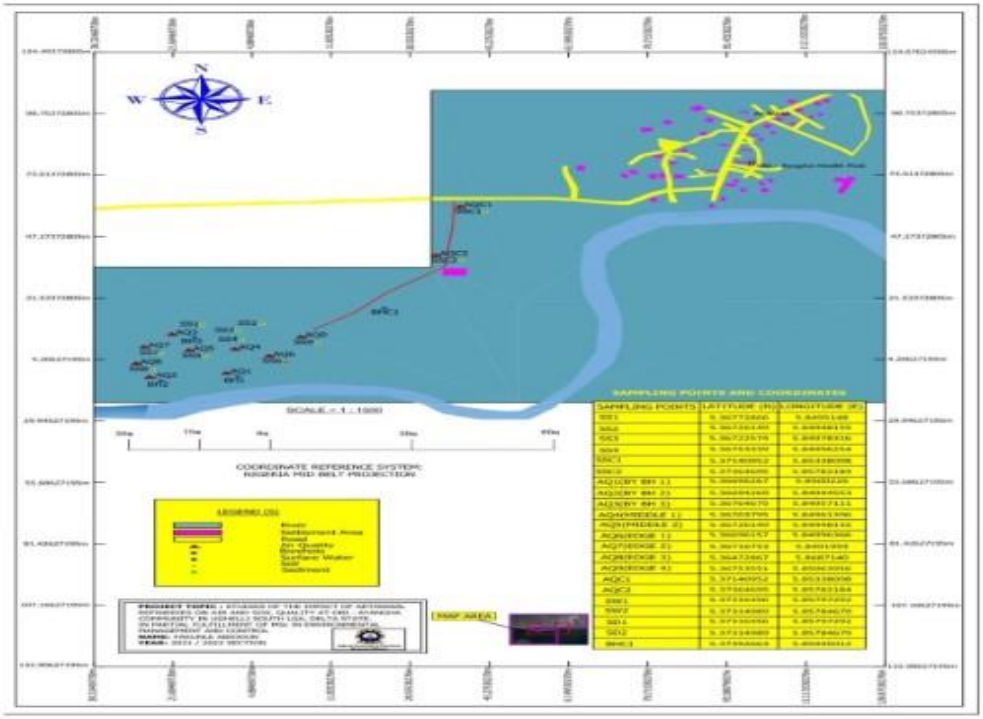

Fig 1: Map of the Study Artisanal Refinery site at Obi-Ayagha Community, Delta State

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Collection of Soil samples

Soil samples were collected at pre-determined sampling points on the map to ensure adequate spread (Table 1). Soil samples were taken with a hand-held soil auger at the depths of 0-15cm, 15-30cm and 30cm-60cm for top, middle and bottom respectively. Samples were kept in polythene bags en route the laboratory. Soil samples were also collected in sterile containers for microbiological studies. All samples were properly tagged with stickers to prevent sample mis-identification. Three (3) soil samples each were collected from the top, middle and bottom as well as from the control point.

Table 1: Soil sampling points with Coordinates

Sampling point	Latitude(N)	Longitude (E)
SS1	5.36772866	5.8495148
SS2	5.36726149	5.84948155
SS3	5.36722574	5.84978316
SS4	5.36753339	5.84996254
SSC (Control)	5.37140952	5.85338098

Laboratory analysis of physicochemical parameters

Determination of Soil pH

The pH of the samples was measured potentio-metrically in a 1:2 (sample – water) ratio suspension. About 25g of each sample was weighed out, air-dried and sieved with a 2mm mesh. The sized sample was transferred into a 100 ml flask and 50 ml of distilled water added and shaken for one hour. The pH meter was calibrated using the pH buffer (KCl), after which the measure of pH of the suspension was taken.

Determination of Electrical Conductivity (EC)

EC was measured in 1:2 (sample-water) ratio suspensions with the help of conductivity meter. The EC meter was calibrated using standard KCl solution and electrical conductivity of the suspensions was determined.

Determination of Nitrate in Soil Using Brucine Method

One gram (1g) of air-dried soil sample (passed a 2mm sieve) was weighed into a 15ml centrifuge tube and 5ml of the extracting solution (Na-acetate and Acetic acid) was added. It was shaken for 1 minute on a mechanical shaker and the suspension was centrifuged at 2,000rpm for 15 minutes, then the solution was filtered and make up with distilled water to 10ml. A number of reaction tubes were set up in a wire rack containing 10ml of sample, blank. Standard solution and were properly spaced. The track was set in a cool water bath; 2ml NaCl was added, mixed thoroughly by swirling and then 10ml of H_2SO_4 solution was also added and swirled again to mix thoroughly and was allowed to cool. The dry tubes were cleaned with tissue paper to remove any turbid or colour observed on it.

The sample blank value was read against the reagent blank at 410nm in the spectrophotometer. The rack tubes were replaced and mix thoroughly and were placed in well – stirred boiling water bath that maintain a temperature of not less than 95ºC. Let them remain there for 20minutes. The samples were removed and immersed in a cold water bath, when thermal equilibrium attained i.e when the temperature of the tubes and the cold water about room temperature, the tubes were removed and dried with tissue paper. Reading was taken with the standard and samples against the reagent blank at 410nm in the spectrophotometer.

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Determination of Total Petroleum Hydrocarbon (TPH) (ASTM D5756-97)

Ten gram (10g) of soil samples were carefully weighed into an organic free amber glass container, 5g of anhydrous sodium sulphate was added to dry the weighed sampled. 10ml of an extract (a mixture of n – Hexane, dichloromethane and Acetone in the ratio of 2:1:1) was added, mechanical shaker were then used to mix the mixture for about 30 minutes. Sonicator was used to extract the sample, while the extract was the extract was then filtered. Final volume of the extract was taken and the extract was stored in a dried organic free and chromic acid pre – clean vial. A sample of the extract was withdrawn with an automated gas-tight syringe and analyzed by direct injection into the GC-FID preset at specific condition. Analysis was run and data quantified at the end of the analysis as follows:

TPH concentration (mg/kg) of wet sample (R)

$$= \frac{Total\ Conc.\ \left(\frac{mg}{l}\right) \times Volume\ of\ the\ extract \times DF}{Weight\ of\ the\ Wet\ sample\ (kg)}$$

Actual TPH (mg/kg) = R × CF

Where DF: Dilution factor
CF: Calibration Graph factor
The class name or texture of the soil was determined from the textural triangle.

Determination of Organic Matter Content

The Walkley-Black method was used to determine the organic matter content of the samples. In this the milled soil samples were passed through 0.5mm sieve. One (1) gram of sample was transferred into a 250ml Erlenmeyer flask in duplicate. Ten (10) ml of 1M K2Cr2O7 solution was accurately added to the sample in each flask and swirled gently to disperse the soil. Thereafter, 20 ml of conc. H_2SO4 was added rapidly and immediately swirled gently until the soil and reagents were mixed, and vigorously swirled for one additional minute. The flask was allowed to stand for 30 minutes. One hundred (100) ml of distilled water was added and allowed to stand for 30 minutes. Three to four (3-4) drops of an indicator, diphenylamine, was added to the solution and 0.5N ferrous sulphate solution was titrated. A greenish cast which changes to dark green showed an approach to four (3-4) drops of an indicator, diphenylamine, was added to the solution and 0.5N ferrous sulphate solution was titrated. A greenish cast which changes to dark green showed an approach to the end point. Continuous addition of ferrous sulphate drop by drop changes the solution colour from blue to red. The blank titration was done in the same manner but without sample. Percentage Organic matter was derived from the equation thus:

$$\% \text{ Organic Carbon} = \frac{(Meq\ FeSO_4\ blank - Meq\ FeSO_4\ Sample) \times 0.003F \times 100}{weight\ of\ air\text{-}dry\ soil}$$

Where correction factor, F = 1.33
Meq = Normality of solution × ml of solution used.
% Organic Matter in soil = % Organic Carbon × 1.729.
Where, % organic matter in soil = % organic C x 1.729;
N= Normality of ferrous sulphate solution; V1= ml ferrous ammonium sulphate required for the blank; V2= ml ferrous ammonium sulphate required for the sample, W = weight of sample in gram, f = correction.

Determination of Total Nitrogen Content

25ml of digested soil sample was taken and made up to 50ml with distilled water, 5ml of 12N of Potassium Hydroxide was added. The solution was filtered, 25ml of the filtrate was taken, 1ml of 10% Sodium Tartrate was added and 5ml of Nessler's reagent added. It was then allowed to stand for 15 minutes for colour change. It was read using Spectrophotometer @ Absorbance of 460nm.

NOTE: Blank
1. 25ml of distilled was taken
2. 1ml of 10% Sodium Tartrate was added
3. 5ml of Nessler's reagent was added

Calculation;

$$\text{Total Nitrogen, \%} = \frac{Abs \times cf \times 2 \times 50}{10000}$$

NB: Potassium hydroxide (12N) = Dissolve 160g of KOH pellets in 250ml distilled water in a volumetric flask.
10% Sodium Tartrate = Dissolve 10g of NaOH salt in 100ml distilled water in a standard flask

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Microbiological Analyses of Soil Samples

Procedures for Enumeration of Total Heterotrophic Bacteria (THB) and Total Heterotrophic Fungi (THF) using pour plate method (APHA 9222A)

One (1g) of each soil sample was weighed and diluted with 9ml of sterilized distilled water in sterilized McCartney bottles/test tubes to make serial dilutions of 10^{-1} to 10^{-5}. 1ml aliquot from the serial dilutions was put into a sterile Petri dish. About 20ml of already sterilized nutrient agar for bacteria and potato dextrose agar for fungi, was poured into the Petri dish with the inoculum, swirled, allowed to cool and solidified. The bacteria plates were incubated at 28 ± 2°C for 24 hours in inverted position, while the plates for fungi were incubated for 3-4days. Thereafter, the colonies which developed were counted using colony counter.

Test Procedure for Enumeration of Hydrocarbon Utilizing Bacteria (HUB) and Hydrocarbon Utilizing fungi (HUF) (APHA 9222A)

Bushnell and Hass (1941) Mineral Salt Agar (MSA) with the composition, dipotassium hyrdrogen phosphate (KH_2PO_4) (1g), potassium dihydrogen phosphate (K_2HPO_4) (1g), Ammonium nitrate (NH_4NO_3(1g), Magnessium sulphate heptahydrate ($MgSO_4$) (0.2g), Ferrous sulphate heptahydrate ($FeSO_4.7H_20$ (0.05g), Calcium chloride (CaCl (0.02g), agar agar (15g) all in one litre of distilled water, was used for the enumeration.

The vapour phase method of Okerentugba *et al*. (2016) was adopted for the isolation of HUB and HUF. After sterilization of the prepared medium at 121°C for 15mins, it was allowed to cool and solidify. 1ml aliquot was taken from the serially diluted soil samples and poured on the already prepared MSA plates with antifungal (fungusol) added to suppress fungi growth and spread with a flame sterilized bent glass rod. A sterile filter paper (whatman No.1) was saturated with filter sterilized crude oil and placed inside the cover of the petri dish, to serve as a sole carbon source. The petri dish was closed, inverted and incubated at a temperature of 28 ± 2°C for 4-7 days in an inverted position. Thereafter, the colonies were counted on the plate, using colony counter.

Colony forming units (CFU) per milliliter (ml) was calculated using the formula:

$$\text{CFU/ml} = \frac{Number\ of\ colonies \times \frac{1}{dilution\ factor}}{volume\ of\ sample\ used\ (ml)}$$

Digestion of Heavy Metals in Soil Using Tripple Acid Wet Oxidation Method

Soil sample which had been dried at room temperature was sieved with 2mm mesh sieve. 2.0g of the soil was weighed into a 300cm^3 conical flask; 1ml of conc HCl, 3ml conc HNO_3 and 1ml conc HF were added under a fume hood. The mixture was continuously heated until dense white fumes appeared. It was allowed to cool, and then 40-50 ml distilled water added. The solution was made up to mark with distilled water into 100ml pyrex volumetric flask then filtered completely with Whatman No. 42 filter paper. The soil extracts and the standard solutions were aspirated into the air-acetylene flame of Varian 220 (*fast sequential*) Atomic Absorption Spectrometer and the metals were analysed along with specific standards and computed.

Results

The results of physicochemical properties of hydrocarbon impacted soils are as shown in Table 2 below. The pH of the soils in the sampled soils and control were acidic and ranged from 3.80 (SS3, 0-15cm) to 5.10 (SS1, 0-15cm), while the control ranged from 4.00 (0-15cm) to 5.30 (30-60cm) (Table 2), though pH had no DPR regulatory limit for both intervention value and target values. Total Organic Carbon (TOC) concentrations within the project site were generally low in both the project site and control areas. The soil TOC values ranged from 0.37% (SS 2, 30-60cm) to 2.96% (SS 1, 0-15cm) (Table 2). Available phosphorus (Phosphate ion) was also generally low in the soil samples. Concentrations ranged from 3.02mg/kg (SS 3, 15 -30cm) to 17.36mg/kg (SS 4, 0 -15cm) for the period studied. The Ammonia concentrations of the entire soil were low except the sub-bottom soil of SS1 (15-30cm) which had the highest concentration of 43.10mg/kg.

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The soil values for Ammonia ranged from 1.39mg/kg TPH concentrations from all the points sampled ranged from 1.28mg/kg (SS 3, 30 – 60cm) to 152.58mg/kg (SS 1, 0 - 15cm)(Table 2). All the points sampled were below the NURPC target (50mg/kg) and intervention values (5000mg/kg), except point 1 which exceeded the stipulated target limit (Fig. 2). PAHs were not detected, and were below the measuring instrument detection limits. NUPRC target value for PAH is 1.0mg/kg while the intervention value is 40mg/kg.

All the heavy metals analysed were below the DPR target and intervention values. Although Iron in contaminated soils does not have available DPR limits, but its concentration was relatively much higher than values obtained for other metals.

(SS 3, 30 – 60cm) to 43.10mg/kg (SS 1, 15 – 30cm). Values obtained ranged from 400mg/kg (SS4, 30-60cm) to 6390mg/kg (SS2, 15-30cm) Table 3. The results of the microbial counts in the soil samples are as shown in Figure 3. The Heterotrophic bacteria and fungi counts ranged between 1.15 x 10^5CFU/g (SS1, 30-60cm) and 2.58 x 10^5CFU/g (SS4, 0-15cm) and from 1.00 x 10^5CFU/g (SS1, 0-15cm) to 2.08 x 10^5CFU/g(SS4, 0-15cm) respectively. The control point had heterotrophic bacteria counts that ranged from 3.00(30-60cm) - 3.15 x 10^5CFU/g (0-15cm), while for fungi the population, the counts ranged from 1.55 (0-15cm) - 2.66x 10^5CFU/g (15-30cm). The HUB counts ranged from 1.00 x10^3CFU/g(SS1, 30-60cm) - 1.93 x 10^3 (SS4, 30-60cm), the HUF had values that were between 1.00 x 10^3 CFU/g (SS1, 30-60cm) and 1.17 x 10^3 CFU/g (SS4, 0-15cm).

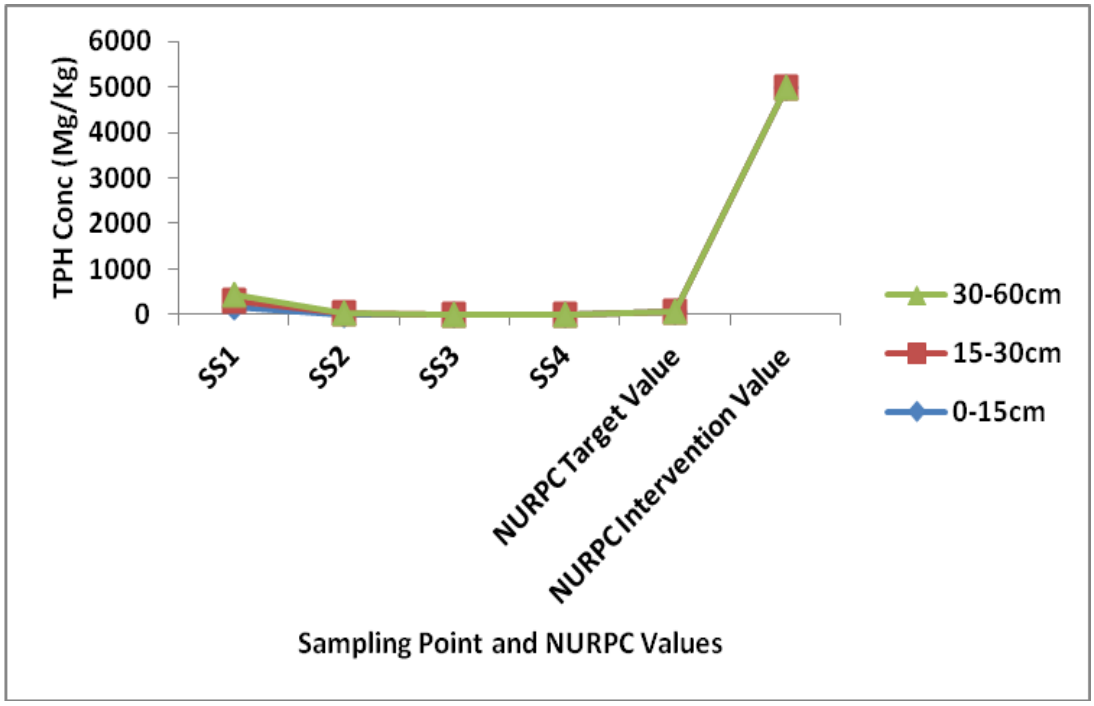

Fig. 2: Total petroleum hydrocarbon (TPH) concentrations of contaminated soils against NURPC Target and Intervention limits

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Table 2: Results of analysis of soil physicochemical properties of hydrocarbon impacted soils in abandoned artisanal refinery site at Obi-Ayagha community

Parameter	Sampling Locations															DPR Target Value	DPR Intervention Value
	SS1			SS2			SS3			SS4			Control				
Depth (cm)	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**		
pH	5.10	4.70	4.50	4.00	4.00	4.70	3.80	3.90	4.00	3.90	4.10	4.00	4.00	4.90	5.30	NA	NA
Temperature (^oC)	29.0	29.0	29.0	29.0	29.0	29.0	29.0	29.0	29.0	29.0	29.0	29.0	30.0	29.0	29.0	NA	NA
Redox Potential	240.00	234.00	287.00	300.00	294.00	252.00	310.00	306.00	304.00	309.00	310.00	311.00	330.00	302.00	283.00	NA	NA
Ammonia, (mg/kg)	2.17	43.10	35.26	10.16	12.57	8.80	4.61	11.21	1.39	11.42	12.08	10.40	0.64	3.93	15.04	NA	NA
Sulphate, (mg/kg)	20.63	25.00	17.50	29.38	18.75	10.00	7.50	9.37	23.13	12.50	18.13	21.88	18.75	9.38	38.13	NA	NA
Nitrate, (mg/kg)	2.81	7.21	4.40	5.20	8.44	2.28	11.26	5.10	5.98	7.74	5.98	5.80	5.72	0.40	13.90	NA	NA
Phosphate, (mg/kg)	6.81	14.18	7.50	5.66	14.53	11.83	8.92	3.02	3.90	17.36	8.89	10.73	4.91	5.29	8.87	NA	NA
Total organic carbon (%)	2.96	2.13	2.00	2.19	0.59	0.37	0.72	0.44	0.42	0.79	0.79	0.46	0.30	0.26	0.72	NA	NA
TPH (mg/kg)	152.58	133.95	115.18	8.46	6.80	4.23	2.34	1.54	1.28	5.16	3.42	2.06	0.42	0.28	0.11	50	5000
PAHs, (mg/kg)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	1.0	40

Legend: SS1: Sampling point 1 SS2: Sampling point 2 SS3: Sampling point 3 SS4: Sampling point 4

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Table 3: Heavy metal concentrations in Hydrocarbon contaminated soils from abandoned artisanal refinery site

Parameter	Sampling Locations															DPR Target Value	DPR Intervention Value
	SS1			SS2			SS3			SS4			Control				
Depth (cm)	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**	**0-15**	**15-30**	**30-60**		
Iron (mg/kg)	5235	3213	6142	4045	6390	4300	4245	895	6645	930	830	400	5200	1400	1350	NA	NA
Zinc (mg/kg)	12.80	3.10	9.60	4.40	7.30	17.60	6.60	3.80	5.80	8.80	5.50	8.30	11.50	5.10	12.10	140	720
Chromium (mg/kg)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	2.60	0.80	3.80	5.10	0.60	4.50	10.90	<0.001	0.40	100	380
Lead (mg/kg)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	85	530
Nickel (mg/kg)	12.20	14.00	8.50	7.10	6.70	3.80	0.40	<0.001	11.00	8.30	2.50	5.90	8.30	12.80	3.70	35	210

Legend: SS1: Sampling point 1 SS2: Sampling point 2 SS3: Sampling point 3 SS4: Sampling point

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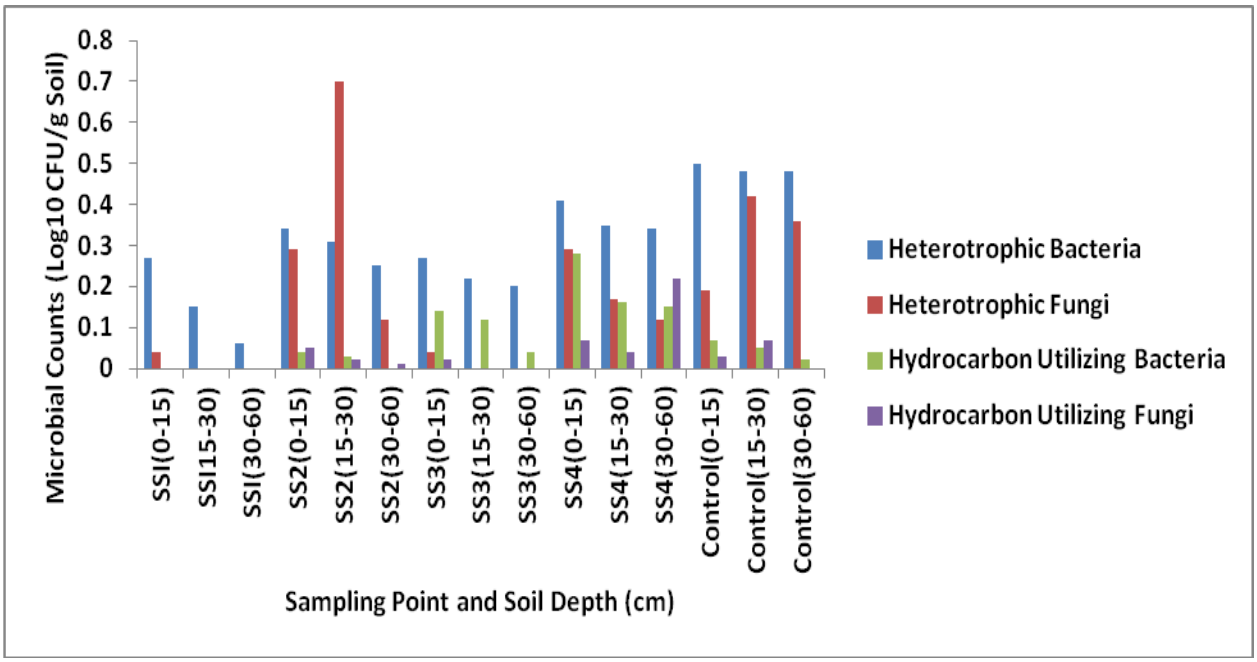

Fig. 3: Heterotrophic and Hydrocarbon utilizing bacteria and fungi counts in contaminated soils from abandoned artisanal refinery site

Discussion

Soil pH value is a measure of the free hydrogen ion (H^+) concentration of soil solution. The value of the free H^+ concentration in a soil influences the availability of nutrient elements and biochemical reactions in the soil. In strongly acidic soils, basic cation uptakes by plants roots are inhibited.

Beneficial soil – borne micro-organisms are also affected by soil reaction. The soil pH values were acidic (Table 2) and ranged from 3.80 (SS 3 at 0 -15cm) – 5.10 (SS 1 at 0-15cm). Low pH can results in poor plant growth (Wright *et al*., 2012).

The pH of 4.80 is set as the lower limit for optimum growth of plants, and conversely the pH of 9.5 is regarded as the extreme upper limit of alkalinity at which plants can still grow (Wright *et al*., 2012).

Soil organic carbon consists of dead, decayed, and decomposing animals and plants remains. The organic carbon of soil is an important element in maintaining its physical conditions and significantly affects its productivity (Bot and Benites, 2005). Low total organic carbon in soils can be attributed to the following (i) low amount of plant residue (ii) high rate of carbon mineralization associated with high microbial activities (iii) high soils moisture content and redox condition of the soil and (iv) combination of these factors. The TOC values from the project site were generally low with values ranging from 0.37 (SS 2 at 30 -60cm) – 2.96% (SS 1 at 0 – 15cm) and mean value of 1.16±0.9%, the control mean had 0.43±0.25 % (Table 2). Organic carbon content of soils is a source of nutrients such as oxidized forms of nitrogen, phosphorus and sulphur. It also serves as source of nutrients for soil microorganisms. Organic carbon binds and stabilizes the soil aggregates which results in greater resistance to erosion as mass movement is less likely when soils are able to retain structural strength under greater moisture levels (Bot and Benite, 2005).

Most soil sources of sulphur are in the organic matter (proteins, nucleic acids and lipids) and are concentrated in the surface soil. Elemental Sulphur is not available to crops as they must be converted to the sulphate (SO4-) form to become available. This conversion is performed by soil microbes (sulphur oxidizing bacteria) and therefore requires soil conditions that are warm, moist and well drained for the process to proceed rapidly. The Sulphur form of S is an anion (negative charge), and therefore is leachable. Sulphate (SO4-) is also an essential macro element because of the relatively large quantity required by plants.

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Plants take up sulphate in the solution form. The sulphate values of the project area range from 7.50 (SS 3 at 0 – 15cm) –29.38mg/kg (SS 2 at 0 – 15cm), while the control mean had 22.09±14.66mg/kg.

Nitrogen is one of the macro nutrients in soils that have very significant effect on plants growth. Plant growth is limited by Nitrogen more than by any other plant nutrient element. Considering all the essential nutrients, nitrogen is required by plants in the largest quantity and is most frequently the limiting factor in crop productivity. The forms of nitrogen available for plant uptake are ammonium and nitrate. Nitrate content of the soil varied from 2.28 (SS 2 at 30 – 60cm) – 11.26mg/kg (SS 3 at 0 -15cm) while the control mean had 6.67±6.80mg/kg for the period under review. Most of the points sampled and the control were below the recommended value of 10mg/kg for fertile soils (Bagshaw *et al*., 2010).

Phosphorus availability in soils is largely influenced by the amount of organic carbon and Iron (Fe) content. Phosphorus is fixed or absorbed to these matrices in soils. In the present scenario, the relatively low amount of Phosphorus is due to the high amount of iron (Fe) as found in the project areas especially the control soil samples. Phosphorus is not affected by solubility but by sorption – desorption processes in soil. The phosphorus concentrations were generally low in the soils sampled and ranged from 3.02 (SS 3 at 15 – 30cm) - 17.36mg/kg (SS 4 at 0 - 15cm) and the control mean of 6.36±2.18mg/kg respectively for the period under review. Most of the points sampled were below the recommended value of 10mg/kg for fertile soils (Bagshaw *et. al*., 2010). Low Phosphorus delays plant maturity and reduces yields; hence the low phosphorus recorded would have an effect on the soil fertility. The low nutrient content of the contaminated site could have resulted in the poor vegetation growth in the contaminated site (Plate 3).

Trace elements are chemical substances that are required in very small concentrations in soils for optimal plants growth. These elements can become hazardous to humans and animals if absorbed in the food chain even in small concentrations as they usually can become bio accumulated and biomagnified. Low levels of heavy metals occur naturally in most soils.

Iron concentration of the soils analysed, ranged from 400 (SS 4, 30 – 60cm) – 6645mg/kg (SS 3, 30 – 60cm) (Table 3). Although Iron has no regulatory limit but it was relatively much higher than all other metals analysed. The control samples also had high Iron values that ranged from 1350mg/kg (30-60cm) to 5200mg/kg (0-15cm). This indicates that Iron is high in the soils in the study area and not attributed to the artisanal refinery contaminants. All other metals analysed were below the DPR target and intervention values (Table 3). Lead was not detected in all the soil samples analysed (Table 3). Low concentrations of heavy metals occur naturally in most soils.

The concentration of heavy metals can be increased to become potential pollutants if heavy metals – containing waste products from industrial or domestic activities are introduced into the environment.

The control heterotrophic counts were higher than both the heterotrophic bacteria and fungi population in the contaminated sites sampled. This could be attributed to the hydrocarbon contamination from the artisanal refinery activities, which has affected the soil's nutrient concentrations, which were observed to be low in all the soils sampled (Fig 3). The HUB and HUF counts were relatively low for effective natural attenuation of hydrocarbon polluted sites by microbes. This could be due to the quantity and components of the crude oil spilled. The high concentration of TPH after one year of spill could have affected the metabolic and physiological functions of the microbes and by extension the biodegradative capabilities (Culbertson *et al*., 2008). This could also have accounted for the poor bioremediation of the environment by natural attenuation.

Total Petroleum Hydrocarbon determines the amount of petroleum hydrocarbon residues left within the areas of concentration / interest and its determined using Gas Chromatography (GC). TPH concentrations were much lower than the NUPRC intervention value of 5000mg/kg. But sampling point 1 had values that were above the NURPC stipulated target value of 50mg/kg (Fig. 2). Other concentration of Organics like PAH were not detected, hence were below instrument detection limits. NUPRC target value for PAH is 1.0mg/kg while the intervention value is 40mg/kg. High TPH compounds have negative effect on soil respiration rate and microbial biomass (Makowsi and Finki, 2018).

It can be concluded that following the analysis of soil quality of the abandoned artisanal refinery site all the parameters analysed were within NURPC regulatory limits except TPH concentrations in sampling point 1

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which were above NUPRC Target Value of 50mg/kg. These could be attributed to the following reasons: Natural attenuation must have taken place given the prolonged period (about 10 years) of abandonment of artisanal activities at the site; residual crude oil might have percolated beneath the surface, and remediation is required on the abandoned artisanal refinery polluted site, especially the subsurface soils, since the crude oil residue might have percolated beneath the surface. Also to restore the nutritional status and microbial biodiversity and density, to make the site fertile to support vegetation this is currently very poor in diversity and density. Restoration of the site for farming would mean restoring the livelihood of the community, farming being their main stay.

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