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Impact of Artisanal Crude Oil Refinery on Physicochemical and Microbiological Properties of Soil and Water in Igia-Ama, Tombia Kingdom, Rivers State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

This study aimed to determine the impact of artisanal refinery operations on the physicochemical and microbiological properties of soil and water in Igia-Ama, Tombia Kingdom, Rivers State, Nigeria. Physicochemical parameters along with concentrations of heavy metals, polyaromatic hydrocarbons (PAHs), total petroleum hydrocarbon (TPH), benzene, toluene, ethylbenzene and xylene (BTEX), and polychlorinated biphenyls (PCB) were determined in soil and water samples using standard methods. Microbial populations were determined using standard plate count. Microbial isolates were identified based on their cultural, morphological and biochemical characteristics. Results show that concentrations of monitored physicochemical parameters differed significantly ($p<0.05$) between impacted sites and control as well as between dry and wet season. Heavy metals, PAHs, TPH, BTEX and PCB concentrations were higher in the impacted sites than in the control (significant, $p<0.05$), and also differed significantly between dry and wet season. Microbial counts varied between polluted samples and control as well as between dry and wet season, though not significantly different ($p>0.05$). Bacterial isolates in polluted soil samples were identified as *Enterobacter* sp., *Bacillus* sp., *Micrococcus* sp., *Staphylococcus* sp. and *Pseudomonas* sp. Bacteria in polluted water samples were identified as *Staphylococcus* sp. and *Escherichia coli*. Fungi in polluted soil samples were identified as *Aspergillus* sp., *Penicillium* sp.

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Fusarium sp., *Rhodotorula* sp., *Exophiala* sp. and *Crypotococcus* sp. While only *Penicillium* sp. was isolated in polluted water sample. Artisanal crude oil refinery operations significantly impacted the physicochemical properties of soil and water in the study area but not the microbiological properties. The levels of heavy metals, PAHs, TPH and BTEX in the soil and water suggest the need for remediation of the impacted environment.

Keywords: Artisanal refinery; physicochemical properties; microorganisms.

1. INTRODUCTION

The discovery and large-scale production of petroleum in Nigeria is an economic blessing and environmental woe. It is well known that crude oil extraction and refining in the Niger Delta plays a major role in impacting on flora and fauna for which the multinational companies have receive much of the blames [1]. The problem of environmental pollution in the Niger Delta is taking a new dimension with the entrant of artisanal crude oil refineries.

Nigeria a major producer of crude oil, still grapples with the problem of refining its crude, as it lacks domestic refining capacity to meet local need [2,3]. To bridge this gap, it relies on import. However, not all refined products in the Nigerian market are imported. In the Niger Delta where crude oil is produced, there exist an illegal sector stealing and refining crude into petrol, diesel and kerosene [4,5].

Artisanal crude oil refineries in the Niger Delta are makeshift setup for the separation of petroleum fractions based on the principle of local gin distillation, as commonly practiced in this region. Artisanal crude oil refinery is relatively cheap to set up, making it an easy venture to enter into, so long there is guarantee of crude supply [3,6]. Operators of artisanal refinery in the Niger Delta are driven by pecuniary motives, in clear disregard to the environmental and health impacts of their operations. As a consequence, their operations lead to the pollution of, air, water, vegetation and soil within the vicinity of their operations [7-9].

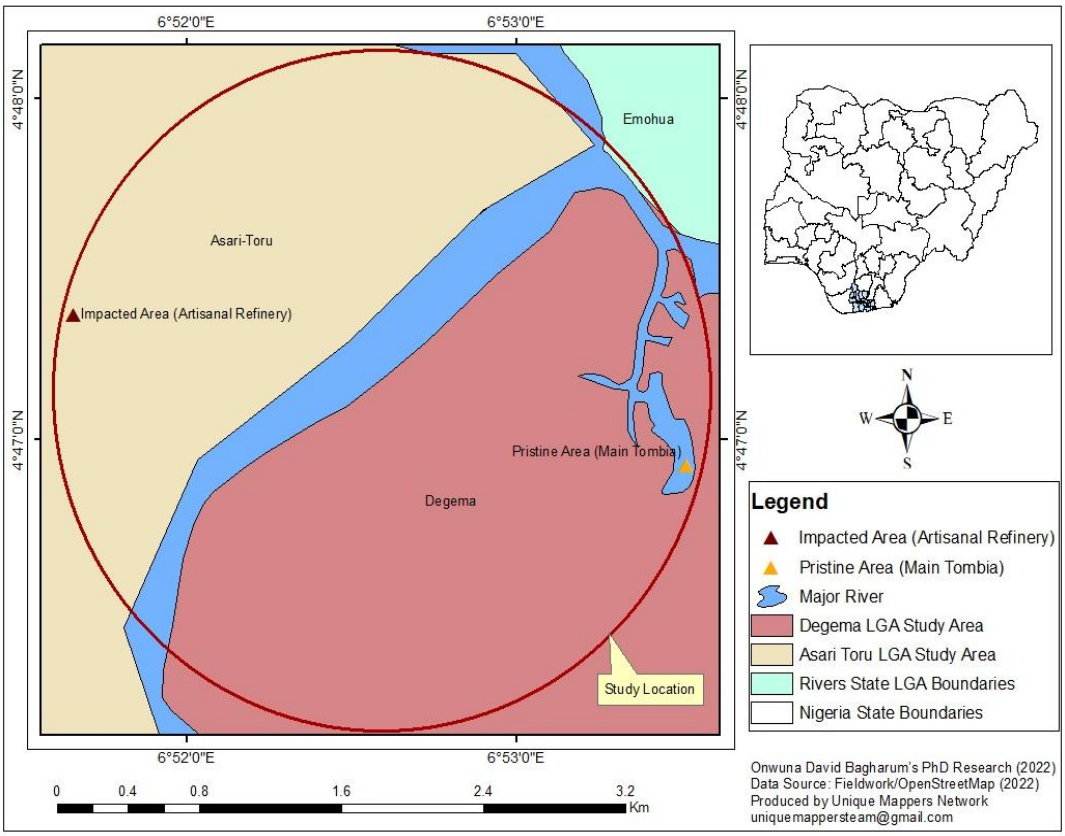
Artisanal refineries in the Niger Delta region of Nigeria have come to be associated with increase pollution of soil and water. The study carried out by Njoku et al. [10] revealed that artisanal refineries operations increased the concentrations of heavy metals and polycyclic aromatic hydrocarbon (PAH) in soil. Ikezam et al. [9] assessed the physicochemical parameters and heavy metals concentration across artisanal refining sites in the core Niger Delta Region and found that soil quality for artisanal refining sites fell below WHO permissible limits. Nwankwoala et al. [11] reported high concentrations of heavy metals in water bodies close to artisanal refineries, which made the water unsuitable for drinking. Also, the soil samples recorded high levels of hydrocarbon content. Lebari et al. [12] reported physicochemical alterations of interstitial water quality as a result of artisanal refining operations in South-Eastern Nigeria. Ugboma et al. [13] reported that artisanal crude oil refining impacted the growth dynamics of microorganisms in soil.

Within the last decade, several artisanal refineries have sprung up within the oil rich but developmentally abandoned Tombia Kingdom. This the locals see as a means of owing their God given resources. The activities of artisanal crude oil refiners in Tombia Kingdom is a source of environmental concern. The aim of this study is to determine the impact of artisanal refinery operations on the physicochemical and microbiological properties of soil and water in Igia-Ama, Tombia Kingdom, Rivers State, Nigeria.

2. MATERIALS AND METHODS

2.1 Study Area

The study was conducted in Igia-Ama, Tombia Kingdom, Rivers State, Nigeria. Tombia Kingdom is positioned in the Northern part of Rivers State, Nigeria, with geographical coordinates 4^0 53' 12.7'' North, 7^0 07' 30.6'' East. The people of Tombia Kingdom with the population of approximately 15,000, are situated in Degema Local Government Area of the State. Tombia people are a force to reckon with among the Kalabari communities which also include Bukuma, Buguma, Buguma, Bille, Abonemma, Harry's Town, Degema, and so on. All Kalabari communities are surrounded by water and Tombia Kingdom is not an exception. It has Iwofe, Ikpokiri, and Bukuma as it closest neighbours. The community can be accessed through its waterways by speedboats, canoes, and ships. There is presence of Nigeria Army at the jetties of the communities which help in the protection of lives and properties of the people of the oil rich region.



Map 1. Map of Tombia Kingdom showing sampling locations

2.2 Sample Collection

Water and soil samples were collected around artisanal crude oil refinery sites at Igia-Ama, Tombia Kingdom between January – March (dry season) and June–August (wet season). The control site was Tombia main town. Sampling points were geo-referenced. Three (3) sampling periods were considered for both dry and wet seasons. Samples were brought to the laboratory for analysis.

2.3 Physicochemical Analysis

Measurements of the physicochemical parameters followed methods described in APHA [14]. Parameters monitored in water were pH, Conductivity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), Turbidity, dissolved oxygen (DO), total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), Alkalinity, SO_4, NO_3, Cl^-, Ammonia, Total Nitrogen, Phosphate, total hydrocarbon concentration (THC) and Temperature. Parameter monitored in soil were pH, Conductivity, TOC, Nitrogen, PO_4, Cl^-, SO_4 and THC.

2.4 Heavy Metals, PAH, TPH and BTEX Analysis

Heavy metals were determined using APHA (3030 E) Atomic Absorption Spectrophotometry (AAS) AA500 PG method [14]. PAH, TPH and BTEX were determined using EPA 8015 [15] and EPA 8100 [16] methods using Gas Chromatography and Flame Ionization Detector (GC/FID).

2.5 Microbiological Analysis

2.5.1 Enumeration of heterotrophic bacteria

Aliquots of 0.1 ml of serially diluted water/soil sample were plated in duplicates on nutrients agar using spread plate techniques, the plates were incubated at 37^{o}C for 24 hours. After incubation colonies were counted to obtain colony forming units (CFU) per gram of the soil sample or CFU/ml for water sample. Discrete colonies were picked and sub-cultured.

2.5.2 Enumeration of fungi

Aliquots of 0.1ml of serially diluted water/soil sample were plated in duplicates on potato

dextrose agar with addition of 0.1 ml of lactic acid to inhibit bacterial growth. The inoculums were spread evenly with a sterile hockey stick. The seeded plates were incubated at room temperature for 48 hours or more.

2.5.3 Screening for hydrocarbon utilizing bacteria (HUB) and hydrocarbon utilizing fungi (HUF)

Vapour phase method was adopted to estimate the population of HUB and HUF using modified mineral salt agar ($MgSO_4$ 0.42 g, KCl0. 28 g, k_2HPO_4 1.25g, KH_2PO4 0.83 g, $NaNO_3$ 0.42 g, NaCl 10.0 g and agar 15.0 g). Aliquots of 0.1 ml of soil suspension were obtained from 10^{-3} and 10^{-4} dilution respectively and plated in duplicates. Sterile filter paper was saturated with sterile crude oil and placed in the lid of each Petri dish, kept in an inverted position, and the plates were incubated at 37^{o}C for 5-7 days. The mineral salt agar for the isolation of HUF was supplemented with lactic acid to inhibit bacteria growth. The crude oil served as sole source of carbon and energy for the growing culture. After incubation, the colonies were counted and the mean counts were recorded.

2.6 Identification of Isolates

Bacterial isolates were examined for morphology and colony characteristics, and microscopically examined by Gram staining and viewed under oil immersion objective (x100 magnification). Biochemical test such as indole test, catalase test, citrate test, motility test, urease test, starch hydrolase test, and sugar fermentation were carried out as described by Cheesbrough [17]. The isolates were identified using Bergey's manual of systematic bacteriology [18]. Fungal isolates were identified based on their microscopic and macroscopic characteristics with reference to descriptions by Salvamani and Nawawi [19].

3. RESULTS

3.1 Physicochemical Properties of Water

Table 1 shows mean values for physiochemical parameter for the water samples. During the dry season, mean pH, Conductivity, COD, BOD, Turbidity, DO, TOC, TDS, TSS, Alkalinity, SO_4,, NO_3, Cl^-, Ammonia, Total Nitrogen, Phosphate, THC and Temperature were 6.76±0.01, 16875.07±0.12 µS/cm, 706.03±0.06 mg/l, 72.07±0.12 mg/l, 18.6±0.01 NCU, 4.83±0.06 mg/l, 0.01±0%, 8400.07±0.12 mg/l, 2800.03±0.06 mg/l, 50.07±0.06 mg/l, 1102.33±1.53 mg/l, 1.21±0 mg/l, 11400.07±0.12 mg/l, 0.2±0.03 mg/l, 0.03±0.01 mg/l, 0.99±0.01 mg/l, 113.03±0.06 mg/l and 28.25±0.21^{o}C respectively. Whereas for the wet season, the values were 5.61±0.01, 5330.07±0.12 µS/cm, 140.07±0.12 mg/l, 64.07±0.12 mg/l, 9.82±0 NCU, 6.07±0.12 mg/l, 0.01±0%, 2665.07±0.12 mg/l, 573.33±30.55 mg/l, 6.07±0.12 mg/l, 20.16±0 mg/l, 0.93±0.01 mg/l, 5700.07±0.12 mg/l, 1.03±0.06 mg/l, 0±0 mg/l, 0.18±0.01 mg/l, 113.02±0 and 26.91±0.01^{o}C respectively.

Table 1. Physiochemical parameter of water samples

Parameter	Polluted (Wet)	Control (Wet)	Polluted (Dry)	Control (Dry)
pH	5.61±0.01a	6.7±0.0b	6.76±0.01d	6.75±0.0c
Conductivity (µS/cm)	5330.07±0.12a	5880.07±0.12b	16875.07±0.12d	15900.1±0.1c
COD (mg/ml)	140.07±0.12c	50.07±0.12a	706.03±0.06d	56±0.1b
BOD (mg/ml)	64.07±0.12c	40.07±0.12b	72.07±0.12d	28.07±0.12a
Turbidity (NCU)	9.82±0c	1.41±0.01a	18.6±0.01d	3.86±0.01b
DO (mg/ml)	6.07±0.12c	6.81±0.01d	4.83±0.06a	5.2±0.0b
TOC (%)	0.01±0b	0±0a	0.01±0b	0.0±0.0a
TDS (mg/ml)	2665.07±0.12a	2940.1±0.1b	8400.07±0.12d	7875.07±0.06c
TSS (mg/ml)	573.33±30.55b	280±60a	2800.03±0.06d	1380.03±0.06c
Alkalinity (mg/ml)	6.07±0.12a	40.07±0.12b	50.07±0.06d	50.07±0.12c
SO_4 (mg/ml)	20.16±0b	16.44±0a	1102.33±1.53d	900.17±0.15c
NO_3 (mg/ml)	0.93±0.01c	0.81±0.01a	1.21±0d	0.82±0b
Cl^- (mg/ml)	5700.07±0.12b	5250.5±0.5a	11400.07±0.12d	10501±1c
Ammonia mg/ml	1.03±0.06c	0.05±0a	0.2±0.03b	0.27±0.03b
Total Nitrogen (mg/ml)	0±0a	0±0a	0.03±0.01b	0.06±0.01c
Phosphate (mg/ml)	0.18±0.01b	0.18±0.01b	0.99±0.01c	0.18±0.01b
THC (mg/ml)	113.02±0b	14.35±0a	113.03±0.06b	14.3±0.3a
Temperature (^{o}C)	26.91±0.01a	27.37±0.06b	28.25±0.21c	27.41±0.01b

Row mean ± standard deviation with different alphabet is significant

3.2 Physicochemical Parameters of soil samples

Table 2 shows the physicochemical parameters of the soil samples. During the wet season, mean values for pH, Conductivity, TOC, Nitrogen, PO_4, Cl^-, SO_4 and THC in the soil at depth 0-15cm were 5.1±0.1,100.03±0.06 µS/cm, 0.12±0.05 mg/kg, 0.09±0 mg/kg, 7.55±0.01 mg/kg, 20.1±0.1 mg/kg, 30±0 mg/kg and 4664.37±89.65 mg/kg respectively, whereas, at depth 15-30 cm the values were 7±0, 393.03±0.06 µS/cm, 4.2±0.1%, 0.07±0 mg/kg, 6.66±0 mg/kg, 1400.1±0.15 mg/kg, 24±0.1 mg/kg and 25836.53±1071.9 mg/kg. During the dry season, mean values for pH, Conductivity, TOC, Nitrogen, PO_4, Cl^-, SO_4 and THC in the soil at depth 0-15 cm were 5.03±0.06, 300.17±0.29 µS/cm, 0.04±0%, 45.47±0.01 mg/kg, 6.67±0.01 mg/kg, 250.23±0.32 mg/kg, 528±12 mg/kg and 914.9±0 mg/kg respectively, whereas, at depth 15-30cm the values were 7.17±0.29,1061.13±0.03 µS/cm, 0.06±0%, 45.43±0.22 mg/kg, 4.22±0.11 mg/kg, 400.37±0.32 mg/kg, 653.33±11.02 mg/kg and 26888.87±48.3 mg/kg respectively.

3.3 Heavy Metals Contents of Water and Soil Samples

Table 3 shows the concentrations of heavy metals in soil samples. During the dry season, all the heavy metals monitored (Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn) were detected in varying concentrations in the polluted soil. The metals As, Cd, Fe, Cu, Ti and Zn were detected in the water samples but not Cr, Ni and Pb. During the wet season, all the heavy metals monitored (Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn) were detected in varying concentrations in the polluted soil and water samples.

3.4 PAH, TPH, BTEX and PCB Contents of Water and Soil Samples

Table 4 shows the concentrations of PAH, TPH, BTEX and PCB in water and soil samples. During the wet season, mean concentrations of PAH, TPH, BTEX and PCB in polluted water were 454.07±26.69 mg/kg, 27512.17±688.58 /Kg, 0.91±0.06 mg/kg, 3.51±2.6 mg/kg respectively. The mean concentrations of PAH, TPH, BTEX and PCB in polluted soil (0-15 cm) were 762.57±31 mg/kg, 18019.27±4618.82 mg/kg, 20.22±4.61 mg/kg, 4.64±0.61 mg/kg, whereas, at soil depth 15-30 cm, the values were 1167.43±126.15 mg/kg, 14820.02±1434.61 mg/kg, 7.52±0.71 mg/kg and7.64±0.62 mg/kg respectively. During the dry season, mean concentrations of PAH, TPH, BTEX and PCB in polluted water were 154.49±33.83 mg/kg, 11767.13±3301.48 mg/kg, 1.44±0.3 mg/kg and 11.12±0.86 mg/kg respectively. The mean concentrations of PAH, TPH, BTEX and PCB in polluted soil (0-15 cm) were 7330.26±80.39 mg/kg, 15013.34±2076.68 mg/kg, 1.31±0.4 mg/kg and 15.51±1.27 mg/kg, whereas, at soil depth 15-30 cm, the values were 942.49±98.27 mg/kg, 23690.29±1668.09, 2.61±0.5 mg/kg and 9.46±0.27 mg/kg respectively.

3.5 Microbiological Properties of Soil

Mean THBC for soil (0-15cm) during the wet and dry season respectively were 7.6 log CFU/g and 8.3 log CFU/g; mean TFC 3.6log CFU/g and 5.1 log CFU/g; mean HUB 4.8 log CFU/g and 5.1log CFU/g and mean HUF 1.1 log CFU/g and 3.8 CFU/g. Mean THBC for soil (15-30cm) during the wet and dry season respectively were 6.5 log CFU/g and 6.4log CFU/g; HUB 4.6 log CFU/g and 4.6 log CFU/g (Fig. 1).

3.6 Microbiological Properties of Water

Mean THBC for water during the wet and dry season respectively were 7.4 log CFU/ml and 7.8 log CFU/ml; mean TFC 0log CFU/g and 5 log CFU/g; mean HUB 4.6 log CFU/ml and 5log CFU/ml and mean HUF 1.1 log CFU/ml and 0 CFU/ml (Fig. 2).

3.7 Bacteria and Fungi in Water and Soil Samples

Bacterial isolates in polluted soil samples were identified as *Enterobacter* sp., *Bacillus* sp., *Micrococcus* sp., *Staphylococcus* sp. and *Pseudomonas* sp. Bacteria in polluted water samples were identified as *Staphylococcus* sp. and *Escherichia coli*. Fungi in polluted soil samples were identified as *Aspergillus* sp., *Penicillium* sp. *Fusarium* sp., *Rhodotorula* sp., *Exophiala* sp. and *Crypotococcus* sp. Fungi in polluted water sample was identified as *Penicillium* sp.

4. DISCUSSION

This study investigated the impact of artisanal refinery operations on the physicochemical and microbiological properties of soil and water in Igia-Ama, Rivers State, Nigeria. Table 1 shows mean values for physiochemical parameter for the water samples. During the dry season, mean pH, Conductivity, COD, BOD, Turbidity, DO, TOC, TDS, TSS, Alkalinity, SO_4,, NO_3, Cl^-, Ammonia, Total Nitrogen, Phosphate, THC and

Temperature were 6.76±0.01, 16875.07±0.12 µS/cm, 706.03±0.06 mg/l, 72.07±0.12 mg/l, 18.6±0.01 NCU, 4.83±0.06 mg/l, 0.01±0%, 8400.07±0.12 mg/l, 2800.03±0.06 mg/l, 50.07±0.06 mg/l, 1102.33±1.53 mg/l, 1.21±0 mg/l, 11400.07±0.12 mg/l, 0.2±0.03 mg/l, 0.03±0.01 mg/l, 0.99±0.01 mg/l, 113.03±0.06 mg/l and 28.25±0.21^{o}C respectively. Whereas for the wet season, the values were 5.61±0.01, 5330.07±0.12 µS/cm, 140.07±0.12 mg/l, 64.07±0.12 mg/l, 9.82±0 NCU, 6.07±0.12 mg/l, 0.01±0%, 2665.07±0.12 mg/l, 573.33±30.55 mg/l, 6.07±0.12 mg/l, 20.16±0 mg/l, 0.93±0.01 mg/l, 5700.07±0.12 mg/l, 1.03±0.06 mg/l, 0±0 mg/l, 0.18±0.01 mg/l, 113.02±0 and 26.91±0.01^{o}C respectively. The ANOVA result revealed that physiochemical parameters of samples are significant different ($p<0.05$). From the result of the physiochemical analysis, the concentrations of these parameters determined for the polluted sites are higher than in the control sites. This could have adverse consequences; concentrations above normal could interfere with normal biological processes, and affect the environmental fate (degradation and persistence) or chemical compounds.

Nwankwoala et al. [11] similarly reported changes in the physicochemical properties of water such as BOD, DO, TDS, sulphate and pH, owing to artisan refining on the aquifer, in parts of Rivers State which render the water of poor quality. Lebari et al. [12] reported physicochemical alterations of interstitial water quality as a result of artisanal refining operations in South-Eastern Nigeria. The study reported significant changes in parameters such as pH, temperature, conductivity, DO, TDS and turbidity over time, same as the present study. Recorded pH values for water in the present study are within range (6.0-8.2) reported in that study, same as EC for wet season. However, the EC in this study averaging 16875µS/cm in dry season, is more than 238 - 7885µS/cm range reported in that study. Similarly, DO, BOD, TDS and sulphate concentrations in the present study were higher than values reported Lebari et al. [12].

In the present study, mean values for pH, Conductivity, TOC, Nitrogen, PO_4, Cl^-, SO_4 THC in the soil at depth 0-15cm during the wet are 5.1±0.1, 100.03±0.06 µS/cm, 0.12±0.05 mg/kg, 0.09±0 mg/kg, 7.55±0.01 mg/kg, 20.1±0.1 mg/kg, 30±0 mg/kg and 4664.37±89.65 mg/kg respectively, whereas, at depth 15-30cm the values are 7±0, 393.03±0.06 µS/cm, 4.2±0.1%, 0.07±0 mg/kg, 6.66±0 mg/kg, 1400.1±0.15 mg/kg 24±0.1 mg/kg and 25836.53±1071.9 mg/kg. During the dry season, the mean values are 5.03±0.06, 300.17±0.29 µS/cm, 0.04±0%, 45.47±0.01 mg/kg, 6.67±0.01 mg/kg, 250.23±0.32 mg/kg, 528±12 mg/kg and 914.9±0 mg/kg respectively, whereas, at depth 15-30cm the values are 7.17±0.29, 1061.13±0.03 µS/cm, 0.06±0%, 45.43±0.22 mg/kg, 4.22±0.11 mg/kg, 400.37±0.32 mg/kg, 653.33±11.02 mg/kg and 26888.87±48.3 mg/kg respectively. The ANOVA result revealed that all samples across parameters are significantly different ($p < 0.05$) in both wet and dry season. Gijo et al. [7] assessed the impact of artisanal crude-oil refineries on the physicochemical features of the sediments of the Nun River, where they showed that the operations similarly leads to increase in total organic carbon and total petroleum hydrocarbon.

During the dry season, all the heavy metals monitored (Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn) were detected in varying concentrations in the polluted soil. The metals As, Cd, Fe, Cu, Ti and Zn were detected in the water samples but not Cr, Ni and Pb. In plant samples, Cd, Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn were detected but not As. During the dry season, all the heavy metals monitored (Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn) were detected in varying concentrations in the polluted soil, water and plant samples. The analysis of variance (ANOVA) result revealed that in the dry season, concentration of heavy metal in sample are significantly different ($p<0.05$) for the following heavy metals As, Cd, Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn except Hg which was same. Also, in the wet season sample are significantly different ($p<0.05$) for the following heavy metals As, Cd, Cr, Fe, Cu, Ni, Pb, Ti, Se and Zn except Hg which was same. Heavy metal concentrations in polluted samples were higher than in control. In an earlier study by Ikezam et al. [9] physicochemical parameters and heavy metals concentration were monitored across artisanal refining sites in the core Niger Delta Region. The study found that soil quality for both the control sites and artisanal refining sites fell below WHO permission limits, however, the soil from control sites were less polluted than soils from artisanal refining sites. Nwankwoala et al. [11] reported high concentration of heavy metals which made the water in areas near artisanal refineries unsuitable for drinking. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure [20,21].

Table 2. Mean values for soil physiochemical parameters

Samples	pH	EC (µS/cm)	TOC (%)	Nitrogen (mg/kg)	PO_4 (mg/kg)	Cl^- (mg/kg)	SO_4 (mg/kg)	THC (mg/kg)
Wet Season								
Polluted Soil (0-15 cm)	5.1±0.1a	100.03±0.06b	0.12±0.05a	0.09±0b	7.55±0.01c	20.1±0.1a	30±0b	4664.37±89a
Control (Soil 0-15 cm)	5.7±0b	80±0a	0.42±0.01b	0.1±0c	7.1±0b	20.1±0.1a	66.1±0.1c	9239.17±89b
Polluted Soil (15-30 cm)	7±0d	393.03±0.06c	4.2±0.1c	0.07±0a	6.66±0c	1400.1±0.15c	24±0.1a	25836.53±107d
Control (Soil 15-30 cm)	6.5±0c	420±0d	7.2±0.1d	0.2±0d	9.44±0.01b	1000.1±0.1b	216±0d	23949.9±0c
Dry Season								
Polluted Soil (0-15 cm)	5.03±0.06a	300.17±0.29b	0.04±0a	45.47±0.01a	6.67±0.01d	250.23±0.32a	528±12c	914.9±0b
Control (Soil 0-15 cm)	5.52±0.03b	216.17±0.29a	0.07±0d	51.91±0.3c	6.22±0.11c	250.37±0.32a	465.33±16b	466.4±8.9a
Polluted Soil (15-30 cm)	7.17±0.29d	1061.13±0.03c	0.06±0b	45.43±0.22a	4.22±0.11b	400.37±0.32b	653.33±11d	26888.87±48d
Control (Soil 15-30 cm)	6.42±0.03c	1135±1d	0.07±0c	47.52±0.03b	3.18±0.17a	500.37±0.32c	360±6a	23942.63±0.55c

Row mean ± std. with same alphabet is not significantly different

Table 3. Mean heavy metal concentrations in water and soil

Samples	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Ti (mg/kg)	Se (mg/kg)	Zn (mg/kg)
Wet Season										
Polluted Water	16.11c	5.96e	0.85b	470.63a	7.14f	5.45e	6.66d	0.79a	8.47a	18.96g
Control	0.05a	0.03a	0a	0.26a	0.05a	0.1a	0.04a	0a	0a	0.04a
Polluted Soil (0-15 cm)	43.06d	10.43g	10.49c	9063.95c	11.54i	46.59g	22.24f	87.16c	127.54b	31.39i
Control	0a	5.38d	0a	6240.78b	2.09e	3.38c	0.44a	1.38a	23.65a	14.23c
Polluted Soil (15-30 cm)	59.67e	12.48h	11.87d	9530.9c	10.38h	41.71f	15.41e	76.24b	101.37b	22.69h
Control	0a	3.97c	0a	4716.52b	1.69d	2.7b	2.27b	2.57a	40.18a	16.21e
Dry season										
Polluted Water	0.18a	1.31c	0a	2194.82c	0.71c	0a	0a	0.02a	0a	39.46d
Control	0a	0.06a	0a	0.14a	0.04a	0.14a	0.46a	0a	0a	0.23a
Polluted Soil (0-15 cm)	26.33b	2.52e	32.88b	8360.7h	2.24e	28.61b	16.47e	51.56e	110.68c	46.78e
Control	0a	1.38c	0a	5925.81f	0a	0a	0a	0a	0a	12.91b
Polluted Soil (15-30 cm)	35.41c	0.79b	0a	7647.96g	1.29d	1.38a	8.13d	47.53d	41.62b	75.35h
Control	0a	0.05a	0a	5527.64e	0a	0a	5.09c	0a	40.65b	19.47c

Row mean with same alphabet is not significantly different

Table 4. Mean value of PAH, TPH, BTEX and PCB

Samples	PAH (mg/kg)	TPH (mg/kg)	BTEX (mg/kg)	PCB (mg/kg)
Wet Season				
Polluted Water	454.07±26.69b	27512.17±688.58d	0.91±0.06a	3.51±2.6b
Control	0±0a	0±0a	0±0a	0±0a
Polluted Soil (0-15 cm)	762.57±31c	18019.27±4618.82c	20.22±4.61c	4.64±0.61b
Control	0±0a	0±0a	0±0a	0±0a
Polluted Soil (15-30 cm)	1167.43±126.15d	14820.02±1434.61b	7.52±0.71b	7.64±0.62c
Control	0±0a	0±0a	0±0a	0±0a
Dry Season				
Polluted Water	154.49±33.83b	11767.13±3301.48b	1.44±0.3c	11.12±0.86d
Control	0±0a	0±0a	0±0a	0±0a
Polluted Soil (0-15 cm)	330.26±80.39c	15013.34±2076.68c	1.31±0.4c	15.51±1.27f
Control	0±0a	0±0a	0±0a	0±0a
Polluted Soil (15-30 cm)	942.49±98.27d	23690.29±1668.09d	2.61±0.5d	9.46±0.27c
Control	0±0a	0±0a	0±0a	0±0a

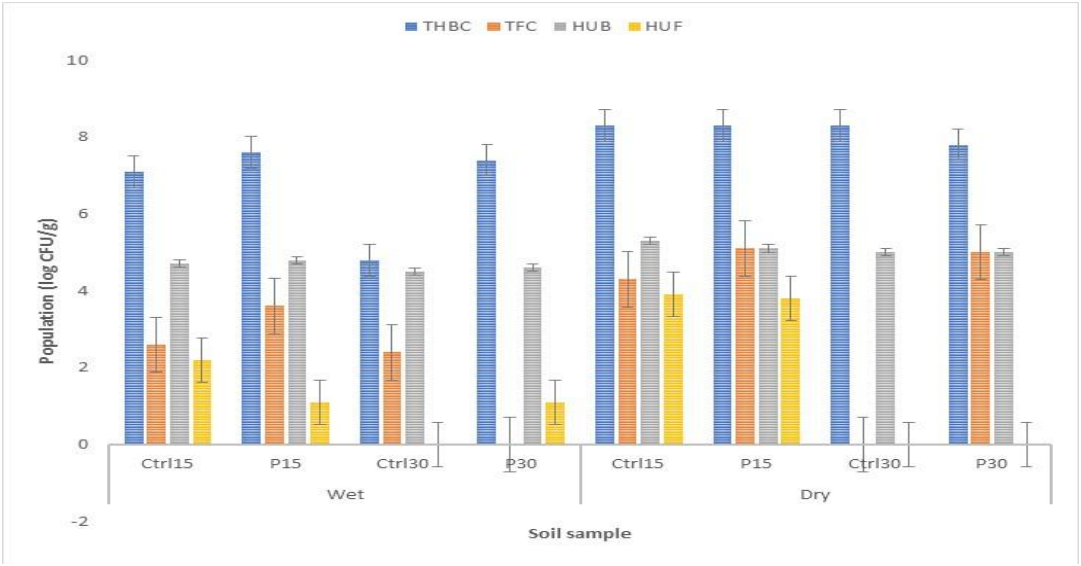


Fig. 1. Bacterial and fungal counts in soil sampled at depth 0-15cm (P_{15} and C_{15}) and 15-30 cm (P_{30} and C_{30})

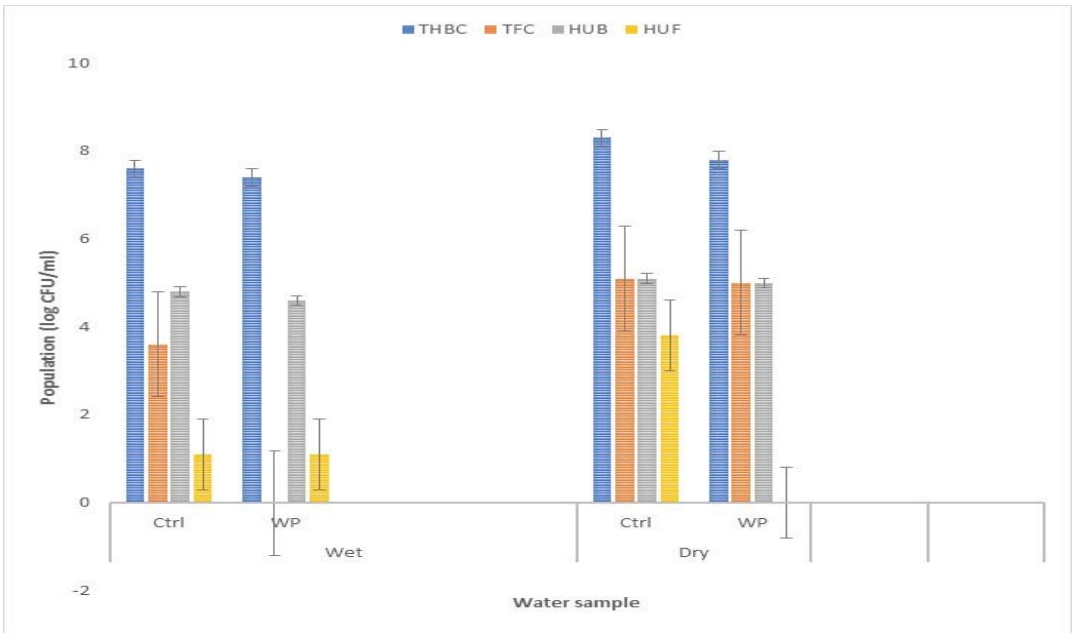


Fig. 2. Bacterial and fungal counts in water samples

For both wet and dry seasons, PAH, TPH, BTEX and PCB concentrations in polluted samples was higher than in control The analysis of variance (ANOVA) result revealed concentrations of PAH, TPH, BTEX and PCB in the soil, plant and water samples are significantly different ($p<0.05$). PAH, TPH, BTEX and PCB are known to be carcinogenic [22,23].

Mean THBC for water during the wet and dry season respectively are 7.4 log CFU/ml and 7.8 log CFU/ml; mean TFC 0 log CFU/g and 5 log CFU/g; mean HUB 4.6 log CFU/ml and 5 log CFU/ml and mean HUF 1.1 log CFU/ml and 0 CFU/ml. Microbial counts of water from polluted sites were not significantly different ($p<0.05$) from control, except for HUF. One of the big problems in the twenty – first century is providing safe industrial or domestic water, and this has been made worse by anthropogenic activities such as artisanal oil operation Nwankwoala et al. [11] reported high impact of microorganisms in the alteration of the quality of water near artisanal refinery sites, particularly by coliforms.

Table 5. Bacterial and fungal isolates obtained from water and soil samples

Sample	Bacteria	Mold	Yeast
Soil 0-15			
	Citrobacter sp.	*Aspergillus* sp.	*Rhodotorula* sp.
	Bacillus sp.	*Penicillium* sp.	
	Escherichia coli		
	Pseudomonas sp.		
Control			
	Enterobacter sp.	*Fusarium* sp.	*Crypotococcus* sp.
	Bacillus sp.	*Aspergillus niger*	
	Bacillus sp.	*Penicillium* sp.	
	Micrococcus sp.		
	Staphylococcus sp.		
	Pseudomonas sp.		
Soil 15-30			
	Staphylococcus sp.	*Aspergillus niger*	*Exophiala* sp.
	Pseudomonas sp.	*Penicillium* sp.	*Rhodotorula* sp
	Citrobacter sp.		
	Pseudomonas sp.		
Control	*Bacillus* sp.		
	Bacillus sp.	*Fusarium* sp.	
	Pseudomonas sp.	*Penicillium* sp.	
	Citrobacter sp.		
Water			
	Staphylococcus sp.	*Penicillium* sp.	
	Escherichia coli		
Control			
	Acinetobacter sp.	*Fusarium* sp.	
	Micrococcus sp.	*Penicillium* sp.	
	Escherichia coli		

Bacterial isolates in polluted soil samples were identified as *Enterobacter* sp., *Bacillus* sp., *Micrococcus* sp., *Staphylococcus* sp. and *Pseudomonas* sp. Douglas and Tamunonegiye [24] likewise isolated bacteria belonging to Bacillus and Enterobacter in artisanal crude oil polluted soil. Bacteria in polluted water samples were identified as *Staphylococcus* sp. and *Escherichia coli*. Fungi in polluted soil samples were identified as *Aspergillus* sp., *Penicillium* sp. *Fusarium* sp., *Rhodotorula* sp. and *Exophiala* sp. Only *Penicillium* sp. was isolated from the polluted water sample. Douglas [25] likewise isolated *Aspergillus* sp., *Penicillium* sp. and *Fusarium* sp. in polluted soil samples.

The bacterial and fungal counts in soil sampled at depth 0-15cm and 15-30 cm in polluted soil were high. Mean THBC for soil (0-15 cm) during the wet and dry season respectively are 7.6 log CFU/g and 8.3 log CFU/g; mean TFC 3.6 log CFU/g and 5.1 log CFU/g; mean HUB 4.8 log CFU/g and 5.1 log CFU/g and mean HUF 1.1 log CFU/g and 3.8 CFU/g. Mean THBC for soil (15-30 cm) during the wet and dry season respectively are 6.5 log CFU/g and 6.4 log CFU/g; HUB 4.6 log CFU/g and 4.6 log CFU/g. Microbial counts of soil from polluted sites were not significantly different ($p<0.05$) from control. The THBC and TFC in the present study are higher than values reported by Douglas and Tamunonegiye [24], where mean THBC ranged from 2.5 x 10^5 to 1.8 x 10^6CFU/g and TFC from 2.1 x 10^3 to 4.4 x 10^4CFU/g. However, HUB which ranged from 4.2 x 10^4 to 6.4 x 10^5CFU/g and HUF from 1.5 x 10^3 to 4.0 x 10^3CFU/g are similar in range to values reported in the present study. Douglas [25] investigated the effect of illegally refined crude oil residue on soil fungi, and reported a mean TFC ranging from 2.4 x 10 CFU/g - 6.7 x 10^4 CFU/g, while the mean HUB counts ranged from 1.6 x10 CFU/g to 3.4 x 10^3CFU/g.

5. CONCLUSION

This study revealed that artisanal crude oil refinery operations have effects on the quality of soil and water. This is evident by changes in physicochemical and microbiological parameters.

Monitored physicochemical parameters, heavy metals, PAHs, TPH and BTEX were higher in the contaminated soil than in the control. The levels of heavy metals, PAHs, TPH and BTEX in the soil and water suggest the need for remediation of the impacted environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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