

Assessment of the Impacts of Artisanal Refinery of Crude Oil On Surface Water, Ground Water And Sediment Quality At Obi-Ayagha Community In Delta State Nigeria

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ARTICLE INFO

Article History:

Accepted: 05 June 2023

Published: 29 June 2023

Publication Issue

Volume 10, Issue 3

May-June-2023

Page Number

1164-1181

ABSTRACT

Aim: This study aims to assess the impacts of artisanal refinery activities on the quality of surface water, ground water, sediment and microbial density of the recipient environment at the abandoned artisanal refinery site in Obi-Ayagha community, Ughelli South, Delta State.

Place and Duration of Study: Abandoned artisanal refinery hydrocarbon impacted site, Obi-Ayagha, Ughelli South, Delta State, Nigeria. During was from September 2021- February 2022.

Methodology: Field sampling techniques were consistent with established and standards methodologies, Environmental Guidelines and Standards for Petroleum Industries in Nigeria (EGASPIN) and Federal Ministry of Environment (FMENV) procedural guidelines. Composite surface water samples were collected using a water sampler, ground water was collected using a water pump from drilled boreholes in the study site. Sediment sample was collected using Eckman dredge (grab) from the surrounding river around the study site. Physicochemical, microbial and metal parameters were analysed in the collected samples and controls, using standard methods to assess the impact of hydrocarbon contaminant from the artisanal refinery activities on the recipient environment.

Results: The study revealed that there was a significant difference in Biochemical Oxygen Demand (BOD₅) values for the three borehole water sampled, with a mean value of 5.23 ± 3.0 mg/l and the control borehole site (3.00 ± 2 mg/l). Total Petroleum Hydrocarbon results were below the instrument detection limit for the surface and ground water samples, while it recorded 5.38mg/kg for the sediment sample. Polyaromatic hydrocarbon results for all samples analysed were below the instrument detection limit

of $<0.0001\text{mg/kg}$. Total heterotrophic Bacteria counts obtained were between $2.08 - 2.13 \times 10^3$ CFU/ml, $1.13 - 1.26 \times 10^3$ CFU/ml and 2.36×10^5 CFU/g for surface water, groundwater and sediment samples respectively. Values obtained for all metals analysed in the study samples were within regulatory stipulated limits. Iron metal, though does not have available limits for sediment samples, recorded the highest concentration of 5585 ± 2.12 mg/kg in relation to other metals.

Conclusion: Results obtained from the environmental samples analysed showed the parameters assessed were within regulatory limits. This could have been due to natural attenuation (remediation) of the environment giving the prolonged period of abandonment of the artisanal refining activities.

The integration of artisanal and modular refinery operations into the oil and gas sector will curtail illegal oil activities in the Niger Delta regions and will also promote the availability of petroleum products, stabilize prices, eliminate shipping costs and provide employment opportunities for the inhabitants in the region and Nigeria in general. It is further recommended that with enough artisanal and modular refineries being granted license by the Federal Government in the country, Nigeria should be able to conserve foreign exchange currently utilized for the importation of petroleum products and promote socio-economic development.

Keywords : Artisanal refinery site, Hydrocarbon contamination, Surface and ground water, Microbial density

I. INTRODUCTION

The extraction of crude oil in the Niger Delta Area of Nigeria is made possible through a diverse network of onshore and offshore oil wells, pipelines and flow-stations located in the creeks of the mangrove forest and the shallow waters. These infrastructures are mostly exposed to constant exploitation through vandalism by breaking of pipelines and siphoning crude oil for sale in the 'international black market' or to local unconventional refineries, found within the swamps of the regions mangrove forest for Artisanal Refining (Bebeteidoh, 2020).

Artisanal oil refining is defined as a small-scale crude oil processing or subsistent distillation of petroleum that is often outside the boundaries of the state law. Artisanal refining activities pose a huge threat to the oil producing areas and its impacts on surface water, sediments and ground water quality is required to be carried out quite carefully aided by professionals in the relevant fields (Bebeteidoh, 2020).

Surface water, sediment and ground water quality pollution depletes aquatic ecosystems and triggers unbridled proliferation of phytoplankton in lakes - eutrophication, contamination of the food chain, lack

of potable water, disease, Infant mortality and destruction of biodiversity.

The turbidity causes the already existing contaminations to spread further into the water-body which also affects the oil producing environment adversely in terms of its surface water, sediment and ground water quality. The impacts of artisanal refinery on water column due to excavation and bottom sediments removal includes increase in turbidity which is detrimental to the re-suspension of sediments. The soil deposits in any water-body have a certain pre-disposed composition. Through artisanal refinery activities this composition is altered and the existing habitat of creatures and organisms that depends on the original composition of the soil dies out due to the unfavourable impacts caused by the oil (Bebeteidoh, 2020).

High turbidity because of algae can also affect fish because when large amounts of algae die, oxygen is used up to decompose them, leaving less oxygen for the fish. Large amounts of suspended soils or clay may clog the gills of fish and kill them directly. High turbidity can also make it difficult for fish to see and catch prey, and it may bury and kill eggs laid on the bottom of lakes and rivers. Pollutants and harmful bacteria may also be attached to particles that cause turbidity (Wokoma *et al.*, 2020). Monitoring the dynamics of artisanal refinery activities with respect to its impacts on surface water, sediment and ground water quality is necessary to evaluate as well as to predict its long-term physical and chemical effects on the oil producing environment in general. This could be accomplished by considering the results of parameters collected in pre-oil mining and extraction phases. However, a more inclusive phase should be post-extraction phase, to establish the recuperative capability of sediment and ground water quality and adjoining coastal areas to their natural state after oil mining or extraction operations (Bebeteidoh, 2020).

According to several researchers, the artisanal petroleum refineries in Obi-Ayagha Community, Obi-Ayagha, Ughelli South, Delta State have been discovered to impact its environment. This is similar to findings by, Obenade and Amangabara, (2014); Ikezam *et al.*, (2021a) who reported the negative environmental, public health and socio-economic consequences, including the economic gains of the refining process. Igben, (2021), reported on the effect of artisanal refinery on occupational dynamics in the Niger Delta, Asimiea and Omokhua (2013), reported the environmental impact of the refineries on vegetation, while Nwankwoala *et al.* (2017) reported its impact on soil and water quality. Substances are often released by artisanal petroleum refineries as acid rain to the soil, plants, and water bodies after undergoing possible atmospheric reactions (Aiswarya and William, 2017; Onakpohor *et al.*, 2020)). In the environment, these substances could build-up in adipose tissues of living things and also move up the trophic web or chain (Nriagu *et al.*, 2016). Hydrocarbon compounds (HC) are the principal pollutants emitted by the petroleum industry, while other fuel combustion devices emit criteria pollutants [oxides of nitrogen (NO_x), carbon monoxide (CO), oxides of sulphur (Sox), particulate matter (PM) and Lead (pb)] (Akeredolu. and Sonibare, 2015).

Analysing the impact of artisanal crude refining on the environment, Ogwu *et al.*, (2022), pointed out that the activities of illegal refineries severely impacted biodiversity, aesthetic scenery of the forest, regeneration of plant species and destruction of wildlife habitat, disruption of the water cycle, and loss of medicinal plant species. From the scientific research carried out by Nwankwoala *et al.*, (2017) on the effect of artisanal refining on water bodies and soil in rivers, the water analysis showed a high concentration of Fe and Zn which made the water in such areas unsuitable for drinking. Also, the soil samples recorded high levels of crude content from 1m, with concentration reducing with depth up to 3m.

Over the years, there has been artisanal refining of crude oil in Obi-Ayagha Community, Obi-Ayagha, Ughelli South, Delta State, which upon physical observation has greatly impacted the ecological system of the area; dried crude oil can be seen at the adjoining lands while crude oil sheen can be seen on the surface of the sediment, mangrove roots and water, which has resulted in stunted mangrove trees, retarded stem girth of mangrove trees and roots, low photosynthetic rates; hence, there is a need to assess the impact of artisanal refinery on surface water, sediment and ground water quality in order to provide information on possible risks to the environment and human health of the inhabitants of the area.



Plate 1: Collection of crude oil into drums | The Guardian 2021



Plate 2: Fire outbreak from artisanal crude oil refinery site | The Guardian 2021



Plate 3: Storage drums of diesel oil from artisanal refineries | The Guardian 2021

II. MATERIALS AND METHODS

2.1. Area of study

The project area is the abandoned artisanal hydrocarbon polluted site at Obi – Ayagha community, in Ughelli South Local Government Area (LGA) of Delta State, Nigeria. The local Government Area is made up of Six Urhobo kingdoms namely: Ughievwen, Arhavwarien, Effurun Otor, Eghwu, Okparabe and Olomu. Otu Jeremi is the headquarters of LGA. It is the fourth most populated Local Government Area in Delta State. The Project population size is 213,576 as of the 2006 census and had an area of 786 square Kilometres (303 sq mi)

2.0. Sample Collection

2.1. Collection of Surface water

Surface water samples were collected as composite from the river around the study site using a water sampler. Two(2) litres polyethylene gallons were appropriately labelled and used to hold the water samples for physicochemical parameters. Two water samples were collected and were kept in an ice chest en route the laboratory.

2.2 Ground water sampling

Three bore holes were drilled (Fig 1) to sample the ground water around the study area. One was drilled out of the study site as a control. Drilling was done by manual percussion involving the use of hand auger, pipe range, bailer, casing pipes, etc. For proper logging

and stratigraphic display, soil samples were collected from drill cuttings at 10 ft interval from surface to depth. Water level measurement was also obtained in all holes along with water samples after flushing. The casings were well capped to serve as reference points in future. Average depth reached in the boreholes was 60 feet. This was considered appropriate in view of the project objective and the hydro geological environment.

Water samples for metals were held in 1litre polyethylene gallons and preserved with 1:1 tetraoxonitrate(IV) acid, while samples for total petroleum hydrocarbons(TPH) and Polyaromatics(PAHs), were kept in glass bottles and preserved with 1:1 tetraoxo-sulfate VI acid to pH of < 2. Water samples for physicochemical parameters were preserved in an ice chest en route the laboratory. In situ analysis was carried out on the surfacand ground water samples for pH, temperature, TDS, Conductivity, DO with hand held meters before transportation to the laboratory for further studies.

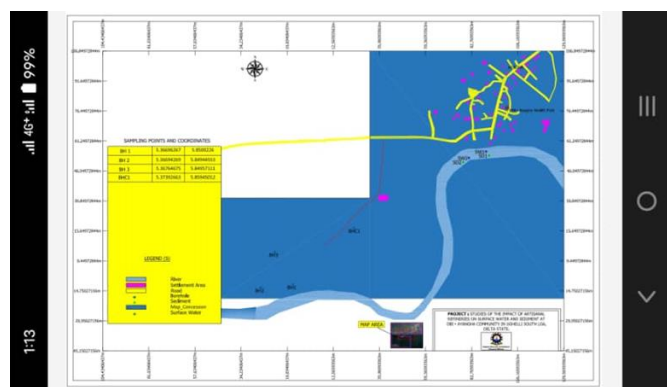


Fig 1: Map of Boreholes for groundwater sampling at abandoned artisanal refinery site, Obi-Ayagha, Delta State.

2.3. Collection of Sediment

Composite sediment samples were collected with an Eckman grab from the river bed around the study site, kept in Polythene bags and labeled appropriately.

Samples were kept in an ice chest and transported to the laboratory for further analysis.

2.4.1 In-Situ Analysis of water samples

In situ parameters were assessed on site using the following procedures; pH (APHA 4500-H+ B using Hanna pH electronic meter), temperature (APHA 2550 - B laboratory and field methods), electrical conductivity and total dissolved solids (APHA 2510-B using Hanna desktop conductivity meter) and dissolved oxygen (DO) (APHA 4500-O C by azide modification method).

2.4.2 Laboratory analysis

These physicochemical parameters were assessed using the following procedures; Salinity (Mohr Argentometric Method, 4500 B-Cl-), Biochemical oxygen demand (BOD) (APHA 5210 B, by 5-Day test method), Total suspended solids (APHA 2540D), Nitrates (APHA 4500-NO₃- B) and Phosphate (APHA 4500-PE). Oil and grease and THC of the samples was analysed using ASTM D3921 method.

A) Microbiological Analyses for water and Sediment samples

i) Enumeration of Total Coliforms in surface water samples.

Total coliforms in the surface water samples was determined using Standard Total Coliform membrane filters Procedure (APHA 9222 B). The method involved the filtration of 100ml of the water samples through a filter membrane of 0.45um. The filter membranes were removed and placed on the surface of an already prepared MacConkey agar. Inverted plates were incubated at 37oC for 24 hours. The colonies exhibiting coliform characteristics (pink colonies) were counted and recorded as CFU/100ml.

ii) Enumeration of total heterotrophic bacteria (THB) count using pour plate method.

Nutrient agar (NA) was used for bacteria enumeration. The media were prepared according to manufacturer's specification. Ten-fold serial dilution was carried out using 1ml of the test water samples and 0.85% (w/v) sodium chloride (normal saline) as diluent to 10⁻³ dilution. For the sediment samples, 1g was serially diluted with normal saline to 10⁻⁵ dilution. The standard pour plate method was used by inoculating 1ml aliquot of the different dilutions into sterile Petri dishes and 15ml- 20ml of sterilized and cooled nutrient agar was poured into each of the plates. The culture plates were swirled for homogenization, allowed to solidify and incubated at 28 ± 2°C for 18-24 hours. After incubation, individual colonies were recorded as CFU/ml for the water samples and CFU/g for the sediment samples.

iii) Test Procedure for Total heterotrophic Fungi (THF) count Using Pour Plate Method

1ml of aliquot from the serial dilutions was taken and poured on the already prepared Potatoe dextrose agar plates and then incubated at 28±2°C for 4-7 days and then the colonies on the plate were enumerated or counted.

iv) Test Procedure for Hydrocarbon Utilizing Fungi (HUF) using Pour Plate Method

The procedure of Bhattacharya et al. [19] was adopted for this study. Bushnell-Haas (BH) media with the following composition (g/L): K₂HPO₄ (1.0 g), KH₂PO₄ (1.0 g), NH₄NO₃ (1.0 g), MgSO₄·7H₂O (0.2 g), FeCl₃·6H₂O (0.05 g), CaCl₂·2H₂O (0.02 g), was used as an enrichment medium with 1% crude oil (v/v) as the sole carbon source to isolate the crude oil degrading fungi from the water and sediment samples. Sediment samples (10g) were added to 90mL (10⁻¹)BH media in 250mL Erlenmeyer culture flasks. It was then incubated at 28 ± 2°C for 7 days. After 7 days incubation, 9ml of normal saline in McCartney bottles were sterilized and used to make serial dilutions of 10⁻² to 10⁻⁵. The water samples were also serially diluted to 10⁻³ dilution. 1ml aliquot of the serial dilutions (inoculum) were put into sterile petri dishes

and already prepared, sterilized and cooled mineral salt agar (Bushnell Haas Agar) was poured into the petri dishes with the inoculum and antifungal (fungusol) added to suppress fungi growth. A filter paper was saturated with sterile crude oil on the inside of the inverted petri dishes of the cultured plate and the plates were incubated at 28 ± 2°C for 7 days. The colonies on the plate were counted using colony counter and expressed as CFU/ml for water samples and CFU/g for the sediment samples.

v) Analysis for Hydrocarbon Utilizing Bacteria (HUB) using Pour Plate Method

1ml aliquot of the serial dilutions were taken and poured into sterile petri dishes and already prepared and sterilized mineral salt agar was poured into the plates with streptomycin added to suppress bacteria growth. A filter paper saturated with sterile crude oil was aseptically placed on the inside of the inverted Petri dishes of the cultured plate and incubated at 28±2°C for 7 days after which the colonies on the plate were counted and expressed as CFU/ml for water and CFU/g for the sediment.

B) 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 1MK₂Cr₂O₇ solution was accurately added to the sample in each flask and swirled gently to disperse the soil. Thereafter 20 ml of conc. H₂SO₄ 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 so far 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 blustered. The blank it rations was done in the same manner but without sample.

Percentage Organic matter was derived from the equation thus:

$$\% \text{ Org.C} = \frac{(V1 - V2) \times 0.3f}{w}$$

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.

C) Determination of Total Nitrogen Content

Precisely 10g of the sample was weighed, air-dried, ground and made to pass through a 0.5mm sieve into a dry 500ml micro-Kjeldahl flask and 20ml of distilled water was added. The flask was swirled for a few minutes and allowed to stand for 30 minutes. A tablet of mercury catalyst and 10 grams of SO₄ was added, thirty (30) ml of conc. H₂S was added using automatic pipette. Low heat was applied cautiously on the stand. The heat was increased when the water has been removed and frothing ceased. The mixture was boiled for 5 hours, then, allowed to cool and 100ml water was added to the flask. The digest was transferred into another clean micro-flask (750ml capacity). Fifty (50) ml of H₃BO₃ indicator solution was added into a 500ml Erlenmeyer flask and was placed under the condenser of the distillation apparatus. The 750ml Kjeldahl flask was attached to the distillation apparatus and 150ml of 10M NaOH solution was poured through the distillation flask via the opened funnel stopcock and distilled. The distillation was ended after the collection of 150ml of distillate. The distillate was titrated with 0.01M standard HCl to determine the NH₄- N content. Colour change from green to pink indicated the end point.

Percentage nitrogen was calculated as shown:

$$\% N =$$

Where, T = Titre value, M = Molarity of HCl, Wt. = weight of soil used.

D) Chemical Oxygen Demand (COD)

To determine the COD levels of the water sample, precisely 10 ml of water sample was measured and transferred into a glass beaker. There after 0.2 g of mercuric sulphate (HgSO₄) was weighed and added to the sample and mixed properly before 1 ml of concentrated sulphuric acid was added and left to cool before 5 ml of 0.25N potassium dichromate (K₂Cr₂O₇) solution was also added. Thereafter, 14 ml of sulphuric acid with silver sulphate reagent was slowly added and swirled until the solution was thoroughly mixed. The beaker was covered with aluminium foil and heated to 100°C for 30 minutes. The mixture was allowed to cool before diluting the acid solution to 150 ml mark with distilled water. Five drops of ferroin indicator were added to the solution until a sharp colour change was noticed; changing from blue green to reddish brown (dark red) colour. There adding on the COD Agilent meter 4510N was taken and recorded in mg/l.

E) Procedure for Metal Analysis

Heavy metals analysed include Cd, Cr, Cu, Pb and Zn. Samples were digested with a mixture of nitric, sulphuric, and hydrochloric acid to make the metals available for determination and the concentration levels of the metals analysed using Atomic Absorption spectrophotometer (A.A.S, Buck Scientific Model VGP-210). ICP-AES analysis (Inductively Coupled Plasma - Atomic Emission Spectroscopy) provides analysis of metals down to trace levels. Iron, copper, and lead are fire-refined by selective oxidation. In this process, oxygen or air is added to the impure liquid metal; the impurities oxidize before the metal and are removed as an oxide slag or a volatile oxide gas.

F) Method for the Determination of Total Petroleum Hydrocarbon (TPH) in Soil Solid Sample Extraction Method (ASTM D5756-97)

10g soil samples were carefully weighed into an organic free amber glass container while 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 then mechanical shaker were used to mix the mixture for about 30 minutes. Sonicator was used to extract the sample, while the extract was filtered. Final volume of the extract taken. Extract stored in a dried organic free and chromic acid pre – clean vial. A sample of the extract withdrawn with an automated gas-tight syringe of the auto-sampler 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.

Data Processing and Reporting For Soil and Sediment

Using GC:

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

$\frac{\text{Instrument reading (total conc.in mg/l)} \times \text{Volume of the extract} \times \text{DF}}{\text{Weight of the wet sample (in kg)}}$

Weight of the wet sample (in kg)

Actual TPH (mg/kg) = R x CF

Where DF: Dilution factor

GF: Calibration Graph Factor

2.5 Statistical Analysis

The data obtained from the field work in the study area was subjected to SPSS Version 17.0 Statistical Analysis, whereby descriptive statistics- i.e. mean, range, standard error, standard deviation, variance, maximum and minimum values and inferential statistics- i.e. linear regression, analysis of variance at confidence limits of $p > 0.01$ and $p > 0.05$, were obtained, for data analysis. The ArcGIS version 10.3, ENVI version 4.7, Surfer 10, SPSS 22 and Microsoft Enterprise were also used for the interpretation.

III. RESULTS AND DISCUSSION

3.1 Results

3.1.1 Analysis of Borehole Water (Ground Water)

The temperature of the borehole water sampled at Obi-Ayagha artisanal refinery site was 28.0°C while the control borehole had same value of 28.00C (Table 1)

Biological Oxygen Demand (BOD₅) value for the borehole at BH1, BH2 and BH3 were 4.60mg/l, 6.60mg/l and 4.50mg/l respectively; while the control borehole recorded 3.00mg/l. No regulatory limits for ground water sampled (Table 1). The Chemical Oxygen Demand (COD) value recorded was 8.40mg/l, 9.20mg/l and 7.20mg/l for BH1, BH2 and BH3, respectively. The control borehole had value of 6.00mg/l. The TPH values of the borehole water sampled were less than 0.001mg/l (below the measuring instrument detection limit) in all the boreholes drilled and as well as the control (Table 1). The concentration of heavy metals in the borehole water sampled and the control point were all below the instrument detection limits except zinc and iron that had values for BH1 (0.08mg/l and 0.11mg/l), BH2 (0.05mg/l and 0.13mg/l) and BH3 (0.04mg/l and 0.11mg/l), respectively with the control point (0.15mg/l & 0.10mg/l) for the period under review. All the concentrations of metals recorded were below the available regulatory NURPC limits (Table 2). The observed pH values were 5.80, 5.80 and 6.10 for BH1, BH2 and BH3, respectively while the control point had 6.10. These showed that the water from the boreholes did not comply with the NUPRC limit of 6.50 – 8.50 (Table 1). The microbial analyses of the ground water indicated the hydrocarbon degrading bacteria and hydrocarbon degrading fungi were not detected, while the heterotrophic bacteria counts ranged from 1.13 x 10³CFU/ml (BH3) - 1.86 x 10³CFU/ml (BH1) and heterotrophic fungi population were between 1.00 x 10³ CFU/ml (BH2) and 1.15 x 10³ CFU/ml (BH3) (Table 3).

Table 1 : Mean concentrations of physicochemical parameters of borehole water samples

Parameters	BH 1	BH 2	BH 3	BH Control	NURPC Limit	FMENV Limit
pH	5.80 ±0.14	5.70 ±0.14	6.10±0.14	6.10±0.14	N/A	6-9
Temp. , 0C	28.00±0.04	29.00±0.04	28.50± 0.04	28.00 ±0.04	N/A	30
Elect. Conductivity, µs/cm	110.00±0.24	90.00 ±0.20	50.00 ±0.23	20.00 ±0.24	N/A	3.0
Total Dissolved Solids (TDS) mg/l	58.20 ± 2.24	47.70 ±2.10	26.50 ± 2.22	10.60 ± 2.12	N/A	2000
Total Suspended Solid (TSS) mg/l	52.00 ±1.26	65.00 ±1.24	1.80 ±0.62	1.00 ±0.23	N/A	N/A
Dissolved Oxygen (DO) mg/l	6.80 ±1.42	4.40 ±1.32	6.00±1.42	5.50 ±1.23	N/A	N/A
Turbidity, NTU	32.60 ±2.23	47.20 ±2.34	1.10±0.42	0.40 ± 0.22	N/A	N/A
Chemical Oxygen Demand (COD) mg/l	8.40 ±1.22	9.20 ±1.23	7.20 ±1.24	6.00 ±1.24	N/A	N/A
Biochemical Oxygen Demand (BOD) mg/l	4.60 ±0.64	6.60 ±0.66	4.50 ±0.43	3.00 ±0.070	N/A	N/A
Ammonia mg/l	1.48 ±0.23	5.97 ±0.24	9.82 ±1.23	±0.14	N/A	N/A
Anions Salinity as Chloride, mg/l	7.09 ±1.20	10.64 ±1.26	10.64 ±1.24	7.09 ±1.25	N/A	N/A
Nitrate, mg/l	0.82 ±0.42	1.44 ± 0.23	0.51±0.24	1.24 ± 0.22	N/A	N/A
Bicarbonate, mg/l	7.32 ±1.22	4.88±1.23	3.66±1.23	1.22±0.62	N/A	N/A
Total Petroleum	<0.001	<0.001	<0.001	<0.001	50	N/A

Hydrocarbons (TPH) $\mu\text{g/l}$ Polycyclic Aromatic Hydrocarbons (PAH) $\mu\text{g/l}$	<0.001	<0.001	<0.001	<0.001	0.02	N/A
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Table 2: Mean heavy metals concentration in borehole water samples

	BH1	BH2	BH3	BH Control	NURPC Limit	FMEN _v Limit
Iron, mg/l	0.11±0.24	0.13 ±0.23	0.11 ±0.24	0.10 ±0.21	0.30	0.05
Zinc, mg/l	0.08 ±0.02	0.05±0.02	0.04 ±0.01	0.15 ±0.04	0.80	5.0
Chromium, mg/l	<0.001	<0.001	<0.001	<0.001	N/A	N/A
Lead, mg/l	<0.001	<0.001	<0.001	<0.001	0.075	0.01
Nickel, mg/l	<0.001	<0.001	<0.001	<0.001	N/A	N/A

Table 3: Heterotrophic and Hydrocarbon Utilizing bacteria and fungi counts in borehole water samples

Parameters	BH1	BH2	BH3	BH Control	NURPC Limit	FMEN _v Limit
Heterotrophic Bacteria $\times 10^3$, CFU/ml	1.86	1.18	1.13	1.39	N/A	N/A
Heterotrophic fungi $\times 10^3$, CFU/ml	1.14	1.00	1.15	1.07	N/A	N/A
Hydrocarbon degrading Bacteria , CFU/ml \times 10^2 ,	ND	ND	ND	ND	N/A	N/A
Hydrocarbon degrading fungi, CFU/ml \times 10^2 ,	ND	ND	ND	ND	N/A	N/A

Legend: N/A: Not available ND: Not detected.

3.2. Results of Analysis of Surface Water

The temperature of the surface water sampled at Obi-Ayagha (SW1 and SW2) recorded 28.0°C for the two sampling stations respectively. All the samples analysed complied with the NUPRC limit of 30°C (Fig 2). The observed pH values was 5.70 for both SW1 and SW2. The NUPRC limit for pH is 6.50 – 8.50; indicating a non-compliance (Fig 2). Biological Oxygen Demand (BOD₅) value for the surface water at SW1 and SW2 recorded 4.50mg/l and 5.50mg/ respectively. All complied with NUPRC Limit of 10mg/l(Fig 2). COD value recorded were 8.00mg/l and 7.60mg/l for SW1 and SW2 respectively, which were in compliance with the NUPRC limit of 40.0mg/l. (Fig 2). Total petroleum hydrocarbon (TPH) was not detected by the measuring instrument in both locations sampled(<0.001mg/l). This was in compliance with the NUPRC limit of 10.0mg/l for surface water from nearshore environment (Table 4). The total dissolved solids (TDS) in aqueous substances consist of inorganic salts and dissolved materials. The value observed for TDS was 15.90mg/l for both SW1 and SW2. This was in compliance with the NUPRC Limit of 2000mg/l(Fig 2). Concentrations recorded for Salinity as chloride were 5.32mg/l and 7.09mg/l for SW1 and SW2 respectively, which were in compliance with the NUPRC limit of 600mg/l for freshwater environment. (Table 4). The concentrations of heavy metals in the surface water from SW1 and SW2 recorded values below the measuring instruments detection limits except Iron and Zinc which recorded SW1 0.27mg/l and 0.061mg/l in SW1 and 0.21mg/l and 0.059mg/l SW2 respectively, and were all in compliance with corresponding NUPRC limits(Table 4). The results of microbiology parameters analysed for the surface water were as follows; hydrocarbon degrading bacteria and hydrocarbon degrading fungi were not detected in the surface water samples but the heterotrophic bacteria and heterotrophic fungi recorded 2.13 x 10³ CFU/ml and 2.24 x 10³CFU/ml for SW1, respectively while 2.08 x 10³CFU/ml and 1.59 x 10³ CFU/ml were recorded for SW2, respectively (Table.4).

Table 4: Mean concentrations of Physicochemical parameters of Surface Water Samples

Parameter	SW 1	SW 2	Control	NUPRC
				Limit
pH	5.72 ±0.02	5.74 ±0.02	6.3 ±0.02	6.5-8.5
Temp.	28.00 ±0.20	29.00 ±0.20	29.00 ±0.20	30
Elect. Conductivity, µs/cm	30.00 ±0.14	32.00 ±0.14	92.0 ±0.22	N/A
TDS, mg/l	15.50 ±0.02	15.90 ±0.02	45.2±0.04	2000
TSS, mg/l	20.48 ±0.14	27.00 ± 2.22	13.40 ± 0.20	30
DO, mg/l	6.00 ±0.02	5.10 ±0.02	6.50± 0.03	N/A
Turbidity, NTU	12.80± 0.14	17.00 ±0.02	3.30± 0.20	N/A
COD, mg/l	8.00 ±0.28	7.60 ±0.22	5.70 ± 20	10
BOD, mg/l	4.50± 0.14	5.50 ±0.12	1.20 ±0.01	10
Ammonia mg/l	0.62±0.06	0.53±0.04	0.48 ±0.02	N/A
ANIONS				
Salinity as Cl, mg/l	5.32±0.12	7.09±0.14	19.14 ±0.13	600
Nitrate, mg/l	0.55 ±0.12	0.38 ±0.13	6.20 ± 0.22	N/A
Bicarbonate	1.71 ±0.02	2.44 ±0.03	2.18 ± 0.20	N/A
Organics				
TPH, mg/l	<0.001	<0.001	<0.001	10
BTEX, mg/l	<0.001	<0.001	<0.001	N/A
PAHs, mg/l	<0.001	<0.001	<0.001	N/A
Heavy Metals				
Iron, mg/l	0.27 ±0.12	0.21 ±0.12	0.18 ± 0.20	1
Zinc, mg/l	0.06 ±0.02	0.06 ± 0.02	0.05 ± 0.20	0.03
Chromium, mg/l	<0.001	<0.001	<0.001	0.05
Lead, mg/l	<0.001	<0.001	<0.001	N/A
Nickel, mg/l	<0.001	<0.001	<0.001	N/A
Microbiology				
Heterotrophic bacteria, CFU/ml x 10 ³	2.13±0.14	2.08±0.14	2.62 ± 0.20	N/A
Heterotrophic fungi CFU/ml x 10 ³	2.24±0.12	1.59 ±0.14	2.15 ± 0.12	N/A
Hydrocarbon degrading				
Bacteria, CFU/ml	ND	ND	ND	N/A
Hydrocarbon degrading Fungi, CFU/ml	ND	ND	ND	N/A

Legend: N/A Not available. ND: Not detected.

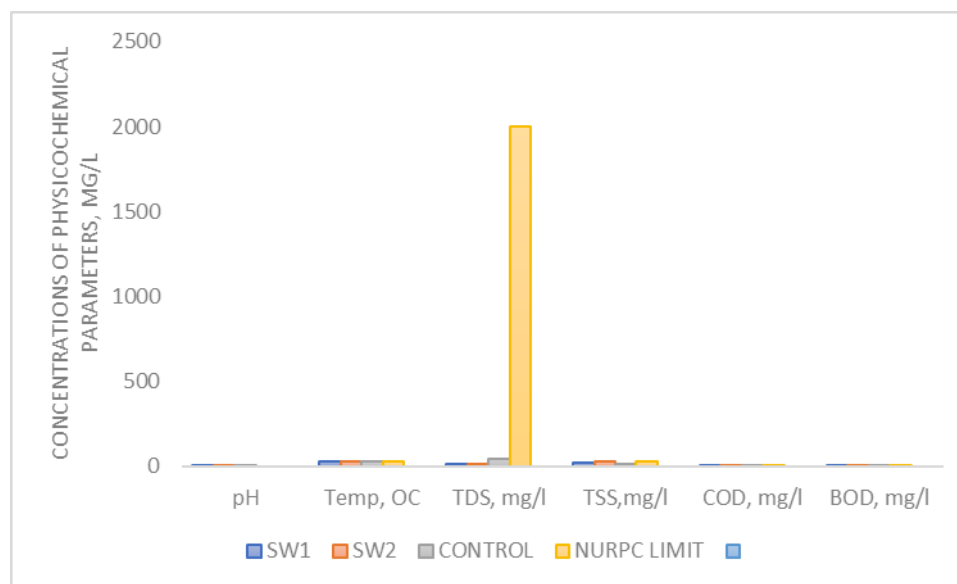


Fig 2 : Concentrations of physicochemical parameters in surface water samples in comparison with NURPC regulatory

3.3 Results of sediment analysis

The physical and chemical characteristics of the bottom sediments of the water station indicated the sediment pH values were moderately acidic for the period under review, which is 4.90 (Table 5). The total organic carbon content (TOC) had mean value of 2.02%. (Table 5). The predominant anions in the study area were sulphate, nitrate and phosphate with values of 16.40mg/kg, 3.22mg/kg and 3.71mg/kg respectively (Table 5). All the physicochemical parameters with NURPC regulatory limits complied with the available NURPC stipulated limits (Fig 2). Concentrations recorded for Iron was 5587 mg/kg, zinc recorded 0.12 mg/kg, chromium value was 5.20 mg/kg, nickel recorded 6.10 mg/kg and lead was not detected (<0.001 mg/kg) (Fig 3). Iron concentration was relatively high in comparison with other metals. The metal concentrations in the bottom sediment of the study station except Iron, were on the low side, suggesting degradation over the long period of time. The metals were all below the stipulated NURPC target and intervention limit (Fig 3). Total petroleum hydrocarbon concentration in the sediment was 5.46mg/kg while Polycyclic Aromatic Hydrocarbons (PAH) was not detected by the measuring instruments. All the metals analysed, TPH and PAH concentrations were below NURPC target and Intervention limits (Table 5). The heterotrophic bacteria and heterotrophic fungi counts were 2.36×10^4 and 2.18×10^4 CFU/g respectively. Hydrocarbon utilizing bacteria and fungi were detected and recorded 1.13×10^2 and 1.30×10^2 CFU/g respectively (Table 5).

Table 5 : Mean concentrations of Physicochemical parameters in Sediment samples

Sample ID	Sediment	NUPRC LIMIT (Target Value)	NUPRC LIMIT (Intervention Value)
pH	4.94± 0.06	NA	NA
Temperature, °C	27.30 ±0.14	NA	NA
Redox Potential	3.33 ± 0.07	NA	NA
ANIONS			
Sulphate, mg/kg	16.50 ±0.14	NA	NA
Nitrate, mg/kg	3.23 ± 0.01	NA	NA
Phosphate, mg/kg	3.72 ±0.01	NA	NA
Organic, mg/kg			
TOC, %	2.03 ±0.01	NA	NA
Organics			
TPH, mg/kg	5.48 ± 0.03	50	5000
PAHs, mg/kg	<0.001	0.02	1
Microbiology			
Heterotrophic Bacteria, CFU/g x 10 ⁴	2.36 ± 0.01	NA	NA
Heterotrophic Fungi, CFU/g x 10 ⁴	2.18 ± 0.02	NA	NA
Hydrocarbon degrading Bacteria, CFU/g x 10 ²	1.13 ± 0.01	NA	NA
Hydrocarbon degrading fungi, CFU/gx 10 ²	1.30 ± 0.14	NA	NA

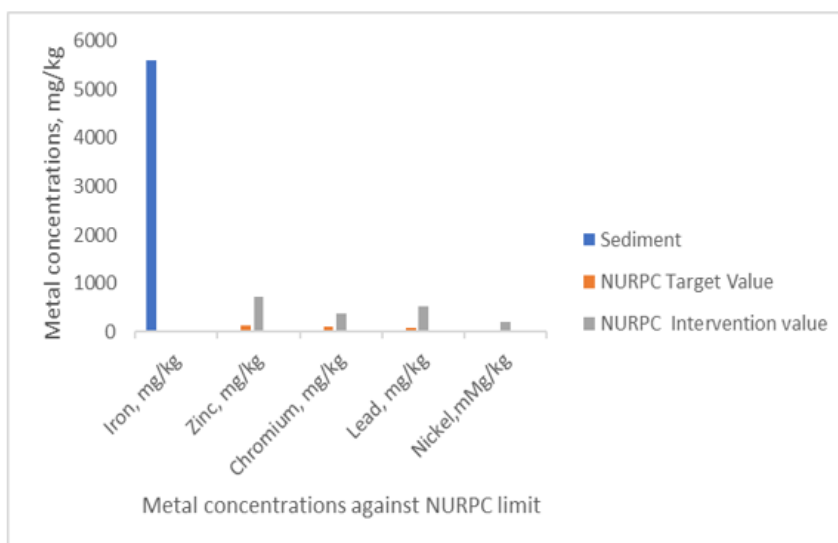


Fig 3 : Metals concentrations in sediment in comparison with NURPC regulatory limit

IV. DISCUSSION

The mean concentrations of physicochemical parameters of water samples from surface and ground water (boreholes) as well as the controls samples were in compliance with NURPC stipulated standards except pH was slightly acidic in all the locations and below the NURPC range of 6.5-8.5. The results showed that borehole water pH level fell between 5.8 (Obi-Ayagha Community Location BH1) to 6.8 (Obi-Ayagha Community location BH2) The control recorded a value of 6.3 also in non-compliance with the NURPC water quality standard threshold of 6.5 -8.5. pH is one of the most important operational water quality parameters and it usually has no direct impact on consumers, but could lead to corroding of infrastructures, especially metallic in nature, such as pipelines, the acidic particles corrode metal and cause paint and stone to deteriorate more quickly. They also dirty the surfaces of buildings and other structures such as monuments (USEPA, 2011).

The values for Total Dissolved Solid (TDS) in all the ground and surface water sampled, when compared to NURPC standard (2000mg/l), fell within the recommended standard. The river water, like all other aquatic medium possesses an ability to carry electric current due to the presence of soluble salts (ions) in the water. This parameter is dependent on water body temperature at the point of measurement, total concentration of dissolved ions, ionic mobility and valence. Therefore, river water conductivity is a measure of its ability to conduct electric current. Electrical conductivity of the river water, within the project area, had 30.0 μ S/cm for the two surface water samples collected. This result is consistent with the work of Uzoekwe and Oghosaine (2011) but slightly different from that of Wokoma and Etori (2017) which recorded higher electrical conductivity of the river water in the study area.

The Turbidity of samples from the study area were higher than that of the control. This correspond with other research work (Okoro, 2017) that artisanal

refinery have negative impacts on surface water, sediments and ground water quality and its effects are short lived generally, lasting a minimum of 4 to 5 tidal cycles ; are confined mainly to an area of few hundred metres from the point of operation (Newell et al, 2016). elements are essential micronutrients at lower doses (Hashim et al. 2011).

The heavy Metals analyzed in this cause of this study included Copper (Cu), Iron (Fe), Zinc (Zn), Chromium (Cr) and Lead (Pb). The results obtained for the metals in the surface and ground water samples showed that the heavy metals have low concentration and some (Lead, and Chromium) were below detection limit. Iron (Fe) recorded the highest concentration especially in the sediment sample (5587mg/kg), though no available regulatory limit for Iron in sediment. In the borehole water samples Iron ranged from 0.10-0.13mg/l, while for the surface water samples, it ranged from 0-21-0-27mg/l. The values were below NURPC intervention limit of 0.3mg/l but above FMENV limit of 0.05mg/l. Iron concentrations however do not pose potential health risk as they fell well within the recommended daily dietary allowance (7mg – 18mg) (Hurrell and Egli, 2010). Water with high iron concentrations may discolour and stain washed clothing. The iron in the sediment could bioaccumulate up the food chain and be a risk factor in agreement with findings of (Sorensen et al. 2015; Peiyue et al., 2021) who reported that toxic metals and metalloids are a risk factor for the health of both human populations and for the natural environment in ground water. Exposures at high concentrations can lead to severe poisoning, although some of these elements are essential micronutrients at lower doses (Hashim et al. 2011).

The TPH and PAH values in the surface and ground water samples were below the measuring instruments detection limit (<0.001mg/l). The river(surface) water below the regulatory limit of 10.00mg/l. This show that the surface and ground studied site were not polluted with petroleum hydrocarbon as a result of

the stoppage of the artisanal refinery activities in the study area over a long period of time. This could be as a result of various weathering processes, including dilution, volatilization, chemical reactions, adsorption on suspended particles and biodegradation

Chemical Oxygen Demand (COD) is the amount of oxygen required to decompose, via acid oxidation to CO₂ and water, of the organic matter present in water sample. Mean COD values of 7.80mg/l were recorded in the river water for period of this study. The BOD and COD values were generally below the NUPRC maximum allowable limit of 10.0mg/l for surface water (EGASPIN 2018). The Microbiology parameters analyzed for heterotrophic bacteria and heterotrophic fungi ranged from 1.13 x 10³CFU/ml to 1.26 x 10³CFU/ml and 1.00 x 10³CFU/ml to 1.15 x10³CFU/ml, respectively. Hydrocarbon degrading bacteria and hydrocarbon degrading fungi were not detected. This result is consistent with the work of Bashorun & Olamiju (2013) but slightly different from that of Oguzie & Okhagbuzo (2010) wherein Hydrocarbon degrading bacteria and hydrocarbon degrading fungi were detected. In the sediments, total heterotrophic bacterial loads recorded 2.36 x 10⁵ CFU/mg/g. Total Heterotrophic Fungi (THF) populations had 2.18 x 10⁵ CFU/mg/g. Hydrocarbon degrading bacterial had concentrations of 1.13 x 10²CFU/mg/g and hydrocarbon degrading fungi with the concentration of 1.30 x 10² CFU/mg/g. The microbial load was relatively low as a result of the low concentration of hydrocarbons which might have been degraded by natural attenuation

V. CONCLUSION

This study assessed the impact of artisanal refinery activities on surface water, sediment and ground water quality. The study showed that following the assessment (analysis) carried out on the various samples collected and water quality measurement, it was observed that; a few of the parameters analysed, in the surface water, sediment and ground water

samples did not comply(Iron and Zinc) while a large number of them complied. The reasons could be attributed to natural attenuation which must have taken place.

The water quality results obtained in the course of the study showed that the abandoned artisanal refinery has no significant impact on the surface water, sediment and ground water quality and the surrounding environment at large at the time of sampling as almost all the parameters and TPH analysed complied with the regulatory limits. Although the pH values of the ground and surface water samples were consistently lower than that of the regulatory limits. While there was an increased level of phosphate in the source station, there was a reduction of Nitrate and total organic matter in the same source. However, some of the parameters such Iron (5548mg/kg) in the sediments was high and some related studies within and outside the study area indicating some impacts which could be mostly anthropogenic. These impacts if not checked and the make-shift refining of the crude oil regulated, could have some deleterious effects on the surface water, sediment and ground water quality in the near future. The study therefore, concluded that the Nigeria artisanal petroleum refineries could be sources of surface water, sediment and ground water quality pollution in the environment. Although, due to prolonged (about 10 years) abandonment of the artisanal refining activities in the studied site, natural attenuation had degraded most of the contaminants hence most were within regulatory limits.

The integration of artisanal and modular refinery operations into the oil and gas sector will not only promote the inclusion of more local content in the industry; it will advance the use of home-grown technology in the refining of petroleum products and also curtail illegal oil activities in the Niger Delta regions.

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Cite this article as :

Tudararo-Aherobo Laurelta, Maya Bright, "Assessment of the Impacts of Artisanal Refinery of Crude Oil On Surface Water, Ground Water And Sediment Quality At Obi-Ayagha Community In Delta State Nigeria", *International Journal of Scientific Research in Science and Technology (IJSRST)*, Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 10 Issue 3, pp. 1164-1181, May-June 2023. Available at doi : <https://doi.org/10.32628/IJSRST52310325>
Journal URL : <https://ijsrst.com/IJSRST52310325>