Heavy Metal Contamination Index, Metal Index and Polycyclic Aromatic Hydrocarbon Content of Ochani River in Ogoni, 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.

Original Research Article

ABSTRACT

The Heavy metal Pollution Index (HPI), Metal Index (MI) and the Polycyclic Aromatic Hydrocarbon (PAH) contents of crude oil-polluted Ochani River in Ejamah-Ebubu community were investigated using physicochemical properties, Heavy Metal Analytic Method (AAS), GC-MS method and heavy metal pollution model. The results showed that Ochani River sampling station 2 (ORPS 2) had highest values of temperature, conductivity, turbidity, total solid (TS), total dissolved solid (TDS), Total Suspended Solid (TSS), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and nitrates with values as (32^oC, 260 μScm^{-1}, 42NTU, 460 mg/L, 526 mg/L, 400 mg/L, 15 mg/L, 10 mg/L, 25 mg/L and 7.5 mg/L respectively) compared to Ochani River sampling station 1 (ORPS 1) with values as (30^oC, 200 μScm^{-1}, 38NTU, 400 mg/L, 500 mg/L, 380 mg/L, 13 mg/L, 9.0 mg/L, 22 mg/L and 6.8mg/L respectively). However, these values of ORPS 1and 2 were higher than the unpolluted water sample (UWS) and WHO standard limits. Heavy metals obtained in Ochani River were rankedas Fe > Cu >Pb> Zn > Cr > Cd >As. The values obtained from crude oil polluted water samples were highest when compared with the values obtained of the UWS and WHO standard limit. The heavy metal pollution index of Ochani River was calculated as 402.32 mg/L which was higher compared with the critical pollution index value of 100. The metal index obtained was 49.88mg/L showing that the water quality classified to be seriously polluted. The Polycyclic Aromatic Hydrocarbon (PAH) components present in Ochani River include

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fluorene, naphthalene, dibenzyl(a,h)anthracene, benzo(k)fluoranthene and benzo(a)pyrene. However, these values of PAH components obtained were highest in ORPS 2 compared to ORPS 1. No PAH content was detected in UWS. However, the values of PAH obtained in both ORPS 1 and 2 were higher compared with WHO standard limit. In conclusion, Ochani River which is an important river used for irrigation and domestic activities by the populace in that community, is highly polluted with heavy metals and carcinogenic PAHs. We therefore recommend that Ochani River is unsafe for drinking, domestic and agricultural activities of the community where it is sited.

1. INTRODUCTION

The emphasis on pollution is limited without heavy metal and Polycyclic Aromatic Hydrocarbon (PAH) impact. Heavy metals are group of elements that exist in nature with relatively high density than water at $5gcm^{-3}$ and exhibit the properties of metal [1]. Further, Polycyclic Aromatic Hydrocarbon (PAH) is an organic pollutant that are formed due to incomplete combustion of organic substances at elevated temperature and are obtained either from natural or anthropogenic activities [2]. PAH can exist in air and soil but, the occurrence are of two phases: gaseous and particulate phase. The hydrophobic nature of PAH increase the soil retention efficiency which leads to high rate of precipitation in soil and sediment [3]. The disastrous consequences of heavy metal and PAH exposure in the ecosystem has been proven via researches over the years. There route of exposure are mainly through anthropogenic activities which are on the increase due to industrial revolution [2]. However, the influence of such activities has led to pollution and also rendered the water bodies unfit for domestic and life form support [4]. The importance of water in the ecosystem cannot be over-emphasize as its utilization in agricultural sector especially contaminated water suggest it can be harmful considering that these pollutants possess the capacity to bio-accumulate. Moreover, the absorption of water by plants is affected through factors such as metal solubility, plant species, pH, soil type etc. [5]. Crude oil contain heavy metals, polycyclic aromatic hydrocarbon etc., and these pollutants poses a danger to the environment when not properly managed [6]. Consequently, crude oil spillage in Nigeria has affected its water bodies although the impact is localized more in the riverine area of the country as they contain more deposit of crude oil. The production and transportation processes have released unprecedented quantity of crude oil in the environment. Moreover, several factors such as drilling rigs, corrosion of oil piping and installations, rusting of pipeline, leakage, operational discharges, vandalism, etc., has contributed to environmental exposure of crude oil pollutant [7]. Additionally, political vices and poverty have contributed to aggressive vandalisation of pipelines to steal products in Nigeria. Crude oil impacts on aquatic environment involves alteration of physicochemical properties, depletion of dissolved oxygen, alteration or variability of the water temperature, reduction in the populations of aquatic animals which is attributed to reduces life cycle and breeding owing to contaminations with toxic substances, loss of biodiversity, decrease in amphipod population, wildlife habitats become too hostile for continued existence of it habitants [8]. Therefore, the exposure of crude oil pollutant in the bodies has led to various health challenge and economic loss. Impacts of the health challenges are stomach irritations, muscle weakness, change in nerve reflex, brain and liver swelling, kidney and heart damage, ulcer, cancer and eventual death of the victim [9] while, the government of Nigeria revenue base through crude oil production are dwindling. This study examines the Heavy metal Pollution Index (HPI), Metal Index (MI) and the PAH content of Ochani River, located in Ejama-Ebubu Community, Eleme Local Government Area of the southeastern part of Ogoniland in Rivers State, Nigeria. The investigation helps to determine the extent of crude oil pollution in Ochani River after thirty (30) years of oil spillage.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

The study area is Ochani River, located in Ejama-Ebubu community of Eleme Local Government Area of the Southeastern part of Ogoniland in Rivers State is a freshwater ecosystem used by the populace community as source of drinking water and a focal point of most commercial and cultural activities. The geographical dimension of the river is

approximately on latitude 05° N and longitude 07° 8° E, covering a land mass of approximately 24.19ha and almost completely flanked by farmland except at North-West end. The river runs through the southeast and eastwest directly into Ogu Creek of Bonny River in Okirika L.G. A. [10]. This river is the source of water for the surrounding community, it is beneficial to the farmlands and other life supports systems. Though, beyond the river is a swamp with observable crude oil pollution [11].

2.2 Collection of Water Sample

The samplings of crude oil polluted Ochani River were carried out during the rainy season in order to ensure total mix up of activities in the water body including tidal current during run-off. The containers were thoroughly washed, sterilized with 70% ethanol, rinsed with distilled water severally and finally with the sample solution before collection of the sample for analysis. The collection of the crude oil polluted Ochani River water sample followed the procedure reported by Olukanni et al. [4]. The water samples were collected with a 2 liter plastic cup and then transferred into 25 liter containers with screw caps, labeled appropriately as ORPS 1, ORPS 2 (at a depth of 8 – 10cm in separate pre-conditioned and alkaline rinsed plastic cans indicating the collection points) and UWS (unpolluted tap water sample away from the point of pollution) and conveyed to the laboratory where they were stored in a fridge at 12°C temperature range. The crude oil polluted water samples were analyzed within 48 hrs of arrival.

2.3 Physicochemical Analysis

The physicochemical properties (pH, temperature, color, conductivity, turbidity, total solid, total suspended solid, total dissolved solid, total hardness, dissolved oxygen, biochemical oxygen demand and chemical oxygen demand) of the water samples were analyzed using the AOAC [12].

2.4 Heavy Metal Analysis

An aliquot of these heavy metals iron, zinc, copper, chromium, cadmium, arsenic, lead were concentrated and analyzed using Agilent FS240AA Atomic Adsorption Spectrometer according to the method of APHA [13].

2.5 Heavy Metal Pollution Index

The overall quality of water with respect to individual heavy metal concentration is estimated

using the Heavy Metal Pollution Index (HPI). This technique of ranking offers the water quality rating which the value is between zero and one. This affords the parameter to obtain its individual quality and its inverse proportionality to the recommended standards [S_i] [14].

The calculation of HPI involves the 3 major steps which includes:

1. Determination of weightage of ith parameter

The weightage of ith parameter

$$Wi = \frac{k}{Si} \tag{1}$$

Where

W_i = the unit weightage
S_i = the recommended standard for i[th] parameter
k = the constant of proportionality

2. Calculation of the individual quality rating for each of the heavy metal

$$Qi = \frac{100\ Vi}{Si} \tag{2}$$

Where

Q_i = the sub index of ith parameter,
V_i = the monitored value of the ith parameter and
S_i = the standard or permissible limit for the ith parameter.

3. Summation of these sub-indices in the overall index

$$HPI = \frac{\sum (QiWi)ni}{\sum (Wi)ni} \tag{3}$$

Where

Q_i = the sub-index of ith parameter.
W_i = the unitweightage for i[th] parameter
n_i = the number ofparameters considered.

The critical pollution index value = 100.

2.6 Metal Index (MI)

This model determines the suitability of the water for consumption. This borders on the water quality through its effects on human health [14].

$$MI = \frac{\Sigma\,[Ci\,/]}{(MAC)i} \tag{4}$$

Where

C$_i$ = Mean concentration of each metal and
MAC = Maximum allowable concentration

The higher the concentration of individual metals compared to its respective MAC value, the worse the water quality. MI value > 1 is a threshold of warning to pollution severity as depicted in the Table 1 [15].

Table 1. Water quality classification using mean index

MI	Characteristics	Class
<0.3	Very Pure	I
0.3 – 1.0	Pure	II
1.0 – 2.0	Slightly affected	III
2.0 – 4.0	Moderately affected	IV
4.0 – 6.0	Strongly affected	V
>6.0	Seriously affected	VI

2.7 Polycyclic Aromatic Hydrocarbon Content Analysis

The PAH contents of the crude oil polluted Ochani River water samples was analyzed using the Gas Chromatography – Mass Spectroscopy (GC-MS) to detect polycyclic aromatic hydrocarbon compounds using the method of AOAC [12].

2.8 Statistical Analysis

Bonferroni test was used to test for significance of the different parameters considered in the study. Bonferroni was applied because of its flexibility, simplicity and ability to prevent possibility of type 1 error. In addition, Beanplot was used to compare the distributions of the different groups in term of their means. R software was to generate the results and plot.

3. RESULTS

3.1 Physicochemical Properties of Crude Oil Polluted Ochani River and the Unpolluted Water Samples

The results of the physicochemical properties of the crude oil polluted Ochani River and the unpolluted water samples using mean and standard are shown on Table 2. The recorded

parameters such as color, pH, temperature, Electrical Conductivity (EC), turbidity, total solid, total suspended solid, total dissolved solid, total hardness, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand and exchangeable bases. These results obtained from Ochani River sampling station 2 (ORPS 2) had highest values of temperature, conductivity, turbidity, Total Solid (TS), Total Dissolved Solid (TDS), Total Suspended Solid (TSS), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and nitrates (32°C, 260µScm^{-1}, 42NTU, 460mg/L, 526mg/L, 400mg/L, 15mg/L, 10mg/L, 25mg/L and 7.5mg/L respectively) compared to Ochani River sampling station 1 (ORPS 1) with values as (30°C, 200µScm^{-1}, 38NTU, 400mg/L, 500mg/L, 380mg/L, 13mg/L, 9.0mg/L, 22mg/L and 6.8mg/L respectively) while ORPS 1 had higher values of pH, hardness, calcium, magnesium, sodium, potassium, chloride, phosphates and sulphates when compared with ORPS 2.However, the polluted water samples had higher values when compared with the Unpolluted Water Sample (UWS) and WHO standard limits. The study observed the color of Ochani River polluted water samples were dark brown when compared to the colorless property of the Unpolluted Water Sample (UWS). The temperature of the polluted samples (ORPS 1 and 2) were slightly higher than the WHO standard limit. The results showed there was a decrease in pH of the Ochani River polluted water sample (5.8 & 6.0) compare to the pH of the unpolluted water sample and the permissible values given by WHO. The UWS values were either equal to or slightly lower than the WHO standard limit.

However, to test for the significance of the different parameters, the physical and chemical properties were separated in the statistical analysis. The test showed significant difference between TDS and Turbidity. (p value=0.0075) as well as between TS and Turbidity (p value=0.0400). For the chemical properties, the test showed significant difference between EC and all the other chemicals; TH and (BOD, COD, DO, K, Na, NO$_3$, PO$_4$) as well as Cl and (BOD, COD, DO, K, NO$_3$, PO$_4$).

The distributions of the different groups in the physical and chemical properties in terms of their means are shown in Figs. 1 & 2. In Fig. 1, the mean of TDS is higher than that of the other physical properties with Turbidity having the least mean. For Fig. 2, the mean of EC is higher than that of the other chemical properties.

Table 2a. Physicochemical properties of the crude oil polluted and the unpolluted water samples

Parameters	ORPS 1	ORPS 2	UWS	WHO
Color	Dark brown	Dark brown	Colorless	Colorless
pH	6.0	5.8	7.8	6.5 – 8.5
Temperature ^{o}C	30	32	26	25 – 30
Conductivity μScm^{-1}	200 ±10.0	260 ±10.0	10 ±0.5	133.5
Turbidity NTU	38 ±0.2	42 ±0.5	12 ±0.4	5
Total Solid (mg/L)	400 ±15.0	460 ±10.0	10 ±0.1	140
Total Dissolved Solid (mg/L)	500 ±10.0	526 ±1.0	15 ±0.5	500
Total Suspended Solid (mg/L)	380 ±5.0	400 ±2.0	8 ±0.2	150
Total Hardness mg/L	125.0 ±0.4	100.0 ±1.0	32.03 ±0.03	20 – 40
Dissolved Oxygen mg/L	13.0 ±0.3	15.0 ±0.2	6.0 ±0.15	9.44
BOD mg/L	9.0 ±1.0	10.0 ±0.5	4.0 ±0.1	4.0
COD mg/L	22.0 ±0.2	25.0 ±0.4	10.0 ±0.3	10.0
Calcium (Ca) mg/L	80.0 ±0.2	60.0 ±0.7	32.0 ±0.1	50 – 100
Magnesium (Mg) mg/L	45.0 ±0.5	40.0 ±0.3	0.3 ±0.1	10.0
Sodium (Na) mg/L	30.0 ±1.0	28.0 ±2.0	6.2 ±2.0	23.0
Potassium (K) mg/L	10.0 ±0.15	7.22 ±0.02	4.8 ±0.05	20.0
Chlorine (Cl) mg/L	98.0 ±1.0	80 ±0.2	57.2 ±0.05	16.0
Nitrates (NO_3)mg/L	6.8 ±0.05	7.5 ±0.07	1.0 ±0.10	1.08
Phosphates (PO_4) mg/L	18.45 ±0.1	16.23 ±0.38	2.1 ±0.10	6.00
Sulphates (SO_4) mg/L	43.34 ±0.02	38.90 ±0.1	4.0 ±0.10	21.02

Legend: ORPS1 = Ochani River Polluted Sample station 1, ORPS 2 = Ochani River Polluted Sample station 2, UWS = Unpolluted Water Sample, WHO = World Health Organization, BOD = Biochemical Oxygen Demand, ± = Standard deviation, COD = Chemical Oxygen Demand

Table 2b. Bonferroni test

Pairwise comparisons using t tests with pooled SD

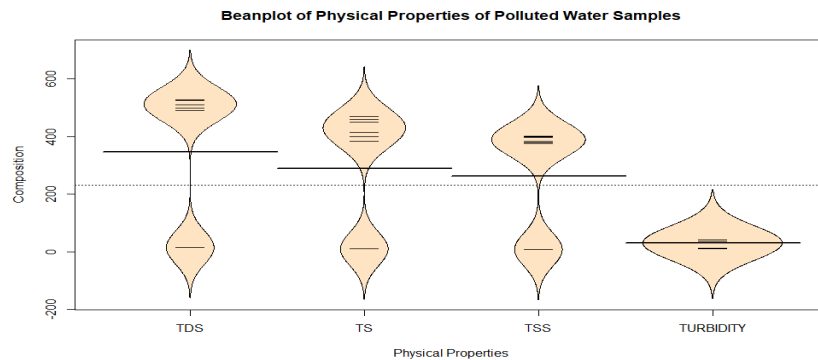|	BOD	Ca	Cl	COD	DO	EC	K	Mg	Na	NO3	PO4	SO4
Ca	0.29	-	-	-	-	-	-	-	-	-	-	-
Cl	0.00	1.00	-	-	-	-	-	-	-	-	-	-
COD	1.00	1.00	0.04	-	-	-	-	-	-	-	-	-
DO	1.00	0.55	0.00	1.00		-	-	-	-	-	-	-
EC	0.00	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-
K	1.00	0.27	0.00	1.00	1.00	0.00	-	-	-	-	-	-
Mg	1.00	1.00	0.27	1.00	1.00	0.00	1.00	-	-	-	-	-
Na	1.00	1.00	0.07	1.00	1.00	0.00	1.00	1.00	-	-	-	-
NO3	1.00	0.18	0.00	1.00	1.00	0.00	1.00	1.00	1.00	-	-	-
PO4	1.00	0.64	0.01	1.00	1.00	0.00	1.00	1.00	1.00	1.00	-	-
SO4	1.00	1.00	0.29	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	-
TH	0.00	1.00	1.00	0.00	0.00	0.00	0.00	0.06	0.02	0.00	0.00	0.07

Fig. 1. Beanplot showing the physical properties of polluted water samples
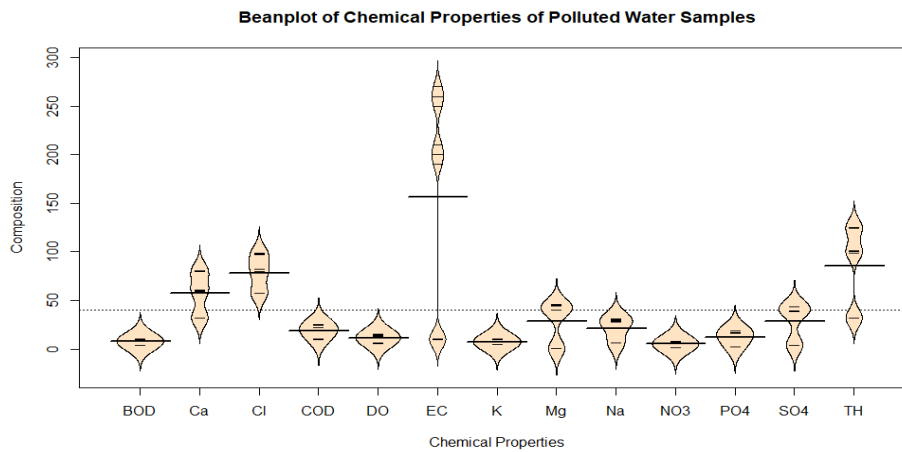
Fig. 2. Beanplot showing the chemical properties of polluted water samples

3.2 Heavy Metal Content of Crude Oil Polluted Ochani River and Unpolluted Water Sample

The results of the heavy metal content of the crude oil-polluted Ochani River and the unpolluted water samples are presented on Table 3. The results obtained showed that seven heavy metals were obtained in the three sampling stations; they include copper, zinc, iron, cadmium, lead, chromium, and arsenic. Among the sampling stations, most of the heavy metals in ORPS 2 contained higher values of heavy metals compared to the ORPS 1 and the unpolluted water sample. This is followed by ORPS 1 and the least heavy metal values were obtained in the UWS. The concentrations of Iron were observed to be higher in all the stations sampled (10.76mg/L and 10.23mg/L), compared to the values obtained from unpolluted sample (0.03mg/L) and standard limit (0.3mg/L) given by

WHO. The values obtained for copper was higher in ORPS 2 and ORPS 1 (3.5mg/L and 3.0mg/L respectively) compared to the UWS. The concentration of lead was found to be higher in ORPS 1 (3.0mg/L) than in ORPS 2 (1.0mg/L). However, the two sampling points have lead (Pb) concentrations more than the unpolluted sampling station (-0.02mg/L) and WHO limit (0.01mg/L). These results also show that the values obtained forelements such as; zinc, chromium and arsenic concentrations were higher in ORPS 2 than in ORPS 1 and both sampling stations were higher when compared with values obtained from the UWS and WHO standard limit. Generally, the concentrations of heavy metals obtained in Ochani River polluted with crude oil were higher in the two polluted sampling points compared with the values obtained in the unpolluted sampling point and the values are greater than that standard value given by World Health Organization (WHO).

Table 3. Heavy metal content of Ochani River, polluted and unpolluted with crude oil

Heavy Metals	ORPS 1 (mg/L)	ORPS 2 (mg/L)	UWS (mg/L)	WHO Standard	SEM
Copper (Cu)	3.0 ±0.1	3.5 ±0.1	0.01 ±0.0	2.0	0.25
Zinc (Zn)	0.25 ±0.01	0.45 ±0.01	-0.01 ±0.0	3.0	0.10
Iron (Fe)	10.23 ±0.01	10.76 ±0.02	0.03 ±0.01	0.3	0.27
Cadmium (Cd)	0.07 ±0.01	0.07 ±0.01	0.01 ±0.01	0.03	0.00
Lead (Pb)	3.00 ±0.1	1.00 ±0.1	-0.02 ±0.01	0.40	1.00
Chromium (Cr)	0.06 ±0.02	0.11 ±0.02	0.01 ±0.01	0.05	0.03
Arsenic (As)	0.02 ±0.01	0.06 ±0.01	-0.07 ±0.01	0.01	0.02

Legend: ORPS 1 = Ochani River Polluted Sample station 1, ORPS 2 = Ochani River Polluted Sample station 2, UWS = Unpolluted Water Sample, WHO = World Health Organization, mg/L = Milligram per liter, ± = Standard deviation, SEM = Standard Error of Mean

3.3 Heavy Metal Pollution Index (HPI) of Ochani River Polluted with Crude Oil

The results of the heavy metal pollution index of the crude oil–polluted water samples ofOchani River are presented on Tables 4 – 7. The concentration of heavy metals in Ochani River ranked as Fe > Cu >Pb> Zn > Cr > Cd >As with the concentration of Iron (Fe) being the highest and Arsenic (As) the smallest in value. Among the elements in the polluted water samples, only Zn was obtained below permissible limit. However, all elements of the UWS were obtained at concentration below the WHO permissible limits. In Table 4, the methodology of HPI calculation was presented with the mean concentrations of ORPS 1 & 2 and the value

obtained was 402.32mg/L and this value obtained was greater than the critical index value of 100 with revere to heavy metals.

The HPI values of the two (2) sampling points were also calculatedseparately for each sampling point on Table 5 and Table 6. The concentration of HPI for Ochani River polluted sampling station 1 (ORPS1) recorded as 377.27mg/L (Table 5) while for ORPS 2, the HPI value obtained was 565.43mg/L (Table 6) respectively. This shows that Ochani River polluted sampling station 2 had higher value than the ORPS station 1 with revere to heavy metals.This could be ascribed to the directional flow of the water or because of the various activities that are being carried out at the river bank.

Table 4. Mean HPI for Ochani river sampling stations (ORPS 1 & ORPS 2)

Heavy Metals	Range	Mean Conc. V_i (mg/L)	WHO (2011) highest permitted value S_i (mg/L)	Unit weightage W_i (mg/L)	Sub-index Q_i (mg/L)	$W_i \times Q_i$ (mg/L)
Cu	3 – 3.5	3.25	2.0	0.50	162.50	81.25
Zn	0.25 – 0.45	0.35	3.0	0.33	11.67	3.85
Fe	10.23–10.76	10.50	0.3	3.33	3500.00	11655.00
Cd	0.07	0.07	0.03	33.33	233.33	7776.89
Pb	1.0 – 3.0	2.00	0.40	2.50	500.00	1250.00
Cr	0.06 – 0.11	0.09	0.05	20.00	180.00	3,600.00
As	0.02 – 0.06	0.04	0.01	100.00	400.00	40000.00
				$\sum W_i$ 159.99		$\sum Q_iW_i$ 64,366.99
HPI = $\sum Q_iW_i / \sum W_i$		HPI= 402.32 mg/L				

Table 5. HPI for Ochani river sample station 1

Heavy Metals	Mean Conc. V_1 (mg/L)	WHO (2011) highest permitted value S_1 (mg/L)	Unit weightage W_1 (mg/L)	Sub-index Q_1 (mg/L)	$W_1 \times Q_1$ (mg/L)
Cu	3.00	2.0	0.50	150.00	75.00
Zn	0.25	3.0	0.33	8.33	2.75
Fe	10.23	0.3	3.33	3410.00	11355.30
Cd	0.07	0.03	33.33	233.33	7776.89
Pb	3.00	0.40	2.50	7500.00	18750.00
Cr	0.06	0.05	20.00	120.00	2,400.00
As	0.02	0.01	100.00	200.00	20,000.00
			$\sum W_1$ 159.99		$\sum Q_1W_1$ 60,359.94
HPI$_1$ = $\sum Q_1W_1 / \sum W_1$		HPI$_1$ = 377.27mg/L			

Table 6. HPI for Ochani river sample station 2

Heavy Metals	Mean Conc. V_2 (mg/L)	WHO (2011)highest permitted value S_2 (mg/L)	Unit weightage W_2 (mg/L)	Sub-index Q_2 (mg/L)	$W_2 \times Q_2$ (mg/L)
Cu	3.5	2.0	0.50	175.00	87.50
Zn	0.45	3.0	0.33	15.00	4.95
Fe	10.76	0.3	3.33	3586.67	11943.60
Cd	0.07	0.03	33.33	233.33	7776.89
Pb	1.00	0.40	2.50	2500.00	6250.00
Cr	0.11	0.05	20.00	220.00	4400.00
As	0.06	0.01	100.00	600.00	60000.00
			$\sum W2$ 159.99		$\sum Q2W2$ 90,462.94
$HPI_2 = \sum Q2W2 / \sum Wi$		HPI_2 = 565.43 mg/L			

A summary of the HPI calculated was presented on Table 7. The mean value of the individual sample stations of ORPS 1 and ORPS 2 was obtained as 471.35mg/L (Table 7). When comparing the mean concentration of the sampling stations and the mean of the individual sampling stations, the values obtained was similar (402.32mg/L and 471.35mg/L respectively) and both are still higher than the critical pollution index value of 100 showing that the whole Ochani River was exceedingly polluted with heavy metals after 30years of crude oil contamination.

3.4 Metal Index (MI) of Ochani River Polluted with Crude Oil

The Metal Index (MI) of crude oil polluted Ochani River was calculated on Table 8. The results obtained showed that the value of the metal pollution index was 49.88 mg/L.

3.5 Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) from Crude Oil-Polluted Ochani River

The results of the concentration of Polycyclic Aromatic Hydrocarbon (PAH) in crude oil polluted Ochani River are presented on Table 9. The PAH content in Ochani River showed 10 different PAH compositions which includes Fluorene, Naphthalene, Dibenzyl (a,h) anthracene, Anthracene, Benzo (a) anthracene, Benzo (k) fluoranthene, Benzo (g,h,i) perylene, Acenapthylene, Benzo (a) pyrene and Phenanthrene. The result obtained showed that nine (9) PAH components were detected in ORPS 1, ten (10) PAH components were

Table 7. HPI recorded at different sampling stations

Sampling Stations (ORPS 1 & 2)	ORPS 1	ORPS 2
402.32 mg/L	377.27 mg/L Mean of HPI (ORPS 1 & ORPS 2) 471.35 mg/L	565.43 mg/L

Table 8. Metal index of Ochani River polluted with crude oil

Heavy Metals	Mean Conc. C_i (mg/L)	WHO (2011)highest permitted value $(MAC)_I$ (mg/L)	MI (mg/L)
Fe	10.50	0.3	35.00
Cu	3.25	2.0	1.63
Zn	0.35	3.0	0.12
Cd	0.07	0.03	2.33
Pb	2.00	0.40	5.00
Cr	0.09	0.05	1.80
As	0.04	0.01	4.00
$\sum$ **MI**			**49.88**

detected in ORPS 2 while none was detected in the UWS. Naphthalene had the highest concentration in both sampling points (0.51mg/L and 0.46mg/L) while acenapthylene had the least value of (0.01mg/L) on both sampling stations. Compounds such as naphthalene and benzo (a) pyrenewere higher in ORPS 1 than in ORPS 2 while compounds such as fluorene, benzo (g,h,i) perylene, anthracene and phenanthrenewas higher in ORPS 2 than ORPS 1. Benzo (g,h,i) pyrene was obtained in ORPS 2 but none was detected in ORPS 1. However, all the values obtained were higher than the value given by water quality guideline of Environmental Protection Agency.

Statistical test of significance for the parameters in Table 9a indicated that there exists significant difference between FLUORE and all others except NAPH; NAPH and others except FLUORE; PHENAN and (ACENAP, FLUORE, NAPH); ANTHRA and ACENAP; as well as BA PYRE and ACENAP.

The distributions of the different groups in the PAH content of polluted Water Samples in terms of their means is shown in Fig. 3. In Fig. 3, the mean of NAPH is higher than that of the other PAH, with BGHI PERY having the least mean.

Table 9a. Concentration of Polycyclic Aromatic Hydrocarbons (PAH) from Ochani river, polluted with crude oil

Polycyclic Aromatic Hydrocarbon	ORPS 1 (mg/L)	ORPS 2 (mg/L)	UWS (mg/L)	WQG (mg/L)	Carcinogenicity
Fluorene	0.36 ±0.01	0.40 ±0.012	NF	0.0030	None Carcinogen
Naphthalene	0.51 ±0.002	0.46 ±0.004	NF	0.0011	None Carcinogen
Dibenzyl(a,h)anthracene	0.08 ±0.002	0.09 ±0.002	NF	-	Carcinogen
Anthracene	0.14 ±0.002	0.29 ±0.002	NF	0.00001	None Carcinogen
Benzo(a)anthracene	0.22 ±0.002	0.27 ±0.075	NF	-	Carcinogen
Benzo(k)fluoranthene	0.04 ±0.01	0.06 ±0.013	NF	-	Carcinogen
Benzo(g,h,i)perylene	NF	0.18 ±0.001	NF	-	None Carcinogen
Acenapthylene	0.01 ±0.002	0.01 ±0.002	NF	-	None Carcinogen
Benzo(a)pyrene	0.43 ±0.003	0.34 ±0.007	NF	0.00002	Strong Carcinogen
Phenanthrene	0.16 ±0.003	0.24 ±0.003	NF	0.0004	None Carcinogen

Legend: NF = Not Found, ORPS 1 = Ochani River Polluted Sample station 1, ORPS 2 = Ochani River Polluted Sample station 2, UWS = Unpolluted Water Sample, WQG = Water quality guideline, mg/L = Milligram per liter, ± = Standard deviation, SEM = Standard Error of Mean, – = unknown, ± = Standard deviation

Table 9b. Bonferoni test

Pairwise comparisons using t tests with pooled SD

	ACENAP	ANTHRA	BA ANTH	BA PYRE	BGHI PERY	BK FLORAN	DAH ANTH	FLUORE	NAPH
ANTHRA	0.00	-	-	-	-	-	-	-	-
BA ANTH	0.21	1.00	-	-	-	-	-	-	-
BA PYRE	0.02	1.00	1.00	-	-	-	-	-	-
BGHI PERY	1.00	0.44	1.00	1.00	-	-	-	-	-
BK FLORAN	1.00	0.05	1.00	0.25	1.00	-	-	-	-
DAH ANTH	1.00	0.43	1.00	1.00	1.00	1.00	-	-	-
FLUORE	0.00	0.04	0.00	0.01	0.00	0.00	0.00	-	-
NAPH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	-
PHENAN	0.01	1.00	1.00	1.00	0.97	0.13	0.97	0.02	0.00

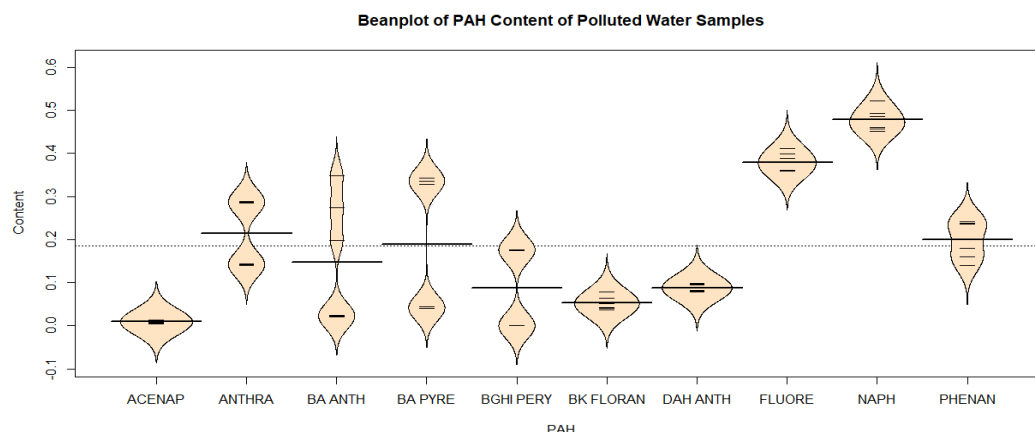**Beanplot of PAH Content of Polluted Water Samples**

Fig. 3. Beanplot showing the PAH contents of polluted water samples

4. DISCUSSION

4.1 The Quality of Water from Ochani River

The physiochemical analysis of Ochani River in both sampling station 1 and 2 reveals the rivers level of contamination. Though, sampling station 2 is less toxic than sampling station 1 but, both of the sample stations are appears to be toxic when compared to the control and WHO standard limit. The dark brown color observed may be attributed to microbial metabolism which changed the color property of Ochani River. The difference in the contamination level of the sampling stations indicates that the hydrocarbon contamination in the water was not uniformly distributed along the perceptible route of the river [11]. Consequently, the acidic nature of the Ochani River is probably because of the carbonates influx emanating from microbial activities within the water [16]. Acidity in such aquatic environment has altered various ecological niches of organisms. Depletion in oxygen level reveals the impact of microbial degradation of the crude oil as such activity renders oxygen unavailability in aquatic environment thereby, suffocates aquatic life form [17]. However, the heavy metals analyzed for sampling station 1 and 2 were all above the control and WHO standard limit. This suggests that water from both sampling stations are contaminated therefore, the toxicity of the water is imminent. The highest heavy metal concentrations were within iron, copper and lead. However, lead is the most toxic metal which precipitates on the sediments [18]. According to Mitra et al. [19], the presence of heavy metal in the crude oil polluted Ochani River is attributed to heavy metal content of crude oil released in the water through spills and other man made activities carried out in the water. The Metal Index (MI) records water quality classifications thus result reveals that Ochani River is grossly polluted with heavy metals which indicate low water quality [15]. The heavy metal calculated the pollution index value was higher than the critical pollution index of 100. This indicates that Ochani River is critically polluted [14]. Further, within the detected PAH compositions are carcinogenic PAHs. Though, out of the ten PAHs, only 4 carcinogenic PAHs were detected. These further implicate the low quality of water as thereis numerous health challenges associated with these pollutants [20]. According to Munyengabe et al. [21] the PAH compounds obtained in Ochani River that are implicated in causing cancer were benzo(a)pyrene, dibenzyl(a,h)anthracene, benzo(a)anthracene, benzo(k)fluoranthene while fluorene, naphthalene, anthracene, benzo(g,h,i)perylene, acenapthylene and phenanthrenewere reported as non-carcinogens [22].

5. CONCLUSION

The result shows that the HPI value of the two sampling stations analyzed (ORPS 1 and ORPS 2) was 402.32mg/L which exceeded the critical pollution index of 100. Also recorded was the metal index value of 49.88mg/L which supersedes the values for water quality regarding heavy metal pollution. Comparing these critical situations to their physicochemical properties, it was observed that the values obtained exceed the standard permissible limits of World Health Organization (WHO). The presence of carcinogenic PAH components in the river is also of great concern therefore, it is recommended that Ochani River is unsafe for drinking, domestic and agricultural purpose to the populace around the environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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