



## **Evaluation of the Total Dispersion and Distribution of Petroleum Hydrocarbons in the Aya Stream, Located in Niger Delta: Implications on the Quality and Health of Aya Water Stream**

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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**

Globally, oil spills are known catastrophic events with harmful consequences that tend to endanger plant, animal and human life. The dispersion and distribution of petroleum hydrocarbons levels were investigated to evaluate its effect on the quality and health of Aya stream, located in the Niger Delta sub region, south east Nigeria. Water samples were collected from the stream, which is the most available source of water in Ikot Ada Udo local community, five years after an extensive oil spillage between the months of June and November 2012. These samples were analyzed to assess the level of total petroleum hydrocarbon (TPH) and physicochemical enrichment using Spectrophotometric with 1g of Bonny Light and Bonny Medium Crude Oils dissolved in 1000 ml of tetrachloromethane were used as standards as well as *insitu* measurements of water temperature and dissolved oxygen. TPH concentrations ranged from 0.21mg/l in dry season (September, October, November) to a maximum level of 0.33 mg/l in wet season (June, July, August) during the

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study. The mean concentrations found for physicochemical parameters during wet and dry seasons respectively were: temperature ( $27.67 \pm 0.29$  &  $27.83 \pm 0.29$  °C), DO ( $3.47 \pm 0.65$  &  $3.44 \pm 0.67$  mg/l), Cd ( $0.03 \pm 0.003$  &  $0.03 \pm 0.01$  mg/l), Pb ( $0.17 \pm 0.06$  &  $0.18 \pm 0.04$  mg/l), Ni ( $0.08 \pm 0.01$  &  $0.08 \pm 0.005$  mg/l), V ( $0.02 \pm 0.01$  &  $0.02 \pm 0.01$  mg/l). The distribution pattern of trace heavy metals in the stream water followed the sequence: Pb>Ni> Cd>V. In all cases, Pb was the most abundant and V the least abundant metal. Elevated levels of some physicochemical parameters shown to correlate significantly ( $p=0.05$ ) and associate with the oil spill infer that Aya stream has been severely polluted. Statistical analysis (t-test) of seasonal levels of TPH in water samples showed positive relationship ( $t=0.55$ ,  $p=0.05$ ). The implication of these results is that the concentrations of the studied parameters did not depend on seasonal influence but were connected with the incessant exposure of the site to oil seeps from the well-head. The high levels of lead above permissible limits in the studied samples poses a health threat, hence, the removal of the well-head and future situation of such structures away from the source of communal water source should be implemented to preserve the quality and health of the water source.

**Keywords:** Total petroleum hydrocarbon; physicochemical parameters; oil spillage; aya stream; niger delta, water quality; health.

## 1. INTRODUCTION

Total Petroleum Hydrocarbons (TPHs) are carbon chains in the range of C6 through C35. Products containing TPH include a wide variety of mixtures that may contain hundreds to thousands of hydrocarbon compounds including aliphatic (straight carbon chain) and aromatic (carbon ring) compounds [1]. Toxicity effects of crude oil have been recorded on aquatic fauna [2], aquatic flora [3] and coastal dwellers [4] who consume contaminated water, fish and shellfish.

Carcinogenic effects are known to be associated with petroleum hydrocarbons [5]. Animal studies have shown effects on the lungs, central nervous system, liver, and kidney from exposure to TPH compounds and subsequent mortality. Some TPH compounds have also been shown to affect reproduction and the developing fetus in aquatic animals [6]. Crude oil affects aquatic flora, as it can easily pass through the cell walls and pores of algae and plants [3]. Oil can harm the scales, tissues and brains of fish. Eggs contaminated with oil become infertile. It may take years for spawning grounds to recover from such pollution, so the effects on fish stocks can be long term [7].

Trace heavy metals such as Ni, V, Cu, Cd, and Pb have been found in crude oil through their association with porphyrins. They are therefore reported as normal constituents of crude oil [8]. Apart from the release of metallic constituents of crude oil during oil spill, this situation can affect the concentration of naturally occurring heavy metals and can bring about an artificial imbalance in the heavy metals concentrations [4]. The present study is geared towards

evaluating the levels of TPH in a communal water source - Aya stream after an oil spill. The impact of the resultant levels of these metals are herein discussed as it affects water quality and health.

## 2. MATERIALS AND METHODS

### 2.1 Study Area

Aya stream is located within Ikot Ada Udo village, Ikot Abasi Local Government Area, Akwa Ibom State of Nigeria. The freshwater stream has a thick tropical vegetation cover along the bank. Its flow is unidirectional, a tributary of Imo river. Geographically, the stream is located within latitudes  $04^{\circ}41'$  N to  $04^{\circ}45'$  N and longitudes  $007^{\circ}40'$  E to  $007^{\circ}43'$  E flowing North – East on the maximum altitude of 62 ft. There exists in the area an abandoned oil well owned by Shell Petroleum Development Company (SPDC). The well head designated as Ibibio 1 is situated on latitude  $04^{\circ}41'8.60''$  N and longitude  $007^{\circ}41'11.0''$  E on the altitude of 140 ft (Fig. 1).

The well head is situated within the river catchment. For over five decades the oil has not been tapped instead oil and gas have been constantly leaking from it to pollute the environment (Fig. 2).

The survey of the area [9] showed that between August and November 2007, a large volume of crude oil had flowed from the corked well down the gentle slope of the streams, farm lands and the main river of the area. The consequence is the release of crude oil into the aquatic environment destroying vegetation, crops and

aquatic life, and causing health problems to the people because of the polluted air and water [9]. However, the spill was stopped on November

7, 2007 followed up with a clean-up exercise by the SPDC but seepage has continued till date.

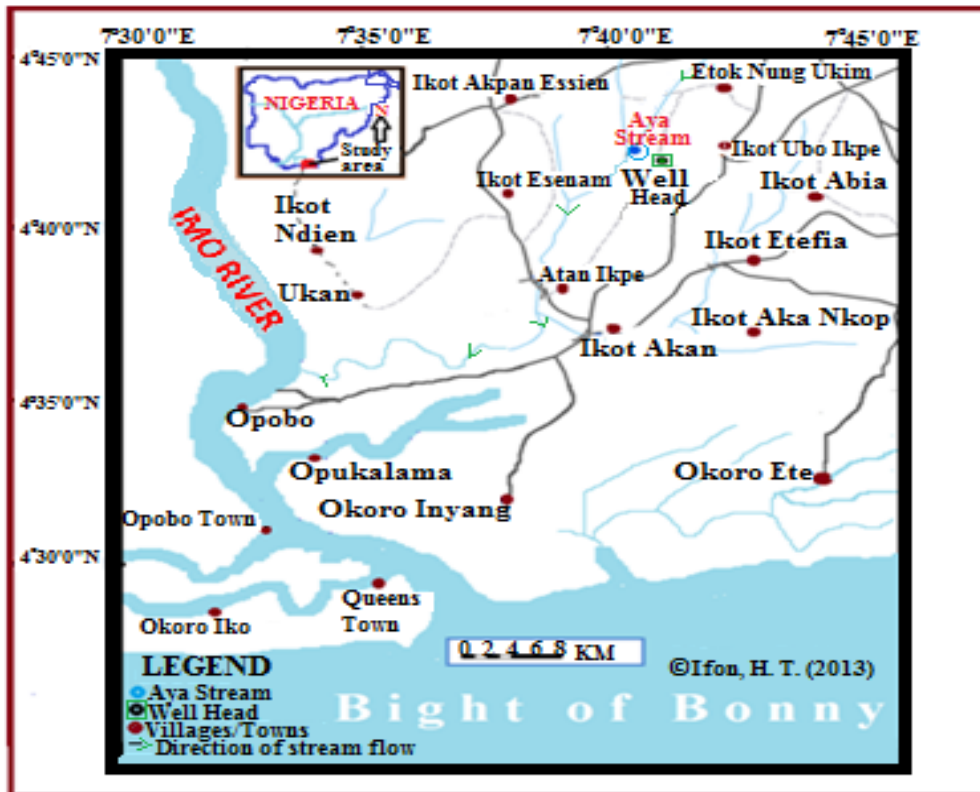


Fig. 1. Map of study area showing Aya Stream and Well Head



Fig. 2. Well head (Ibibio I) at Ikot Ada Udo Community

## 2.2 Field Methods

Field method for water quality assessment involved monthly sampling of surface water from June to November, 2012 to cover the wet and dry seasons. Samples were collected in triplicates and altogether, eighteen (18) water samples were collected. Water samples for physicochemical analysis were collected in 1 litre sterile polyethylene bottles pre-rinsed with site water and stored in an ice chest before analysis in the laboratory within 3 days of collection. Samples for heavy metals analysis were collected in 20ml sterile polyethylene bottles pre-rinsed with site water and preserved by acidifying to pH 2 with concentrated nitric acid until analysis. Water samples for total petroleum hydrocarbons were collected with 500 ml sterile brown glass bottles pre-rinsed with site water and sealed with aluminum foil until extraction within 3 days of collection. Samples for nutrients (nitrate) were sub-sampled and stored frozen at  $-4^{\circ}\text{C}$ .

Temperature and Dissolved Oxygen (DO) were measured in-situ due to their unstable nature using Thermometer and Dissolved Oxygen Meter - SCHOTT-CG867. All other parameters were analyzed in the laboratory.

## 2.3 Analytical Methods

### 2.3.1 Total Petroleum Hydrocarbon (Spectrophotometric Method)

1g of Bonny Light and Bonny Medium Crude Oils dissolved in 1000 ml of tetra chloromethane were used as standards. Working standards of 0.02, 0.04, 0.06, 0.08 and 0.1 mg/l were prepared. The TPH in the sample was extracted using 50 ml of tetra chloromethane for every 20 ml of sample in a separating funnel. The absorbance of both the standards and samples were read at 280 nm

using the Spectrophotometer UNICAM HEXIOS UV-VIS.

### 2.3.2 Metals (Spectrophotometric Method)

1g of each pure metal was accurately weighed and dissolved in 50ml of concentrated Nitric acid and made up to 1 liter with deionized water. That gave the stock that contained 1000mg/l of the element. Working standards were prepared from above stocks depending on their sensitivities with Atomic Absorption Spectrophotometer – Thermo Solar Series. Standards were prepared as follows: 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l for Pb, Ni and Cd; while 0.01, 0.02, 0.03, 0.04 and 0.05 mg/l were prepared for Vanadium.

## 3. RESULTS AND DISCUSSION

The results of Total Petroleum Hydrocarbon and physicochemical analyses of the surface water samples from Aya stream are presented in Tables 1 & 2. In each table, the levels of each parameter for the studied location are compared with World Health Organization (WHO), Federal Environmental Protection Agency (FEPA) and Direct Potable Reuse (DPR) recommended standards. The relationships between each studied parameter and the other are shown in Table 3.

The results obtained for TPH show low levels ranging from minimum concentration of 0.21mg/l in dry season to a maximum level of 0.33 mg/l in wet season during the study as compared to permissible limit of 10mg/l established by FEPA & DPR for discharge of effluents by petroleum industries in Nigeria. However, this range exceeds the WHO [10] permissible limit of 0.1mg/l TPH in drinking water which makes the water unsuitable for drinking as at the time of sampling. This poses a health threat to humans as well as aquatic life ingesting the water.

**Table 1. Physicochemical analysis of surface water samples from Aya stream during wet Season**

WATER PARAMETERS	SAMPLING MONTHS			Mean $\pm$ SD	STANDARDS		
	June	July	August		WHO	FEPA	DPR
Temperature ( $^{\circ}\text{C}$ )	27.5	27.5	28	27.67 $\pm$ 0.29	25	30	30
Dissolved Oxygen (mg/l)	3.2	4.22	3	3.47 $\pm$ 0.65	-	-	-
Cadmium (mg/l)	0.027	0.024	0.029	0.03 $\pm$ 0.003	0.01	0.01	0.01
Lead (mg/l)	0.19	0.11	0.22	0.17 $\pm$ 0.06	0.05	0.05	0.05
Nickel (mg/l)	0.082	0.078	0.09	0.08 $\pm$ 0.01	0.07	-	-
Vanadium (mg/l)	0.012	0.019	0.028	0.02 $\pm$ 0.01	-	-	-
TPH (mg/l)	0.3	0.29	0.33	0.31 $\pm$ 0.02	0.1	10	10

**Table 2. Physicochemical analysis of surface water samples from Aya stream during dry season**

WATER PARAMETERS	SAMPLING MONTHS			Mean $\pm$ SD	STANDARDS		
	June	July	August		WHO	FEPA	DPR
Temperature ( $^{\circ}$ C)	28	27.5	28	27.83 $\pm$ 0.29	25	30	30
Dissolved Oxygen (mg/l)	3.1	4.21	3.01	3.44 $\pm$ 0.67	-	-	-
Cadmium (mg/l)	0.028	0.019	0.028	0.03 $\pm$ 0.01	0.01	0.01	0.01
Lead (mg/l)	0.19	0.13	0.21	0.18 $\pm$ 0.04	0.05	0.05	0.05
Nickel (mg/l)	0.09	0.081	0.082	0.08 $\pm$ 0.005	0.07	-	-
Vanadium (mg/l)	0.028	0.01	0.02	0.02 $\pm$ 0.01	-	-	-
TPH (mg/l)	0.32	0.21	0.32	0.28 $\pm$ 0.06	0.1	10	10

**Table 3. Correlation matrix for physicochemical parameters in surface water from the study area**

	TEM	DO	Cd	Pb	Ni	V	TPH
TEM	1						
DO	<b>-0.777</b>	1					
Cd	0.728	<b>-0.901</b>	1				
Pb	<b>0.778</b>	<b>-0.976</b>	<b>0.828</b>	1			
Ni	<b>0.767</b>	-0.569	0.604	0.704	1		
V	<b>0.833</b>	-0.569	0.720	0.533	<b>0.789</b>	1	
TPH	0.745	<b>-0.819</b>	<b>0.976</b>	<b>0.760</b>	0.564	<b>0.790</b>	1

*Degree of freedom (df) = N-1 = 6-1 = 5; Critical r = 0.754 Significance level for a two-tailed test = 0.05. Calculated r-values greater than critical value (0.754) are considered to be significantly correlated*

The mean temperature values of 27.83 $\pm$ 0.29 & 27.67 $\pm$ 0.29 during the wet and dry seasons respectively were higher than the WHO recommended limit of 25 $^{\circ}$ C in drinking water. This means that the temperature range during the study would pose palatability problem to community dwellers that rely on this stream as the only source of drinking water. Temperature was also found to significantly influence the presence of the heavy metals and total hydrocarbon (Fig. 3) while causing a significant depletion of dissolve oxygen in the stream (Table 3).

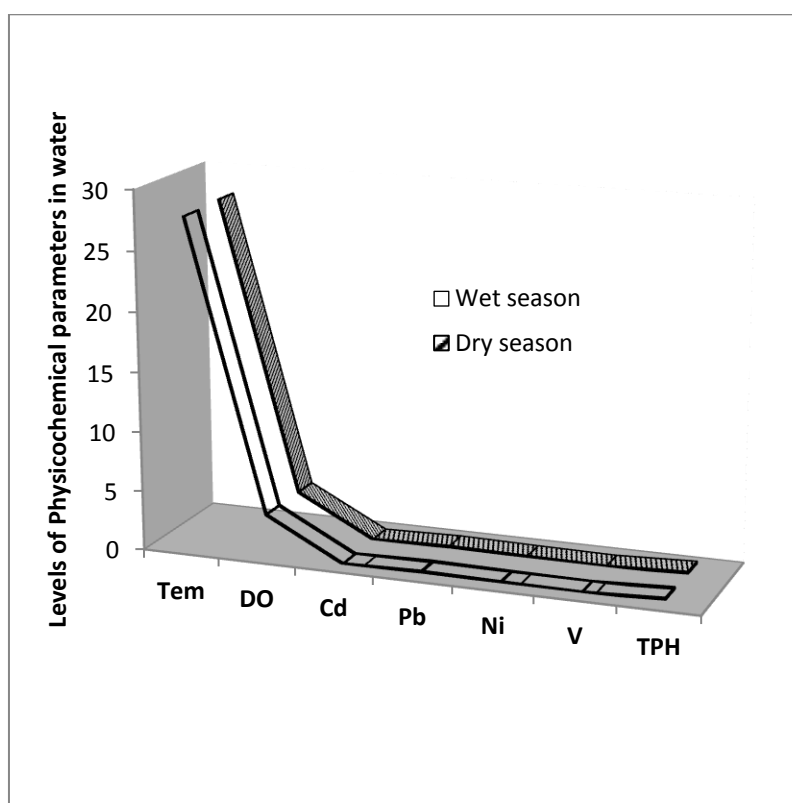
The mean dissolved oxygen concentrations in stream water were low (3.47 $\pm$ 0.65 & 3.44 $\pm$ 0.67 mg/l for wet and dry seasons respectively). Fig. 3 shows a negative relationship between TPH and DO levels in sample water inferring that presence of TPH causes depletion of DO in surface water. This study supports the findings of Dugan [11] who reported that fish and other aerobic organisms die in oxygen deficient waters. Therefore DO depletion is among the factors that have contributed to declining fish stock in global fishery.

The range of concentrations of trace heavy metals for the period of study are Cd (0.019 – 0.029 mg/l), Pb (0.11 – 0.22 mg/l), Ni (0.078 – 0.09mg/l), V (0.01 – 0.03 mg/l). These metals

correlated positively and significantly with TPH in sampled water (Table 3). Nickel is an essential micronutrient required by red blood cells. However, it is known to be toxic at high intakes. The long term exposure can cause decrease in body weight, heart and liver damage and skin irritation. This finding supports the work of Birge & Black [12] who reported that the toxicity of Ni to aquatic life has been shown to vary significantly with organism species, pH and water hardness.

The overall assessment of the water quality of the stream water in the study area indicates that cadmium, lead and nickel were above permissible limits except for vanadium which has no stipulated standard in drinking water. These elevated values prompt environmental concern as these metals are considered generally harmful if above permissible limits, and are associated with several health hazards including anemic, carcinogenic and reproductive effects [13].

T-test statistical analysis of studied parameters (t=0.55, p=0.05) showed no significant difference between data collected during the wet and dry seasons. This homogeneous trend in seasonal data is also depicted in Fig. 3. This means that the concentrations of the studied parameters do not depend on season. Also, this indifference might be connected with the incessant exposure of the site to oil seeps from the well-head.



**Fig. 3. Seasonal variation in levels of physicochemical parameters in water samples**

Socio-economic activities in the area including artisanal fishing have been adversely affected due to levels of TPH and physicochemical parameters found in the analyzed samples. Enhanced levels of trace heavy metals in the stream water may result in enhanced absorption by aquatic floras and faunas which may bring about possible bioaccumulation by such organisms leading to toxic reactions along the food chain.

Furthermore, high values of heavy metals observed in the water samples can be attributed to the retention of heavy metals present in oil by water, while the oil which flows in the water could have been carried away by the current or trapped by sediment and aquatic organism. The river drainage along with the spilled oil as shown in Fig. 1 into Imo River and further into the Atlantic Ocean is a major factor for low TPH observed in the studied samples. Moreover, the lower values of TPH obtained during the present study could have been due to the clean-up exercise carried out by SPDC after the spill. Also the process of biodegradation and physical processes involving dissolution, advection, dispersion, and diffusion, generally referred to as natural attenuation or remediation process could also

account for low concentrations of TPH in sampled water.

#### 4. CONCLUSION

The findings of this work generally imply toxicity effects of crude oil and physicochemical parameters which adversely affect aquatic fauna, aquatic flora and coastal dwellers who consume contaminated water, fish and shellfish. Socioeconomic activities such as swimming, boating and artisanal fishery have been undesirably affected. This in turn implies low economic productivity and reduced source of livelihood in the affected area.

The present study is an analytical approach for TPH in the environment which opts to satisfy the informational needs of regulatory agencies and engineers designing remediation activities. Continuous monitoring of the well-head for impending spills and formulation of strategies to combat pollution at least to reduce it to the barest minimum should be of great concern to all.

Finally, regulations should be promulgated to put necessary sanctions on breaches that tend to derogate and damage the environment. This

involves the removal of the well head and strict laws prohibiting the situation of similar structures near any source of water.

## DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

## DATA AVAILABILITY STATEMENT

The raw data supporting this article will be made available by the authors, without reservation.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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