

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) on Fresh Water Samples from Egbema in Ogba/Egbema/Ndoni L.G.A. in Rivers State.

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ABSTRACT

This study determined the Polycyclic Aromatic Hydrocarbons (PAH's) on Fresh Water Samples from Egbema Communities in OGBA/EGBEMA/NDONI L.G.A of RIVERS STATE. The fresh water samples for this work were collected in February, 2017 from natural water bodies within Egbema Community in Ogba/Egbema/Ndoni Local Government Area (ONELGA) in Rivers State, Nigeria. The concentration of Polycyclic Aromatic Hydrocarbons (PAH's) and physicochemical parameters were determined. The physicochemical parameters were done to ascertain water quality. The parameters determined did not exceed the permissible limit of the World Health Organization (WHO, 2006) and Nigeria (FMENV, 1992). The Total Dissolved Solid was 98.1 ± 16.88 mg/l, Total Suspended Solid was 68.5 ± 10.29 mg/l, Turbidity was 1.6 ± 0.011 NTU and pH was 7.4 ± 1.05 . The mean concentration and standard deviation of PAH's across the sampled areas showed that Egbema sampled communities had 4.7 ± 0.23 $\mu\text{g/l}$, with a range of 4.0 – 5.1 $\mu\text{g/l}$. The mean concentration and standard deviation for the study stood at 3.3 ± 0.18 $\mu\text{g/l}$ with a range of 1.4 – 6.0 $\mu\text{g/l}$.

Key Words: Polycyclic Aromatic Hydrocarbons, freshwater, physicochemical parameters, water quality

1. INTRODUCTION

Water is a unique substance, which exist in the three states of matter (gaseous, liquid and solid states). It is often the most complex of all the familiar substances that are single chemical compounds. It is a very simple chemical compound composed of two atoms of hydrogen and one atom of oxygen, which bond covalently to form one molecule.

In its pure state, water is colourless, odourless and freezes at 0°C and has a boiling point of 100°C. The physical and chemical characteristics of water are important parameters as they may directly or indirectly affect its quality and consequently its suitability for the distribution and production of fish and other aquatic animals (Swingle 1969; Moses, 1983). Water is a marvelous substance which is essential for life. It is the medium in which all living process occurs and it is an indispensable unit of life. Water covers 70% of our earth's surface, it is a necessity for life, but industrialization and urbanization brought about pollution of water bodies. Anthropogenic activities carried out around water bodies have led to the introduction of substances that causes pollution. Water pollution involves the degradation of water bodies; it is an integrated occurrence that must be taken seriously according to the Environmental Protection Agency (EPA). This includes the discharge of unwanted chemicals, biological and physical materials from man's environment into water bodies. The quality of any water is governed by its physicochemical and heavy metal factor. The monitoring of physicochemical characteristics of water body is vital for both long term and short term evaluation of its quality. Lakes, rivers and streams have important multi-usage components, such as source of drinking water, irrigation, fishery and energy production. Water is a scarce and fading resource and its management can have an impact on the flow and the biological quality of rivers and streams. Expanding human population, industrialization, intensive agricultural practices and discharges of massive amount of waste water into the rivers and streams have resulted in the determination of water quality. Modern Technology has provided the means for great changes of the environment and its pollution. The industrial revolution and the World War II have extremely changed the life norms. Modern

lifestyles are largely depending on the benefits derived from the various industries where “specifically”, chemical industries and their derivatives is major contributor to the various life-branches. However, when the relation between modern lifestyles “civilization” and the environment is to be evaluated, disproportionately growth is to be appeared accompanied with great tension on the different environment components. Contaminations as a result of human activities (anthropogenic) through the worldwide industries coupled with other natural contamination feed such tension and are major threat to the environment. “Also, there is a threat to ground waters from waste water dumps and landfills, storage lagoons, treating ponds, and other facilities” (Horsfall *et al.*, 2001). Water pollution by organic compounds, many of which are known to be toxic or carcinogenic, has caused considerable and worldwide concern. Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic compounds produced by incomplete combustion or high-pressure processes. They are formed due to exposure of complex organic substances to high temperatures or pressures. “Some Polycyclic Aromatic Hydrocarbons (PAHs) can also be derived from biogenic precursors such as pigments and steroids” (Wakeham *et al.*, 1980). Polycyclic aromatic Hydrocarbons (PAHs) in soils can arise from a number of sources, and these include hydrocarbon spillage” (Benner *et al.*, 1990), products of incomplete combustion of fossil fuels, e.g. wood burning (Freeman *et al.* 1990), use of organic waste as compost and fertilizer (Smith *et al.* 2001) and power plants and blast furnaces (Van Brummel *et al.* 1996). Evidence is there to indicate that PAH are transported over long distances due to atmosphere movement (Lunde *et al.*, 1977; Aamot *et al.*, 1996; Bakker *et al.*, 2001; Halsall *et al.* 2001). Cracking and refining of crude oil is one of the major activities that produces large amount of Polycyclic Aromatic Hydrocarbons (PAHs) (Inengite *et al.*, 2012).

They often, consist of three or more fused benzene rings containing only carbon and hydrogen. Variation in the configuration of rings may lead to differences in properties. Polycyclic aromatic Hydrocarbons (PAHs) are known by several names: Polycyclic Organic Matter (POM), Polynuclear Aromatic Hydrocarbons, Polynuclear Aromatics (PNAs) and Polynuclear Hydrocarbons (Agency for Toxic Substances and Disease

Registry [ATSDR], 2009). Polycyclic aromatic Hydrocarbons (PAHs) are a natural component of most fossil fuels. Although produced naturally by forest fires and volcanoes, most Polycyclic aromatic Hydrocarbons (PAHs) in ambient air are the result of man-made processes. Sources of Polycyclic aromatic Hydrocarbons (PAHs) can be both natural and anthropogenic (Young *et al.*, 1995). Natural sources include: forest and grass fires, oil seeps, volcanoes, chlorophyllous plants, fungi, and bacteria. Anthropogenic sources of Polycyclic aromatic Hydrocarbons (PAHs) include: petroleum, electric power generation, refuse incineration, home heating, and production of coke, carbon black, coal tar, and asphalt, internal combustion engines, motor vehicle exhaust (Cherng *et al.*, 1996). Polycyclic aromatic Hydrocarbons (PAHs) are of increasing concern in the environment (water) cycle. Before the twentieth century waste water treatment plants were developed to remove contaminants and parameters like heavy metals, nitrate (NO_3^-), chemical oxygen demand (COD), oxygen demand (BOD), phosphate (PO_4^{2-}) and micro-organisms, but recently, industrialization, population and extensive use of chemicals has resulted in organic contaminants like Polycyclic aromatic Hydrocarbons (PAHs) finding its way into the water environment. The need has arisen to get into details, the manner, the sources, flow paths, fate (transport, treatment, natural attenuation) and impact of xenobiotics on both humans and environment in these kind of systems (Janosova *et al.* 2006). The industrialized countries have therefore seen reason to be ahead of time. This has made some of the European Union member countries to participate in a project to mitigate the possible effect of xenobiotics (PAHs) on human health. These includes such countries as Austria, Belgium, Czech Republic, Denmark, Finland, France, Italy, Latvia, Luxembourg, Netherlands, Norway, Portugal, Romania, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom (Dokianakis *et al.* 2006). The EU-Water Framework Directive has noted that current wastewater treatment technologies only takes care of conventional parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), nitrate, phosphate and microorganisms (Dokianakis *et al.*, 2006). Nonetheless, water pollution as a result of atmospheric washout, pesticides application, industrial production, erosion of building materials, traffic emissions, use of household chemicals, personal care products and

other contaminants enters natural water bodies without any proper treatment. The unified nature of the water bodies and the ability of xenobiotics to spread sporadically across structural boundaries and into the environment where ecological systems and humans are exposed calls for holistic, intersectorial and multidisciplinary approach to find affordable solutions to this problem. Information about the biodegradability, metabolic pathways, conjugation and deconjugation, sorption, transport in the environment and persistence of Polycyclic aromatic Hydrocarbons (PAHs) are needed to predict their fate and impacts and to help in the creation of policy to protect humans and ecosystems from their effects. Research is desperately needed to determine the degradation reactions in soil that transform these Polycyclic Aromatic Hydrocarbons (PAHs) compounds to their mineral components (Dokianakis, *et al.*, 2006). Whenever Polycyclic aromatic Hydrocarbons (PAHs) enters the water environment, they distribute themselves among various compartments including water, suspended particles, colloidal matter and sediments. It has been shown that Polycyclic aromatic Hydrocarbons (PAHs) associate themselves strongly with colloidal matter or dissolved organic matter (DOM) in aquatic environment, enhancing their apparent solubility but making them less available to the sediment phases (King *et al.* 2004). Sediment pore water has played an integral role in Polycyclic aromatic Hydrocarbons (PAHs) speciation. In water environment, studies have shown that only the freely dissolved fractions of Polycyclic aromatic Hydrocarbons (PAHs) are available for bio-uptake (fish, shell fish and aquatic plants) (Ditoro *et al.*, 1991). Thus, the existence of Dissolved Organic Matter (DOM) in the water environment can greatly influence the bioavailability and distribution of PAHs in water (Li *et al.* 2001).

Polycyclic aromatic hydrocarbons (PAHs) released into the environment through both natural and human processes causes pollution of the environment. Such releases are of great concern due to their persistent nature with the potential to cause adverse environmental and health effects. Oil spillage is a major contributor to PAHs level in the water environment. Reports on the level of oil spills in the Niger Delta area had varies significantly, the Department of Petroleum Resources (DPR) estimated that about 1.9 million barrels of crude oil were spilled into the Niger Delta area between

1976 and 1996 out of a total of 2.4 million barrels spilled in 4,835 incidents (Vidal, 2010). The World Bank also claims that the true quantity of petroleum spilled into the Niger Delta environment could be as much as ten times the officially claimed amount (Moffat *et al.*, 2012). Another source of PAHs into the environment is gas flaring. There was a claim that about 70% of associated gas produced annually is being wasted through flaring (Friends of the Earth, 2004). The Energetic Solution Conference estimates that the Niger Delta region has about 123 gas flaring sites (Kadafa, 2012), out of which over 10 flare sites are located in the local government area of this study. Majority of these flared gases find their way into the water environment which results in release of pollutants such as NO₂, SO₂, volatile organic compounds (benzene, toluene, xylene and hydrogen sulphide) and carcinogens like benzo (a) pyrene and dioxins.

This research aimed to determine the presence of Polycyclic Aromatic Hydrocarbons (PAHs) in fresh water samples in Egbema Communities in Ogba/Egbema/Ndoni Local Government Areas in Rivers State, Nigeria, and specifically adopted the following objectives: determining the level of polycyclic aromatic hydrocarbon in fresh water samples from Egbema in Onelga, Rivers State; determining the physico-chemical parameters of the water samples collected; identifying the types of PAHs from the water samples; and assessing the human health risk associated with the drinking of the freshwater.

2. STUDY AREA

The Natural Environment in the study area is an integrated mosaic of aquatic, semi terrestrial (Mangrove fresh water swamps) and terrestrial habitat, the species *Rhizophora racemosa* is dominant. The wildlife in the area includes mammals, aves, reptiles, amphibians.

Soil in Egbema Communities in Ogba/Egbema/Ndoni Local Government Area in Rivers State are well drained to deep poorly drained soil; sandy, sandy loam or loamy sand surfaces over sandy loam, sandy clay loam, loam or sandy clay. Previous

analysis of Cone Penetration Test (CPT) logs of soil in the project area revealed that the sub-soil in the swamp and submerge terrain in the site is highly susceptible to compression due to presence of organic clay and peat. It also has increasing compaction state with depth.

Geologically, Egbema is underlain by a sequence of sedimentary formations with a thickness of about 8,000 meters and include from bottom to top. The water table is influenced by tidal regime; it is very close to the ground surface and varies from 0–4 meters. The underground water of the study area is acidic, while that of the surface water is slightly acidic/alkaline.

The ambient air quality of the area is within regulatory standard.

According to Macmillan Nigeria Secondary Atlas (2006), the mean annual rain fall of the area is 2000-2200mm³ with mean annual temperature of 26-27⁰c rain fall onset begins in March with break in August and continues to November..

The local government stretches from longitude 6° 28' 13"E through longitude 6° 47' 34"E and latitude 5° 9' 42" N through 5° 44' 3"N. It is one of the oil producing Local Government Areas of the Niger Delta of Nigeria. The Niger Delta has been said to cover an area of between 19,100 km² to 30,000 km² based on hydrological, ecological as well as political boundaries (Shell Petroleum Development Company [SPDC], 2006) and United Nation Development Programme [UNDP], 2006). The Niger Delta is a vast wetland located in the southern part of Nigeria consisting essentially of Bayelsa, Delta, Akwa Ibom, Ondo, Imo, Edo, Cross River, Abia and Rivers states.

Ogba/Egbema/Ndoni Local Government Area covers an area of over 1500 sq km in the northern part of the Niger Delta region located within the River Niger axis. It is bordered on the west by the Orashi River and on the east by the Sembreiro River. In addition to the two main rivers, there are the Omoku river, Tailor creek, Ndoni creek, and many back swamps/streams, cut offs and interconnecting streams which form a

maze of drainage channels superimposed on the area. At the peak of the rainy season, these interconnected waterways are a prominent feature of the landscape.

The mineral resources are crude oil and natural gas and there are numerous oil fields in the study area which make significant contributions to Nigeria's crude oil output. Crude oil exploration has impacted negatively on the people and economy of the study area. Periodic spills have resulted in destruction of farmland, rubber plantations and aquatic biota; thereby undermining rural economy and leaving the people unemployed. There are numerous gas flare sites in these areas where natural gas associated with crude oil is burnt off. The sample points for this research were chosen in view of various anthropogenic activities in the areas. The major sources of organic contaminants in the areas are from crude oil exploitation and exploration activities, and transportation of crude oil through pipeline, including the contributions from residential and communal heating and transport.

Ten water samples were collected from three different bodies as showed for sampling points, in Ogba/Egbema/Ndoni Local Government Area (ONELGA).

The ten water samples were collected from areas within Ebocha flow station in Egbema community, comprising Ebocha, Aggah, Mgbede and Okwuzi communities.

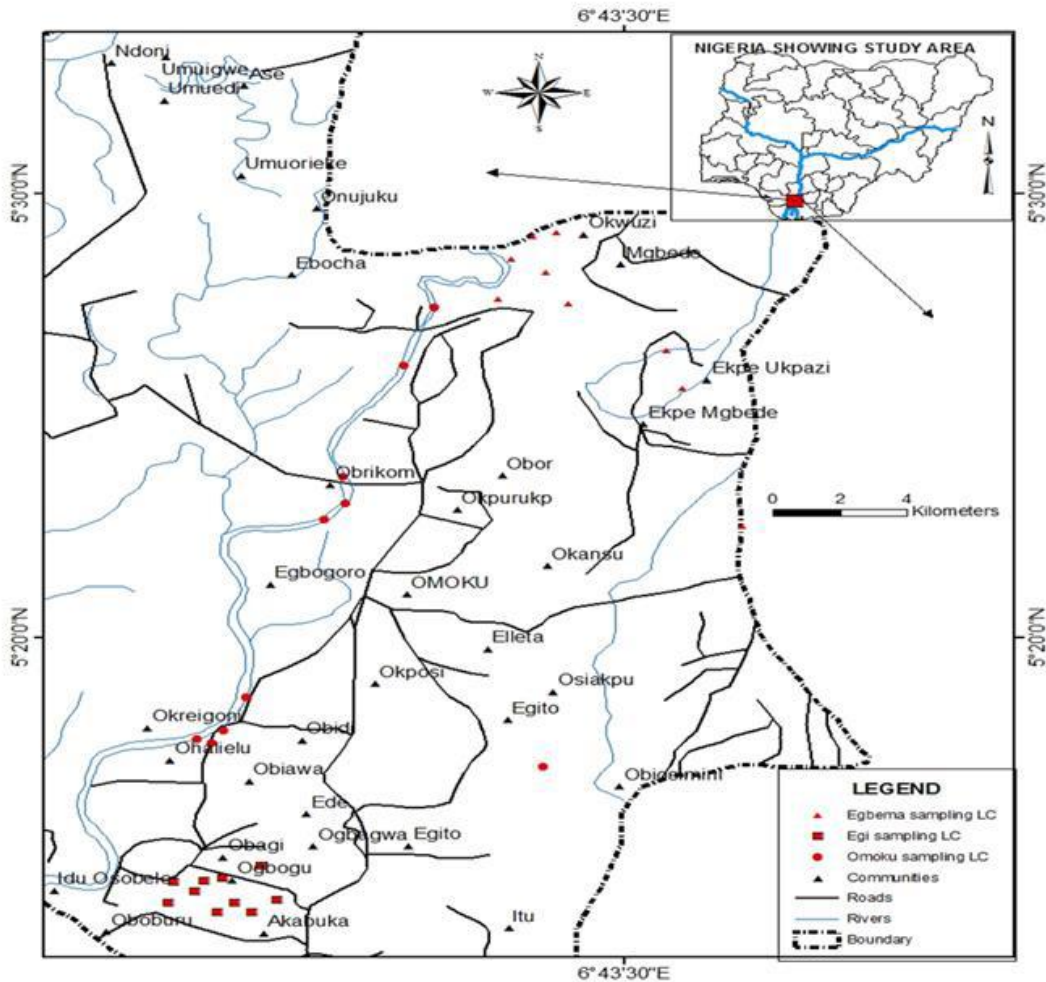


Figure 1: Sampling points in Ogba/Egbema/Ndoni Local Government Area in Rivers State, Nigeria.

3. MATERIALS AND METHODS

A comparative cross-sectional study design was adopted, involving collection of freshwater samples from Egbema sampling communities. A total of 10 grams of freshwater samples from Egbema communities were deliberately collected because they were the most prominent receiving freshwater bodies in the area. Prior to sample collection, the glass bottles were washed and sun-dried; and before collection, the glass bottles were rinsed twice with the same water samples they are to contain. A Geographic Positioning System (GPS) was used to capture the coordinates of each of the sampled location. Table 1 shows the coordinates of the sampled stations. In each case samples were collected at a depth of 20cm below the surface of the water using amber-coloured 1litre capacity glass bottles (Ana *et al.*, 2010). The filled bottles were

immediately covered, properly labeled, and placed in an ice chest with ice for further treatment and analysis in the laboratory. Figure 1 shows the sampling points in ONELGA and the sampling co-ordinates in the Egbema communities in Ogba/Egbema/Ndoni Local Government Area in Rivers State, Nigeria are shown below.

Table 1: Sampled locations in Egbema Communities

Locations Description	Sample Code	Longitude	Latitude
Egbema	EB1	6° 42'02"E	5° 27'53"N
Egbema	EB2	6° 42'36"E	5° 27'32"N
Egbema	EB3	6° 44'11"E	5° 25'55"N
Egbema	EB4	6° 42'05"E	5° 27'50"N
Egbema	EB5	6° 44'30"E	5° 26'08"N
Egbema	EB6	6° 44'11"E	5° 26'28"N
Egbema	EB7	6° 45'36"E	5° 22'31"N
Egbema	EB8	6° 42'25"E	5° 29'08"N
Egbema	EB9	6° 42'09"E	5° 27'49"N
Egbema	EB10	6° 42'02"E	5° 29'03"N

Source: *Researchers' Fieldwork, 2016*

Determination of Physicochemical Parameters

The global water supply and sanitation assessment report found that about one sixth of the world's population (1.1 billion people) was without access to improved water supply and two-fifth (2.4 billion people) lacked access to improved sanitation. The majority of these people live in Asia and Africa, where less than half of all Asians

have access to improved sanitation and two out of five Africans lack improved water supply. The need for improved water quality is evident from the millions that die of water-borne diseases each year.

In view of the objective of the present research, a critical survey of literature was carried out to gather information on various relevant aspects such as physic-chemical features and trace metals. Seasonal variations in water temperature of various aquatic bodies have been recorded by Hannan *et al.* (1974) and Hershey *et al.* (1982). Jolly *et al.* (1966) made a preliminary study on the effects of pollution on farmers and creeks with respect to temperature. pH variations in water are widely studied worldwide. Impact of addition of sewage and industrial effluents on pH levels has been observed by Oswald (1960) with recorded effects of industrial discharges on pH level of water. Dissolved oxygen which is a parameter of primary importance in the aquatic ecosystem by virtue of its role in both chemical as well as biological reactions has been recorded in various water bodies throughout the world by Hutchinson (1957). The changes in dissolved oxygen levels in water with addition of domestic sewage, various industrial wastes and agricultural run-off have been investigated by Otieno (2008). The physico-chemical parameters of water influence the uptake of heavy metals by fish and other aquatic animals.

The pH of surface water samples was determined by probe method according to standard procedures 2500H+B (APHA, 1992). The pH meter was stabilized for 15 minutes, and then the meter was set to the effluent temperature. The electrode was rinsed with jet of distilled water and calibrate with buffer solution. The electrode was further rinsed, then dipped into the water sample and allowed to stabilized, and then the value recorded.

Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended materials in water. Turbidity is caused by suspended and fine insoluble particles and colloidal impurities like clay, silt, algae and plankton. Turbidity refers to how clear the water is. The greater the amount of total suspended solids (TSS) in the water, the murkier it appears and the higher the measured turbidity. The major source of turbidity in the open water zone of most rivers and creek is phytoplankton, but

closer to the banks particulates may also be a form of clay, silt. Erosion, organic detritus from stream and/or waste water discharges can make a river become murky. Dredging operation, channelization, increased flow rate, floods or even too many bottom feeding fish (crap) may stir up bottom sediments and increase the cloudiness of the rivers that leads to turbidity of those particular streams/rivers.

Total dissolved solid in water samples was determined by gravimetric method 2510B. (APHA, 1992). 250ml conical flask was weighed after heating and drying in an air oven; 50ml of the water sample was filtered into the weighed flask, cooled to room temperature in a desiccator. Then the flask and content was reweighed and new weight recorded. The total dissolved solid was calculated as shown below:

$$\text{TDS (mg/l)} = (\text{Wf} - \text{We}) (\times 1000 \times 20)$$

Where:

Wf = Weight of flask with solid residue

We = Weight of empty flask

1000 = conversion factor from gram to milligram

20 = conversion from 50ml to 1000ml

Total suspended solids are defined as the particles in the water larger than 2 microns in diameter. In creeks the majority of suspended solids are fine sediments or algae. Surface runoff carries suspended solids into water. The suspended solids may be inorganic in nature such as clay, silt, sand, silica and calcium carbonate or they may be organic matters. (Due to human activities such as farm and cultivation, quarry of sand and gravel). Suspended materials in water are aesthetically displeasing and provide adsorption sites for chemical and biological agents. The gravimetric method given by APHA 2540B, (APHA, 1992) was adopted. The filter paper was pre-weighed and used to filter 50ml of water sample. It was dried at 105°C to constant weight and reweighed. The total suspended solid was calculated using equations shown below:

$$\text{TSS (mg/l)} = (\text{Wfp} - \text{Wef}) (1000 \times 20)$$

Where:

Wfp = Weight of filter paper + residue

Wef = Weight of empty filter paper

1000 = conversion factor from gram to milligram

20 = conversion from 50ml to 1000ml

Polycyclic Aromatic Hydrocarbons

The determination of Polycyclic Aromatic Hydrocarbons (PAHs) was done following standard protocol as described by Essumang *et al.* (2009). Precisely 250ml of each water sample was measured and spiked with pre-deuterated Polycyclic Aromatic Hydrocarbons (PAHs) Cocktail as internal standard (naphthalene-d8, acenaphthylene-d8, anthracene-d10, acenaphthene-d10, fluoranthene-d10, phenanthrene-d10, fluorene-d10, pyrene-d10, chrysene-d12, benzo[a]pyrene-d12, benzo[b]fluoranthrene-d12, benzo[a]anthracene-d12, benzo[ghi]perylene-d12, dibenzo[a,h]anthracene-d14 and indeno[1,2,3-cd]pyrene-d12) (110 Benner Circle-Bellefonte, PA 16823), and agitated with 25 mL of dichloromethane in a separating funnel. The mixture was shaken well for the needed extraction to take place and left undisturbed. The organic layer was drained through a sample vial into a Zymark tube. With sodium sulphate used to absorb water left in the organic layer. A second extraction was repeated with same procedure as described above, and the extract was added to the first one in the Zymark tube. 1cm of moderately packed glass wool was placed at the bottom of a 10mm I.D. (internal diameter) x 250mm long chromatographic column. Slurry of 2g activated silica in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5g of sodium sulphate. The column was rinsed with additional 10ml of methylene chloride. The column was pre-eluted with 20ml of dichloromethane; this was allowed to flow through the column at a rate of about 2minutes until the liquid in the column was just above the sodium sulphate layer. Immediately, 1ml of the extracted sample was transferred into the column. The extraction bottle (sample vial) was rinsed with 1ml of dichloromethane and added to the receiving end of the column as well. The stop-cork of the column was opened and the eluate was collected into a 10ml graduated cylinder. Just prior to exposure of the

sodium sulphate layer to air, dichloromethane was added to the column in 1-2ml increments. The eluate was collected and labelled “PAHs –sample” up to sample number as applicable. The Polycyclic Aromatic Hydrocarbons (PAHs) fraction was injected into a gas liquid chromatography equipped with flame ionization detector. The GC analysis was conducted on a HP 5890 series II GC with fused silica capillary (HP5) of 30m length, 0.32mm internal diameter, and 0.25µm film diameter at the rate of 6°C/min. The oven temperature was programmed from an initial temperature of 100°C (2min hold) to 260°C at the rate of 6°C/min and was maintained at 260°C for 25 minutes. Injector and detector temperature were maintained at 280°C and 300°C respectively. Helium was used as the carrier gas.

4. RESULT PRESENTATION AND DISCUSSION

The result of the physicochemical parameters obtained from water samples from Egbema communities are summarized and presented in Table 1 below, while Tables 2 shows summary of levels of Polycyclic Aromatic Hydrocarbons (PAHs) in Egbema.

Table 1: Summary and comparism of Physicochemical parameters with permissible limit area .

Area	TDS (mg/L)	TSS (mg/L)	Turbidity (NTU)	pH
Egbema	113.0±23.70	70.8±11.93	0.8±0.00	7.5±1.05
WHO (2006)	1000	100	5	6.5-8.5
India (EPR,1993)	500	100	10	6.5-8.5
Nigeria (FMENV, 1992)	1000	500	5	6.5-8.5

Source: *Researchers’ Fieldwork, 2016*

Table 2: Summary of Measurement of Polycyclic Aromatic Hydrocarbons (PAHs) in freshwater samples ($\mu\text{g}/\text{l}$) collected from Egbema Communities in Ogba/Egbema/Ndoni Local Government Area (ONELGA) of Rivers State, Nigeria.

PAHs		Location
Egbema \pm std		
Nap	Mean	ND
	Range	ND
Ace	Mean	ND
	Range	ND
Can	Mean	ND
	Range	ND
Flo	Mean	ND
	Range	ND
Ant	Mean	$5.2\text{E-}3 \pm 1.2\text{E-}4$
	Range	$1.2\text{E-}3 - 1.2\text{E-}2$
Phe	Mean	$3.0\text{E-}2 \pm 4.5\text{E-}3$
	Range	$1.2\text{E-}2 - 6.0\text{E-}2$
Flu	Mean	$3.6\text{E-}3 \pm 4.6\text{E-}4$
	Range	$5.4\text{E-}4 - 7.1\text{E-}3$
Pyr	Mean	$2.6\text{E-}2 \pm 5.7\text{E-}3$

	Range	1.2E-2-4.6E-2
BaA	Mean	1.6E-3±1.6E-4
	Range	2.1E-4-5.0E-3
Chr	Mean	1.8E-3±3.4E-4
	Range	1.1E-4-3.0E-3
BbF	Mean	4.4±2.1E-1
	Range	3.7-4.8
BkF	Mean	2.3E-3±3.2E-4
	Range	9.9E-4-7.0E-3
BaP	Mean	1.2E-2±1.3E-3
	Range	1.7E-5±4.8E-2
IdP	Mean	2.2E-1±1.8E-2
	Range	1.7E-1-3.0E-1
DbA	Mean	9.7E-4±3.5E-5
	Range	5.8E-4-2.0E-3
BgP	Mean	1.1E3±4.8E-5
	Range	2.3E-4-7.0E-3
Location	Mean	4.7±0.23
Location	Range	4.0-5.1
Overall	Mean	

Note: ND = Not Detected, Nap = Naphthalene, Ace = Acenaphthylene, Can = Acenaphthene, Flo. = Fluorene, Ant. = Anthracene, Phe.= Phenanthrene, Flu =

Fluoranthene, Pyr. = Pyrene, BaA = Benz (a) Anthracene, Chr. = Chrysene, BbF = Benzo (b) fluroranthene, BkF = Benzo (k) Fluoranthene, BaP = Benzo (a) Pyrene, IdP = Indeno (1,2,3-cd) Pyrene, DbA = Dibenz(a,h) Anthracene, BgP =Benzo (g,h,i) Perylene. Source: Researchers' Fieldwork, 2016

Table 3: Comparison of the Concentration of PAHs ($\mu\text{g}/\text{l}$) in ONELGA with Permissible Limits of Countries/Agencies

Countries/Agencies	Types of PAHs	Permissible Limit($\mu\text{g}/\text{l}$)
Canada (DWFPTCDW,2008)	BaP	0.01
USEPA (2009)	BaA	0.1
	BaP,BbF,BkF.	0.2
	DaA	0.3
	IdP	0.4
	Total PAHs	0.2
Europe (NIEA, 2011)	BaP	0.01
	Total PAHs	0.1
Australia (NHMRC, NRMMC, 2011)	BaP	0.01
WHO (2006)	Total PAHs	0.7
Turkey (Emrah, 2012)	Total PAHs	0.1
This Work \pm std	Total PAHS	3.3 \pm 0.18

Source: *Google, 2016*

Table 1 present the summary and comparison of the values of the physico-chemical parameters of freshwater samples from Egbema in Ogba/Egbema/Ndoni Local Government Area (ONELGA) with the limits outlined by WHO, India and Nigeria. The value of Total Dissolved Solids (TDS) obtained in the study was 113.0 ± 23.70 mg/l. In general, this value is lower than limits given by regulatory authorities as shown in Table 1. This low Total Dissolved Solids (TDS) could probably be attributed to the shutdown of operations by the oil and gas companies during the flooding period. Reports by Alabaster *et al.*(1982) suggested that excessive concentration of suspended and dissolved solid might be harmful to aquatic organism, because they decrease water quality, stops the processes of photosynthetic and eventually lead to

increase in bottom sediment and decrease of water depth. The value of Total Dissolved Solids (TDS) may also have depended on differences in organic composition of the water bodies and as well the source of effluent discharge that gets into the water (Ogbeibu *et al.*, 2004).

The mean and standard deviation of total suspended solids concentrations for the sampled communities in Egbema is (70.8± 11.93 mg/l). The TSS is low compared with Federal Ministry of Environment (FMENV) and WHO's standard of 2006. This could be attributed to the level of organic and inorganic materials on the water environment which result from industrial activities from the mining area.

The Turbidity of water depends on the quantity of solid matter present in the suspended state. It is a measure of light emitting properties of water and the test is used to indicate the quality of waste discharge with respect to colloidal matter. The mean Turbidity value obtained for Egbema communities is (0.8 ± 0.00 NTU), which is lower than WHO's maximum permissible limit of 5 NTU. This is also relatively lower than work by Ewa *et al.* (2011) were they reported 29.30 NTU on Omoku creek. This could be attributed to the water current from the flooding which washed away most of the organic particles in the surface of these water bodies. The greater the turbidity the higher the risk of gastro-intestinal diseases (Eric *et al.*, 1997).

The mean values obtained for pH in the study area was within the range of 6.5 to 8.5, recommended by WHO (2006) for drinking water. Although the values indicate that the surface water samples are slightly basic, it is in agreement with what was reported by other researchers in 40 similar studies (Edimeh *et al.*, 2011) and (Aremu *et al.*, 2011). Ewa *et al.* (2011), also reported a pH of 6.0 which is a little below standard. (Chinedu *et al.*, 2011), had pH range of 6.0±0.52 to 7.2±0.52 on surface water around Ota, South West Nigeria. This result recorded for the surface water is agreeable to the fact that Egbema is oil and gas production area which is characterized by industries that discharges effluents made of organic matters. This result which is slightly basic

also agrees to the Polycyclic Aromatic Hydrocarbons (PAHs) concentration to an extent.

Table 2 also indicated that Egbema communities had a mean value of $4.7 \pm 0.27 \mu\text{g/l}$ and range of 4.0 to $5.1 \mu\text{g/l}$. The result further showed that naphthalene, acenaphthylene, acenaphthene and fluorene were not detected. The Polycyclic Aromatic Hydrocarbons (PAHs) with the highest concentrations were BbF ($4.4 \pm 2.05 \times 10^{-1} \mu\text{g/l}$) and IdP ($2.2 \times 10^{-1} \pm 1.8 \times 10^{-2} \mu\text{g/l}$). The ranges were 3.7 to $4.8 \mu\text{g/l}$ for BbF and 1.7×10^{-1} to $3.0 \times 10^{-1} \mu\text{g/l}$ for IdP. DbA was the least concentrated with a value of $9.7 \times 10^{-4} \pm 3.5 \times 10^{-5} \mu\text{g/l}$ and range of 5.8×10^{-4} to $2.0 \times 10^{-3} \mu\text{g/l}$.

Polycyclic Aromatic Hydrocarbons (PAHs) concentrations in freshwater samples from Egbema is higher, this may be attributed to the oil/gas exploration and exploitation activities going on in Egbema communities in Ogba/Egbema/Ndoni Local Government Areas of Rivers State. Generally the Polycyclic Aromatic Hydrocarbons (PAHs) value from Egbema compared with permissible limit is attributed to the oil and gas activities area. The mean concentration of this work ($4.7 \pm 0.23 \mu\text{g/l}$) is far above work reported by Nizzetto *et al.* (2008) on the Biscay bay France that ranged from 0.0007-0.001 $\mu\text{g/l}$. Other reports that are below this work includes Algarra *et al.* (2005), at 0.01-0.03 $\mu\text{g/l}$, Essumang, *et al.* (2009), report on water bodies around oil refinery area in Accra varied from 0.00-0.55 $\mu\text{g/l}$, Celino *et al.* (2012) had 0.0029-0.107 $\mu\text{g/l}$ with a mean value of 0.0344 $\mu\text{g/l}$ at Todos Santos Bay in Northern Brazil and Mirsadeghi *et al.* (2010), reported that water of the peninsular in Malaysia had a value of 0.022 ± 0.0022 - $0.076 \pm 0.010 \mu\text{g/l}$.

The Concentration of total Polycyclic Aromatic Hydrocarbons (PAHs) reported in this work (Table 2) was within range and mean value as those reported by Anyakora *et al.* (2006) reported on Polycyclic Aromatic Hydrocarbons (PAHs) in water bodies in the Niger Delta Region, Nigeria. They have reported 1.95 $\mu\text{g/l}$ for nonoil area and 22.10 $\mu\text{g/l}$ for oil producing areas. Ana *et al.* (2010), has also reported 8.39 $\mu\text{g/l}$ for less industrialised area and 22.10 $\mu\text{g/l}$ for industrialised areas in water bodies in the Niger Delta Region. Environment Canada (1994), reported a value of 2.00 $\mu\text{g/l}$ for

fluoranthene, 1.8 µg/l for Phenanthrene and 0.49 µg/l for Naphthalene for water from ditches next to utility near Vancouver, Canada and Law *et al.* (1997), studied Polycyclic Aromatic Hydrocarbons (PAHs) in surface water in England and Wales had a value of 0.00-10.70 µg/l.

Okoro (2008), reported a Polycyclic Aromatic Hydrocarbons (PAHs) value of 24.39-2883.60 µg/l for Ekpan Creek in Niger Delta, Olajire *et al.* (2007), reported 11.20-3410 µg/l for surface water within the vicinity of Agbabu Bitumen field of South Western Nigeria, Opuene *et al.* (2009), reported 720.46- 857.65 µg/l for total PAHs in Elelenwo Creek, Southern Nigeria, Ogunfowokan *et al.* (2003), reported a concentration of 100-15810 µg/l for surface water at Oshogbo and Ife, 100-73720 µg/l for Lagos water bodies. Kamchanayoon *et al.* (2008), also recorded 50.00-550 µg/l, Adeyemo *et al.* (2012), reported 1863.33 µg/l for some rivers in oil producing areas of Delta State, Nigeria, Falahudin *et al.* (2012), while working on Timor Sea had 54.50-213.70 µg/l and a mean of 99.80 µg/l and Essumang *et al.* (2009), also reported 26.8-105.5 µg/l with arithmetic mean of 68.40 µg/l for water bodies in Esbjerg Denmark. These works by the various researchers were far above this work. Table 3 shows comparison of the Polycyclic Aromatic Hydrocarbons (PAHs) level with permissible limits.

The concentration of the total Polycyclic Aromatic Hydrocarbons (PAHs) is far above the permissible limit set by WHO (2006), of 0.7 µg/l, Europe (NIEA, 2011) of 0.1 µg/l, USEPA (2009), of 0.2 µg/l, Turkey (Emrah, 2012), at 0.1 µg/l and Australia at 0.01 µg/l, this higher value may be of significant health risk to the populace. The Highest concentration of individual PAHs was from benzo (b) Fluoranthene, with concentration higher than permissible limits as shown in Table 3, at this concentration of which may also pose health risk as it is classified by the USEPA as a Group 2B carcinogenic chemical (WHO, 1996). Indeno (1,2,3-cd) pyrene had a concentration also above the permissible limits, may also pose human health risk as it is also classified as group 2B carcinogenic chemical by the USEPA. Other individual

Polycyclic Aromatic Hydrocarbons (PAHs) were in concentration that was too low to pose a threat to human health.

The CDIing recorded for Egbema shows that benzo (b) fluoranthene still had the highest value, $8.93E^{-5}$ mg/kg-day for 10 years, $1.12E^{-4}$ mg/kg-day for 25 years adult, $1.26E^{-4}$ mg/kg-day for 70 years old. The least value was obtained for dibenz(a,h) anthracene at $1.97E^{-8}$ mg/kg-day for 10 years old children, $2.44E^{-8}$ mg/kg-day for an adult of 25 years and $2.77E^{-8}$ mg/kg-day for adults of 70 years. The total PAHs had a CDIing value of $9.41E^{-5}$ mg/kg-day for 10 years of child, $1.18E^{-4}$ mg/kg-day for adult of 25 years and $1.33E^{-4}$ mg/kg-day for an adult of 70 years. Generally other carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) had CDIing value that is lower compare to that of BbF and a bit higher than that of DaA.

5. SUMMARY

This study was aimed at determining the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in water samples from Egbema Communities in Ogba/Egbema/Ndoni Local Government Area (ONELGA), Rivers State, Nigeria. In doing this, cancer risks and physico-chemical parameters were determined. The physico-chemical parameters were done to ascertain water quality. For the parameters determined did not exceed the permissible limit of the World Health Organization (WHO, 2006) and Nigeria (FMENV, 1992). The Total Dissolved Solid was 113.0 ± 23.70 mg/l, Total Suspended Solid was 70.8 ± 11.93 mg/l and Turbidity was 0.8 ± 0.00 NTU and pH was 7.5 ± 1.05 . The mean concentration and standard deviation of PAHs across the sampled areas showed that Egbema sampled communities had 4.7 ± 0.23 μ g/l, with a range of 4.0 – 5.1 μ g/l. The mean concentration and standard deviation for the study stood at 4.7 ± 0.23 μ g/l with a range of 1.4 – 6.0 μ g/l. This concentrations were above the permissible limit as given by Canada (DWFPTCDW, 2008) at 0.010 μ g/L; USEPA, (2009) at 0.20 μ g/l; Europe (NIEA, 2011) at 0.10 μ g/l; Australia (NHMRC, NRMCC, 2011) for BaP at 0.010 μ g/l; WHO (2006) at 0.70 μ g/l and Turkey (Emrah, 2012) at 0.10 μ g/l.

6. CONCLUSION

The results showed that the parameters determined did not exceed the permissible limit of the world Health Organization (WHO, 2006). The water samples analysed in the area was also considered hard although they fall within the WHO specification limit. Generally there is an indication that water quality has been impaired. This study has provided new insights into the distribution pattern of Polycyclic Aromatic Hydrocarbons (PAHs) in the area, as some the Polycyclic Aromatic Hydrocarbons (PAHs) was detected in Egbema, some was not detected like naphthalene, acenaphthylene, acephthene and fluorene. Results obtained from the study clearly demonstrate that the effluent from all the oil/gas exploitation and exploration industrials around Egbema areas discharged into water bodies contain Polycyclic Aromatic Hydrocarbons with concentration ranging from below detection level to 6.0 µg/l. However, seven carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) were detected in different concentrations from the various sites. Benzo [a] anthracene, benzo [b] fluoranthene, chrysene, benzo [k] fluoranthene, benzo [a] pyrene, indeno [1,2,3-cd] pyrene, dibenz[a,h] anthracene occurred at the various sites with total concentration above the safety level set by WHO and USEPA. The current levels of Polycyclic Aromatic Hydrocarbons (PAHs) in surface water in the areas sampled is an indication that there is much high level input into the water environment from the industries including the flow stations, gas plants, pipelines present in these areas.

7. RECOMMENDATION

The present findings suggest that;

Improvements in the existing environmental legislation should be made to avoid adverse effects to public health within the region. Based on these findings, consumers should be advised not to make use of such water but use alternatives provided by multinationals around the areas.

Industries within the Niger Delta area, especially those at Egbema communities must ensure that their effluent containing Polycyclic Aromatic Hydrocarbons (PAHs)

compounds are carefully managed to minimize the pollution of environmental media particularly surface water sources in the region.

Periodic risk assessment of our environments should be carried out from time to time to determine the levels of these Polycyclic Aromatic Hydrocarbons (PAHs) in the water bodies since human activities such as energy generation, oil/gas activities and mining are been carried out daily.

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