Journal of Environmental Health (JEH) ISSN- 0189-5885
https://www.sehon.org/publications *vol 11 (2) 43-53*

ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) CONCENTRATION IN NWORIE RIVER, OWERRI, IMO STATE

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ABSTRACT

Study to establish the concentration of polycyclic aromatic hydrocarbons in Nworie River was executed between March and October,2023. Surface water and fish were the samples collected from Nworie Rivers. Samples were collected from various strategic sampling points from Nworie River: Egbeada (sampling point 1), Alvan/FMC (sampling point 2), Umezuruike hospital(sampling point 3), and Akanchawa (sampling point 4). The Global Positioning System (GPS) was used to establish the coordinates of the sampling points. The analysis of PAH was performed on a BUCK M910 Gas chromatography equipped with a ECD detector. A RESTEK 15 meter MXT-1 column (15m x 250um x 0.15um) was used. The injector temperature was 280^{o}C with splitless injection of 2µl of sample and a linear velocity of 30cms^{-1}, Helium 5.0 pa.s was the carrier gas with a flow rate of 40 ml/min. The oven operated initially at 200^{0}c, it was heated to 330^{0}c at a rate of 3^{0}c min^{-1} and was kept at the temperature for 5min. the detector operated at a temperature of 320^{0}c. PAH was determined by the ratio between the area and mass of internal standard and the area of the identified compounds. The concentration of the different PAH expressed in µg/ml. Egbeada sampling point recorded , 4.0722 mg/ml, Alvan/FMC recorded 4.5459 mg/ml, Umezurike hospital sampling point recorded, 5.2721 mg/ml while Akanchawa sampling point recorded 4.5011 mg/ml of total PAH. The total PAH concentrations in the Nworie River consistently exceeded the Federal Ministry of Environment (FMEnv) standard of 4.0722 mg/ml. This suggests a high level of PAH contamination in the water, which is a cause for concern. High PAH concentrations can have detrimental effects on aquatic ecosystems as well as indicating a potential for adverse human health consequences.

Keywords: Chromatography, Polyaromatic, hydrocarbons, Ecosystem, aquatic, Injector

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of harmful organic compounds that contain more than two fused benzene rings and can be found throughout the environment. There are over 200 known types of PAHs, which are typically categorized as either lower molecular weight or higher molecular weight PAHs. Lower molecular weight PAHs have two or three fused aromatic rings, while higher molecular weights PAHs have at least four benzene rings and are more stable in the environment. PAHs are naturally hydrophobic and lipophilic, meaning they tend to repel water and are attracted to fats, and they also have a strong tendency to bind to suspended particles in aquatic environments. They are primarily deposited in water and water sediment at the bottom of bodies of water, where they can accumulate to levels that are high enough to be toxic to the environment and can enter the food chain, ultimately becoming part of our diet. PAHs are known to have the potential to disrupt the endocrine system and are considered priority organic pollutants due to their ability to form photo-oxidation products and alkylated derivatives, which can make them teratogenic, carcinogenic, and mutagenic, as reported by (Adeniji *et al*. 2018).

Polycyclic aromatic hydrocarbons (PAHs), as persistent organic pollutants commonly encountered in the environment, are particularly challenging to eliminate. They present a significant environmental risk to public health because of their toxic, mutagenic, and carcinogenic properties, (Mekuleyi *et al*. 2018). It has been observed and is often predicted that PAHs can be distributed in water, sediments, particulate matter, and dissolved organic materials. The presence of these substances in both aquatic and terrestrial ecosystems has garnered increased attention due to the hazardous nature of polycyclic aromatic hydrocarbons (PAHs) and their wide-ranging distribution, as highlighted by (Agbozu *et al*. 2020).

Studies of surface water bodies in Asia, United States of America among others, reveals that anthropogenic sources of chemical pollutants which include industrial effluents, fossil fuels, discharges from sewage plants releases chemical substances which contain polycyclic aromatic hydrocarbons (PAHs) pollutants into rivers. Chronic exposure to low concentrations of polycyclic aromatic hydrocarbons (PAH) pollutants might cause brain damage, chronic kidney diseases and other serious health challenges (Selvam, *et al*., 2022; Wang, *et al.,* 2016; and liu, *et al.,* 2020).

In Africa, polycyclic aromatic hydrocarbons are pollutants of major concern in rivers and other aquatic habitats. They are characterized by carcinogenic and non-carcinogenic tendencies, more especially the sixteen priority PAHs in water and sediment pose potential health risks. Polycyclic aromatic hydrocarbons (PAHs) and sundry pollutants are also bio-available to the aquatic animals and finally find their ways into the dietary sources. Studies reveal that they are carcinogenic, teratogenic, and mutagenic and have the potentials for endocrine disruption (Adeniji, *et al.,* 2019).

Furthermore in Nigeria, reports of studies on polycyclic aromatic hydrocarbons (PAHs) reveal that human activities such developmental, agricultural, mining, economic, commercial, social, industrial and biomedical activities, release pollutants directly and indirectly in form of untreated or partially treated effluents containing polycyclic aromatic hydrocarbons (PAHs) into rivers. These pollutants may accumulate in aquatic life, enter the food chain and cause serious harm to human health, where exposure is significant. Studies further reveals that ingestion of contaminated aquatic foods or water is the main route of exposure to polycyclic aromatic hydrocarbons. Chronic intake of polycyclic aromatic hydrocarbons above safe threshold in animals and humans have detrimental health effects such as neurological problems, liver and kidney diseases among others (Ezemonye, *et al.,* 2018; Ezekwe, *et al.,* 2014; Obanya, *et al*., 2019; Okechukwu, *et al.,* 2021; Udofia *et al.,* 2021; Ekere, *et al.,* 2019).

The existence of these chemicals in the aquatic environment has drawn greater attention due to the toxicity of polycyclic aromatic hydrocarbons (PAHs) and their extensive distribution (Agbozu *et al.,* 2020). Consequently, they have been listed in United States Environmental Protection Authority (USEPA) based on their potential for human consumption and health risk. In addition, a major percentage of polycyclic aromatic hydrocarbons which accumulated in fish come from polluted water through water borne exposure. Aquatic animals especially fish have been reported by Food and Agricultural Organization (FAO) data to constitute 16% of the world population intake of animal protein and 6% of all protein consumed. Polycyclic aromatic hydrocarbons in fish tissue can be many times higher than their corresponding waterborne values. Consumption of aquatic animals has been reported as important route of human exposure to varieties of chemical contaminants (Ezemonye, *et al.*, 2018).

In Imo State, there is limited information on the concentration of polycyclic aromatic hydrocarbons in Nworie River. Like many other rivers across the world, Africa and Nigeria, Nworie River may be faced with problems of pollution of polycyclic aromatic hydrocarbons due to precipitation, waste discharge and urban runoff which leach these pollutants from anthropogenic sources into the water bodies. The degradation of surface water quality may also be a significant threat to Nworie River due to urbanization, industrialization and growth of commercial activities around these rivers. It therefore becomes necessary to assess the concentration of polycyclic aromatic hydrocarbons in Nworie River, Imo State Nigeria.

MATERIALS AND METHOD

Study area

They study area was Nworie River of Owerri Imo State, located within 5^o 101 N to 5^o 571 N and longitude 7^o 281 E to 5^o 351 and covered an area of about 24.88km^2. The area has an annual rainfall of 1900-2900 mm and monthly minimum temperature of 25^{o}C and maximum temperature of 35^o C. Owerri municipal area has a tropical wet and dry climate. The north –east trade wind causes the dry season as it advances south wards while the south-west trade wind causes the rainy season as it moves inland towards the north (Ogbomida & Emeribe 2013). There are various land use around Nworie river which include residential, commercial, industrial, institutional and administrative land uses. Manufacturing industries are distributed near the Nworie River along the highway,

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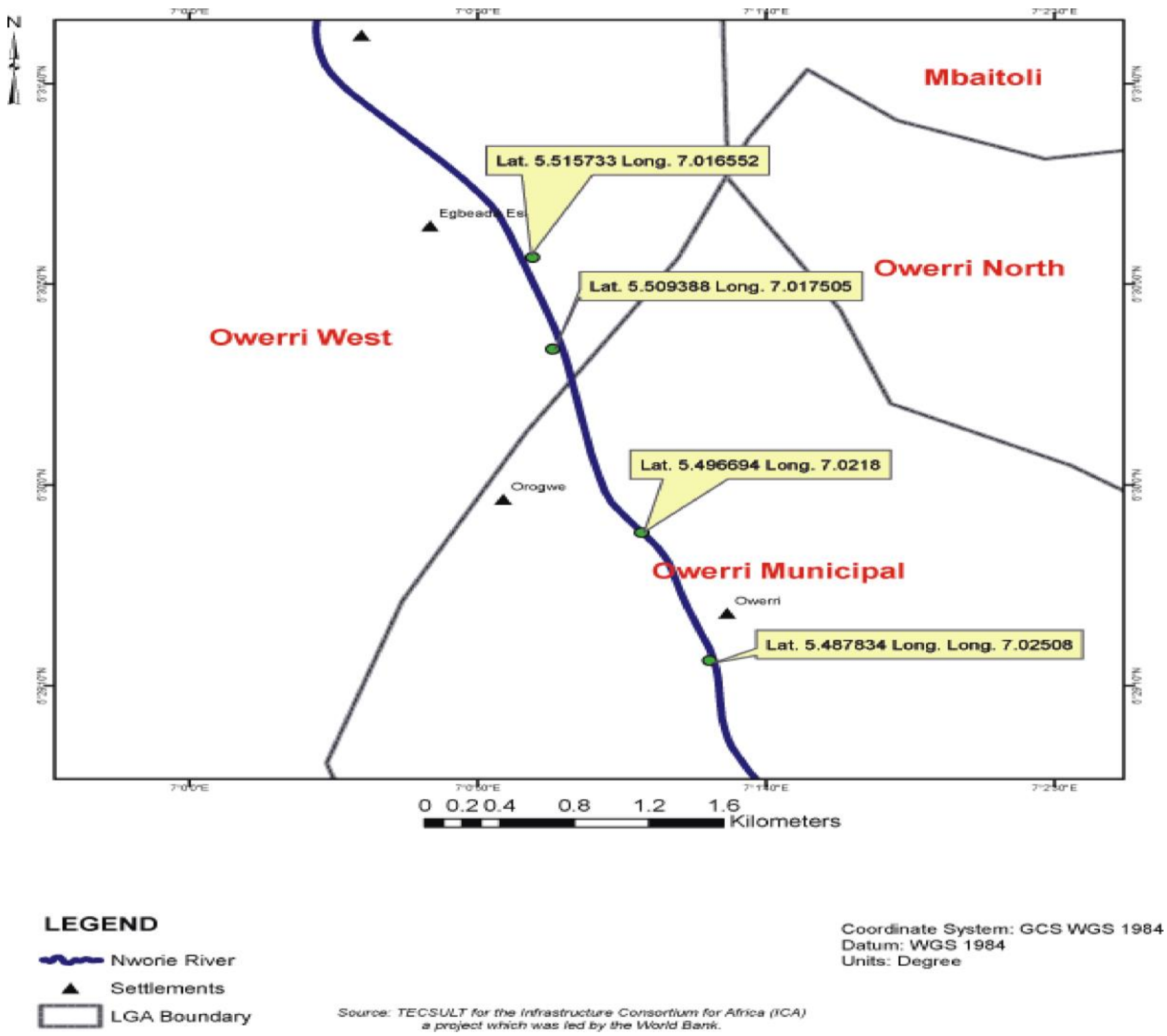

Figure 1: map of Owerri Nworie River showing the study site

Collection of Water Samples

Surface water and Fish were sampled and analysed for polycyclic aromatic hydrocarbons (PAHs). The sampling points were carefully selected to include upstream and downstream regions. Water samples were collected from 0.3m below the water surface. Samples were collected from various strategic sampling points from Nworie River at Egbeada (sampling point 1), Alvan/FMC (sampling point 2), Umezuruike hospital (sampling point 3), and Akanchawa (sampling point 4). The samples were collected and labeled for easy identification and were preserved in an ice pack

Laboratory analysis

Extraction for Polycyclic aromatic hydrocarbons (PAH) Analysis

Water sample Extraction

Equal volume of N-hexane and the water sample (100ml) were measured into a beaker. Mixed thoroughly and transferred into a separating funnel to separate. N-hexane layer was collected for florisil clean-up.

FISH sample Extraction

20g of the fish sample was extracted with the aid of soxhlet apparatus using N-hexane. 100ml of N-hexane was used for the extraction of oil from the fish sample. The extracted oil was used for flosisil clean up for PAH analysis.

Florisil Cleanup for PAH analysis

1. Florisil (magnesium silicate) 1g heated in an oven at 130C and transferred to a 250ml size beaker and placed in a desiccator.
2. A 0.5g anhydrous $NaSO_4$ was added to 1.0g of activated florisil (magnesium silicate) (60-100nm mesh) on an 8ml column plugged with glass wool.
3. Packed column was filled with 5ml n-hexane for conditioning. Open stopcock to allow N-hexane run out until it just reached top of soldium sulphate into a receiving vessel whilst tapping gently the top of the column till the florisil settled well in the column.
4. Extract was transferred on to the column with disposable Pasteur pipette from an evaporating flask.
5. Each evaporating flask was rinsed twice with 1ml portions of n-hexane and added to column.
6. Eluate was collected into an evaporating flask and rotary evaporated to dryness.
7. Dry eluate was dissolved in 1ml n-hexane for fatty acid profile
   The 1ml n-hexane extract was dissolved in 50ml of chloroform and transferred to a 100ml volumetric flask and dilute to the mark. Most of the chloroform was evaporated at room temperature. 1ml of inter-esterification reagent (20 vol benzene and 55 vol methanol) was added. Sealed, and heated at 40^0C water bath for 30 minutes. After addition of inter-esterification reagent, the organic sample was extracted with hexane. The mixture was shaken vigorously by hand for 2min. when a stable emulsion was formed, it was separated by centrifugation. Then about half of the top hexane phase was transferred to a small test tube for injection.

Analysis of PAH using GC-ECD DETECTOR

The analysis of PAH was performed on a BUCK M910 Gas chromatography equipped with a ECD detector. A RESTEK 15 meter MXT-1 column (15m x 250um x 0.15um) was used. The injector temperature was 280°C with splitless injection of 2ul of sample and a linear velocity of $30cms^{-1}$, Helium5.0pa.s was the carrier gas with a flow rate of 40ml/min. The oven operated initially at 200^0c, it was heated to 330^0c at a rate of 3^0c min^{-1} and was kept at this temperature for 5min. the detector operated at a temperature of 320^0c.

PAH was determined by the ratio between the area and mass of internal standard and the area of the identified compounds. The concentration of the different PAH express in ug/ml.

RESULTS

Polycyclic aromatic hydrocarbons

Table 1: concentration of polycyclic aromatic hydrocarbons in water samples (mg/kg) in the four locations (egbeada point, alvan/fmc, umezurike hospital and akanchawa)

PARAMETERS	FMEnv Standard	NWORIE RIVER							
		EGBEADA POINT1 N5.515734^0 E7.016496^0		ALVAN/FMC POINT2 N5.509388^0 E7.017507^0		UMEZURIKE HOSPITAL POINT3 N5.487911^0 E7.025613^0		AKANCHAWA POINT 4 N5.473937^0 E7.030037^0	
		RUN 1	RUN 2	RUN 1	RUN 2	RUN 1	RUN 2	RUN 1	RUN 2
POLYAROMATIC HYDROCARBON									
PAH Total, mg/ml		4.0722	4.0722	4.5459	4.5459	5.2721	5.2721	4.5011	4.5011
Benzo(b) Fluoranthene, mg/ml	0.2	0.1974	0.1974	0.1974	0.1974	0.0052	0.0052	-	-
Acenaphthylene,mg/ml	0.1	1.4688	1.4688	1.4688	1.4688	0.4157	0.4157	0.9917	0.9917
1-2 benzanthracene, mg/ml	0.1	0.3230	0.3230	0.8027	0.8027	0.3875	0.3875	0.6503	0.6503
Benzo(k)fluoranthene, mg/ml	0.1	0.0111	0.0111	0.0111	0.0111	0.0107	0.0107	0.0787	0.0787
Benzo(a)pyrene, mg/ml	0.1	0.0533	0.0533	-	-	0.3197	0.3197	0.3467	0.3467
Phenanthrene, mg/ml	0.02	0.0111	0.0111	0.3199	0.3199	1.0590	1.0590	0.1096	0.1096
Benzo(g-h-i)perylene, mg/ml	0.1	-	-	0.1934	0.1934	1.2770	1.2770	0.3250	0.3250
Acenaphthene, mg/ml	0.1	0.1109	0.1109	0.3202	0.3202	0.0032	0.0032	0.5792	0.5792
Anthracene, mg/ml	0.02	0.2315	0.2315	-	-	1.0955	1.0955	0.4811	0.4811
Dibenzyl(a_h)anthracene, mg/ml	0.2	0.3840	0.3840	0.5761	0.5761	0.2560	0.2560	0.4057	0.4057

Fluorene, mg/ml	0.1	0.9604	0.9604	-	-	-	-	-	-
Xylene, mg/ml	0.2	-	-	-	-	0.4374	0.4374	-	-
Pyrene , mg/ml	0.2	0.0032	0.0032	0.0107	0.0107	0.0042	0.0042	-	-
Naphthalene, mg/ml	0.1	0.0003	0.0003	-	-	-	-	-	-
Flouranthene, mg/ml	0.005	0.3170	0.3170	0.6050	0.6050	0.0011	0.0011	0.5332	0.5332
Chrysene	0.2	-	-	0.0405	0.0405	-	-	-	-

The total PAH concentrations were measured in mg/ml (milligrams per milliliter).

In all runs and at all points, the total PAH concentrations exceeded the FMEnv (Federal Ministry of Environment) standard of 4.0722 mg/ml. This indicates that the PAH pollution levels in Nworie River are above the acceptable regulatory limits.

Benzo(b) Fluoranthene: Concentrations: 0.1974 mg/ml (Egbeada),0.1974 mg/ml (Alvan/FMC), 0.0052 mg/ml (Umezuruike hospital) were generally below the FMEnv standard of 0.2 mg/ml, indicating compliance with this specific PAH compound.

Acenaphthylene: Concentrations consistently exceeded the FMEnv standard of 0.1 mg/ml.

1-2 Benzanthracene: Concentrations exceeded the FMEnv standard of 0.1 mg/ml in some runs, indicating potential pollution. Other individual PAH compounds show varying levels, with some exceeding standards while others remain below standard.

The data indicate that there is a significant pollution issue with respect to PAHs in the Nworie River. The total PAH concentrations consistently exceeded the FMEnv standard, suggesting a high level of PAH contamination in the water. Specific PAH compounds like Acenaphthylene also consistently exceeded regulatory limits, indicating potential harm to the aquatic environment and human health. The presence of certain PAHs, such as Benzo(k)fluoranthene, Benzo(a)pyrene, Phenanthrene, and others, at concentrations above or near regulatory standards raises concerns about the overall water quality and the potential impact on aquatic life and ecosystems.

In overall, the data suggests that urgent action is needed to address the PAH pollution issue in the Nworie River to protect both the environment and public health. The findings from the measurements of polyaromatic hydrocarbons (PAHs) in the Nworie River indicate a serious pollution issue with potential environmental and public health implications.

DISCUSSIONS

The total PAH concentrations in the Nworie River consistently exceeded the Federal Ministry of Environment (FMEnv) standard of 4.0722 mg/ml. This suggests a high level of PAH contamination in the water, which is a cause for concern. High PAH concentrations can have detrimental effects on aquatic ecosystems. This finding aligns with global trends in PAH pollution in water bodies. A study by Zhang *et* *al*. (2018) found that PAH contamination in rivers and lakes is a widespread problem, often exceeding recommended limits. Benzo(b) Fluoranthene: Concentrations are generally below the FMEnv standard of 0.2 mg/ml, indicating compliance with this specific PAH compound. This suggests that some PAHs may not be as prevalent or problematic as others in the Nworie River. Acenaphthylene Concentrations exceed the FMEnv standard of 0.1 mg/ml. This is particularly concerning as it indicates the presence of a specific PAH compound at levels that can be detrimental to aquatic life and public health. The persistence of Acenaphthylene pollution is in line with research by Wei *et al*. (2019), which emphasized the need for strict regulations and monitoring of this compound due to its adverse effects on ecosystems. The varying concentrations of specific PAH compounds, such as Benzo(k)fluoranthene, Benzo(a)pyrene, Phenanthrene, and others, raise concerns about overall water quality and potential impacts on aquatic life and ecosystems. Studies like the one conducted by Chang *et al*. (2017) stressed the importance of monitoring a wide range of PAH compounds due to their diverse toxicological effects and the complex interactions among different PAHs in aquatic environments. The data highlighted the importance of identifying the sources of PAH contamination. Understanding these sources is crucial for developing effective strategies for remediation and pollution control. Research by Wang *et al*. (2014) emphasized the necessity of source identification in PAH pollution management, as this information is fundamental for targeted pollution control efforts. The data strongly suggests the need for immediate action to address the PAH pollution issue in the Nworie River, to protect both the environment and public health. Urgent action in response to PAH pollution is a common theme in recent environmental policy discussions. The findings from the Nworie River indicated an adverse PAH level, with total PAH concentrations exceeding standards, the presence of specific compounds at unacceptable levels, and a need for further investigation.

Conclusion and Recommendation:

Given the severity of the PAH pollution issue in the Nworie River, it is imperative to take decisive action to mitigate its impact and protect the environment and public health. Here are some recommended actions: Immediate Remediation: Implement measures to reduce PAH contamination, such as source identification, pollution control, and cleanup efforts. Stringent

Regulations: Develop and enforce stringent regulations for PAH levels in the Nworie River to prevent further contamination. Monitoring and Assessment: Establish a robust monitoring and assessment program to track PAH concentrations over time and assess the effectiveness of mitigation efforts.

Public Awareness: Educate the public about the risks associated with PAH pollution and encourage responsible environmental practices.

Further Research: There should be Continues research into the specific sources and pathways of PAH contamination, enabling more targeted pollution control strategies.

Collaboration: Collaborate with environmental agencies, local communities, and experts to develop a comprehensive plan for addressing this critical issue. The urgency of the situation requires immediate attention and concerted efforts to safeguard the Nworie River and the well-being of the surrounding community

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