Evaluation of Concentration of Polycyclic Aromatic Hydrocarbons in Otamiri River Owerri, Southeast Nigeria

Abstract

Study to evaluate the concentration of polycyclic aromatic hydrocarbons (PAHs) Otamiri River. Samples of water was collected from Otamiri River and analysed for polycyclic aromatic hydrocarbons (PAHs). Samples were collected from various strategic sampling points from Otamiri River: Abattoir/Shoprite Residence Point 1 (sampling point 1), Abattoir/Shoprite Residence 2 (sampling point 2), Nekede/Ihiagwa Bridge 1 (sampling point 3), and Nekede/Ihiagwa Bridge 2 (sampling point 4). The Global Positioning System (GPS) was utilized to locate the coordinates of the sampling points. The analysis of polycyclic aromatic hydrocarbons (PAHs) was performed using a BUCK M910 Gas Chromatograph equipped with an Electron Capture Detector (ECD). A RESTEK MXT-1 column (15 m × 250 µm × 0.15 µm) was employed for the separation. The injector temperature was set to 280°C, with a splitless injection of 2 µL of sample, and a linear velocity of 30 cm/s. Helium 5.0 served as the carrier gas, flowing at a rate of 40 ml/min. The oven was initially maintained at 200°C, then ramped to 330°C at a rate of 30°C per minute, and held at that temperature for 5 minutes. The detector operated at 320°C. PAHs were quantified by calculating the ratio of the area-to-mass of the internal standard to the area of the identified compounds. The concentration of the different PAHs expressed in mg/ml. Abattoir/Shoprite Residence sampling point 1 recorded 3.920 mg/ml, Abattoir/Shoprite Residence 2 sampling point 2 recorded 7.749 mg/ml, Nekede/Ihiagwa Bridge 1 sampling point 3 recorded 3.841 mg/ml, and Nekede/Ihiagwa Bridge 2 sampling point 4 recorded 5.422 mg/ml. The total PAH concentrations in the Otamiri River was consistently above the Federal Ministry of Environment (FMEnv) standard of 1.845 mg/ml which suggests a high level of PAH pollution in the Otamiri water, which should be a serious public health concern. High PAH concentrations can have detrimental effects on aquatic ecosystems, other animals and humans consuming the water.

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key words : Polyaromatic, hydrocarbons, concentration, surface water

Introduction

Polycyclic aromatic hydrocarbon (PAH) refers to a class of organic compounds composed of multiple interconnected aromatic rings, typically formed by carbon and hydrogen atoms. These compounds are known for their stability and are commonly found in substances like fossil fuels, tar, and the byproducts of combustion. Over 200 known types of PAHs, typically classified as either lower molecular weight or higher molecular weight PAHs. Low molecular weight PAHs consist of two or three fused aromatic rings, whereas high molecular weight PAHs contain four or

Commented [AA3]: Back this sentence up with a reference more benzene rings and exhibit greater environmental stability. These compounds are inherently hydrophobic and lipophilic, meaning they repel water and are attracted to fats. Additionally, they have a strong affinity for binding to suspended particles in aquatic systems. PAHs are mainly deposited in water and sediments at the bottom of aquatic environments, where they can accumulate to toxic levels, posing risks to the ecosystem and potentially entering the food chain, eventually becoming part of human consumption. These compounds are recognized for their ability to disrupt the endocrine system and are classified as priority organic pollutants. Their capacity to form photo-oxidation products and alkylated derivatives further enhances their toxicity, making them teratogenic, carcinogenic, and mutagenic, as reported (Adeniji et al. 2018).

Polycyclic aromatic hydrocarbons (PAHs) are hazardous and persistent organic pollutants frequently found in the environment, making their removal particularly difficult. These compounds are a pervasive group of pollutants present across various environmental media, including sediment, particulate matter, soil, air, and water. Due to their toxic, mutagenic, and carcinogenic characteristics, PAHs pose a substantial environmental threat to public health, as reported (Mekuleyi et al. 2018). PAHs are known to distribute themselves among water, sediments, particulate matter, and dissolved organic materials, a behavior that is both observed and frequently predicted. Their presence in aquatic and terrestrial ecosystems has drawn significant attention due to their hazardous nature and extensive distribution, as emphasized (Agbozu et al. 2020).

Research on surface water bodies in regions such as Asia and the United States reveals that anthropogenic activities, including industrial effluents, fossil fuel combustion, and discharges from sewage treatment plants, introduce chemical substances containing polycyclic aromatic hydrocarbons (PAHs) into rivers. Prolonged exposure to low concentrations of these PAH pollutants may lead to brain damage, chronic kidney disease, and other severe health issues (Selvam, *et al*., 2022; Wang, *et al.,* 2016; and liu, *et al.,* 2020).

In Africa, polycyclic aromatic hydrocarbons (PAHs) are significant pollutants in rivers and other aquatic environments. These compounds, including the sixteen priority PAHs in water and sediment, are associated with both carcinogenic and non-carcinogenic effects, posing potential health risks. PAHs and other pollutants are bioavailable to aquatic organisms, eventually entering the food chain and dietary sources. Research indicates that these substances are carcinogenic, teratogenic, mutagenic, and capable of disrupting the endocrine system (Adenji, *et al.,* 2019).

In Nigeria, studies on polycyclic aromatic hydrocarbons (PAHs) indicate that various human activities—such as developmental, agricultural, mining, economic, commercial, social, industrial, and biomedical operations—contribute to the release of pollutants. These pollutants, often in the form of untreated or partially treated effluents containing PAHs, are discharged directly or indirectly into rivers. Over time, these contaminants can accumulate in aquatic organisms, enter the food chain, and pose significant health risks to humans upon substantial exposure. 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 (Ezeonye, *et al.,* 2019; 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). As a result, polycyclic aromatic hydrocarbons (PAHs) have been classified by the

United States Environmental Protection Agency (USEPA) due to their potential risks to human health through consumption. Additionally, a significant portion of PAH accumulation in fish originates from polluted water via waterborne exposure. According to data from the Food and Agriculture Organization (FAO), aquatic animals, particularly fish, contribute 16% of the global intake of animal protein and 6% of total protein consumption. 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 Eastern Nigeria, there is limited information on the concentration of polycyclic aromatic hydrocarbons in Otamiri River. Like many other rivers across the world, Africa and Nigeria, Otamiri 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 Otamiri River due to urbanization, industrialization and growth of commercial activities around these rivers.

Establishing the concentration of polycyclic aromatic hydrocarbons in surface water in the determination of safety of aquatic ecosystems. Hence, it is significant to ascertain concentration of polycyclic aromatic hydrocarbons in Otamiri River in Imo State Eastern Nigeria.

Materials and methods

Description of study area

The study area was the Otamiri River in Owerri, Imo State, located in southeastern Nigeria, within the coordinates 5° 10'N to 5° 57'N latitude and 7° 28'E to 5° 35'E longitude, covering an area of approximately 24.88 km². The region experiences annual rainfall ranging from 1900 to 2900 mm, with a minimum monthly temperature of 25°C and a maximum of 35°C. Owerri municipal area has a tropical wet and dry climate. The dry season is driven by the northeast trade winds, which move southward, while the southwest trade winds bring the rainy season as they move inland toward the north. The dry season lasts from November to early March, and the rainy season occurs from March to October, reaching its peak in September, with a brief dry period known as the "August break." The study area exhibits various land use patterns, including residential, commercial, industrial, institutional, and administrative areas. The built-up region is located at the confluence of the Otamiri River. The commercial, market and traditional housing district are both in the less elevated central and southern parts of the town are high density residential area. Low density residential area and public establishments and major educational institutions are concentrated in the north east axis of the town. Manufacturing industries are distributed though the largest of them is located near the Otamiri River along the highway,

Map 1 : Otamiri River

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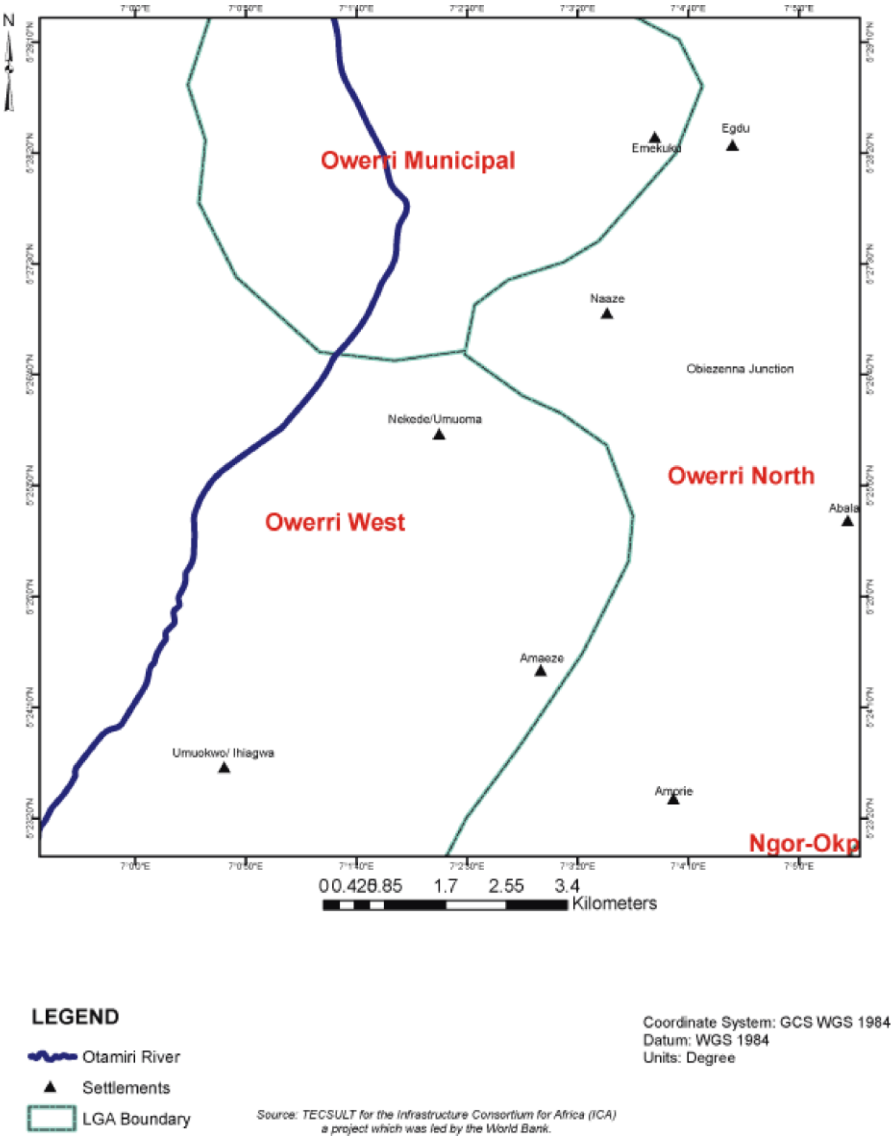

Coordinate System: GCS WGS 1984
Datum: WGS 1984
Units: Degree

Source: TECSULT for the Infrastructure Consortium for Africa (ICA) a project which was led by the World Bank.

Collection of Water Samples and Treatment

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Surface water and fish samples were collected and analyzed for polycyclic aromatic hydrocarbons (PAHs). The samples were taken from the Otamiri River, with sampling sites strategically chosen to represent both upstream and downstream areas. Water samples were collected from a depth of 0.3 meters below the water surface. Samples were collected from various strategic sampling points from Otamiri River at Abattoir/Shoprite Residence Point 1 (sampling point 1), Abattoir/Shoprite Residence 2 (sampling point 2), Nekede/Ihiagwa Bridge 1 (sampling point 3), and Nekede/Ihiagwa Bridge 2 (sampling point 4). The samples were collected, labeled for proper identification, and stored in ice packs to preserve their temperature. Various data collection methods were used in the study, including water and fish sampling, observations, field and laboratory analyses, and global positioning system (GPS) measurements.

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Laboratory analysis

Extraction for Polycyclic aromatic hydrocarbons (PAH) Analysis

Water sample Extraction

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An equal volume of N-hexane and 100 ml of the water sample were measured into a beaker, mixed thoroughly, and then transferred to a separating funnel for separation. The N-hexane layer was collected and subjected to a florisil clean-up process.

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FISH sample Extraction

A 20 g fish sample was extracted using a Soxhlet apparatus with N-hexane. A total of 100 ml of N-hexane was used to extract the oil from the fish sample. The extracted oil was then subjected to florisil clean-up for polycyclic aromatic hydrocarbon (PAH) analysis.

Florisil Cleanup for PAH analysis

1. Florisil (magnesium silicate) 1g heated in an oven at 130°C and transferred to a 250 ml size beaker and placed in a desiccator.
2. A 0.5 g anhydrous $NaSO_4$ was added to 1.0 g of activated florisil (magnesium silicate) (60-100 nm mesh) on an 8 ml column plugged with glass wool.
3. Packed column filled with 5 ml n-hexane for conditioning. Open stopcock to allow N-hexane run out until it just reaches top of sodium sulphate into a receiving vessel whilst tapping gently the top of the column till the florisil settled well in the column.
4. Transfer extract on to the column with disposable Pasteur pipette from an evaporating flask.
5. Rinse each evaporating flask twice with 1ml portions of n-hexane and add to column.
6. Eluate collected into an evaporating flask and rotary evaporated to dryness.
7. Dry eluate dissolved in 1ml n-hexane for fatty acid profile

Dissolve 1 ml of the n-hexane extract in 50 ml of chloroform, then transfer the mixture to a 100 ml volumetric flask and dilute to the mark. Evaporate most of the chloroform at room temperature. Afterward, add 1 ml of the inter-esterification reagent (containing 20 parts benzene and 55 parts methanol), seal the flask, and heat it in a water bath at 40°C for 30 minutes. After addition of inter-esterification reagent, extract the organic sample with hexane. Shake the mixture vigorously by hand for 2min. If a stable emulsion is formed, break it by centrifugation. Transfer about half of the top hexane phase 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^{o}C with splitless injection of 2ul 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 °C, it was heated to 330 °C at a rate of 3^{0}c min^{-1} and was kept at this temperature for 5 min. the detector operated at a temperature of 320 °C.

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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 ug/ml.

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Fixed Setting: Generally, the operator must adjust gas flows to the columns, the inlets, the detectors, and the split ratio. In addition, the injector and detector temperatures must be set. The detectors are generally held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All of these parameters should have been set to the correct values, but double check all the instrument: Buck 530 gas chromatograph equipped with an on – column, automatic injector, Flame Ionization detector, HP 88 capillary column (100 m x 0.25 µm film thickness,) CA, USA

Detector Temperature A: 250 °C

Injector temperature: 22 °C

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Integrator chart speed: 2 cm/min

Set the OVEN TEMP to 180 °C and allow the GC to warm up. While its warming,

Set:

List 1 : Temperature Condition

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Initial Temp	**Hold**	**Ramp**	**Final Temp**
80^{0}C	**5min**	**10min**	**220^{0}C**
220^{0}C	**10min**	**5min**	**295^{0}C**

When the instrument is ready, the ‘’NOT READY’’ light will turn off, and you can begin your Run. Inject a 1 microliter sample onto column A using proper injection technique (Buss and Butler, 2010)

ETHICAL ANALYSIS

The following procedures were adopted by the researcher in the course of this research:

Plagiarism: This was avoided as works of people which was used to substantiate analysis and in the literature was duly acknowledged both in text and reference

Results

Polycyclic aromatic hydrocarbons

Table 1: concentration of polycyclic aromatic hydrocarbons in Otamiri river water samples (mg/ml) in the four sampling locations (Abattoir/shoprite residence point 1, Abattoir/shoprite point 2, Nekede/Ihiagwa bridge 1 point 3 and Nekede/Ihiagwa bridge 2 point 4)

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PARAMETERS	FMEnv Standard	OTAMIRI RIVER								Test METHOD
		ABATTOIR SHOPRITE, RESIDENTIAL POINT1 N5.471855^0 E7.041608^0		**POINT2 N5.443756^0 E7.022936^0**		**NEKEDE / IHIAGWA BRIDGE POINT3 N5.434568^0 E7.012608^0**		**POINT 4 N5.398043^0 E6.99335^0**		
		RUN 1	**RUN 2**	**RUN 1**	**RUN 2**	**RUN 1**	**RUN 2**	**RUN 1**	**RUN 2**	
POLYAROMATIC HYDROCARBON										
PAH Total, mg/ml	1.845	3.9203	3.9203	7.4798	7.4798	3.8411	3.8411	5.4221	5.4221	
Benzo(b) Fluoranthene, mg/ml	0.2	-	-	1.9254	1.9254	-	-	1.4412	1.4412	
Acenaphthylene,mg/ml	0.1	-	-	0.6613	0.6613	-	-	-	-	
1-2 benzanthracene, mg/ml	0.1	1.0030	1.0030	1.0030	1.0030	0.3305	0.3305	0.8065	0.8065	FID Gas Chromatography (GC)
Benzo(k)fluoranthene, mg/ml	0.1	-	-	0.5333	0.5333	-	-	0.9600	0.9600	
Benzo(a)pyrene, mg/ml	0.1	0.7446	0.7446	0.7446	0.7446	-	-	-	-	
Phenanthrene, mg/ml	0.02	-	-	0.4381	0.4381	-	-	0.5341	0.5341	
Benzo(g-h-i)perylene, mg/ml	0.1	-	-	0.0014	0.0014	0.6369	0.6369	0.2554	0.2554	
Acenaphthene, mg/ml	0.1	0.4000	0.4000	0.4000	0.4000	0.2767	0.2767	0.3413	0.3413	
Anthracene, mg/ml	0.02	-	-	-	-	-	-	-	-	
Dibenzyl(a_h)anthracene, mg/ml	0.2	1.6781	1.6781	1.6781	1.6781	1.8080	1.8080	0.2144	0.2144	

Fluorene, mg/ml	0.2	0.0113	0.0113	0.0113	0.0113	0.2132	0.5012
Xylene, mg/ml	0.2	0.0001	0.0001	0.0001	0.0001	0.1389	0.0046
Pyrene , mg/ml	0.1	0.0832	0.0832	0.0832	0.0832	0.4369	0.3410
Naphthalene, mg/ml	0.2	-	-	-	-	-	0.0224
Flouranthene, mg/ml	0.005	-	-	-	-	-	-
Chrysene	0.2	-	-	-	-	-	-

The above table, which includes measurements of polyaromatic hydrocarbons (PAHs) in the Otamiri River at different points (Abattoir Shoprite, Residential Point1 and 2, Nekede / Ihiagwa Bridge Point3 and Point 4). The total PAH concentrations are measured in mg/ml (milligrams per milliliter). The total PAH concentrations at all points and in all runs are significantly higher than the FMEnv (Federal Ministry of Environment) standard 1.845 mg/ml. This suggests that the Otamiri River is experiencing a substantial contamination of PAHs, exceeding acceptable regulatory limits. Individual PAH Compounds: Benzo(b)Fluoranthene, Acenaphthylene, and Benzo(a)pyrene are either not detected or below the FMEnv standards in all runs and at all points. 1-2 Benzanthracene is consistently above the FMEnv standard of 0.1 mg/ml in all runs and at all points.

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Benzo(k)fluoranthene is present at elevated levels in some runs, exceeding the FMEnv standard. Phenanthrene is also present at elevated levels, surpassing the FMEnv standard. Benzo(g-h-i)perylene is detected in some runs at levels above the FMEnv standard. Acenaphthene is consistently detected at various levels, some of which are above the FMEnv standard. Anthracene, Fluorene, Xylene, Pyrene, Naphthalene, Flouranthene, and Chrysene are either not detected or detected at very low levels. The data indicates a significant issue of PAH contamination in the Otamiri River. Total PAH concentrations are consistently above regulatory standards, suggesting a high level of PAH pollution in the water. Specific PAH compounds such as 1-2 Benzanthracene, Benzo(k)fluoranthene, Phenanthrene, and Benzo(g-h-i)perylene are present at concentrations that may raise environmental concerns. The presence of these PAHs at elevated levels could have adverse effects on the aquatic environment and potentially human health, as PAHs are known to be harmful and carcinogenic.

Further investigation is required to identify the sources of PAH contamination and to develop strategies for remediation and pollution control in the Otamiri River. In summary, urgent action is needed to address the PAH pollution issue in the Otamiri River to protect both the environment and public health, given the consistently high levels of PAHs detected in the water.

DISCUSSIONS

The provided data on polyaromatic hydrocarbons (PAHs) in the Otamiri River reveals a significant and concerning issue of PAH contamination. The data indicates that the total PAH concentrations in the Otamiri River are consistently higher than the WHO/FMEnv (Federal Ministry of Environment Nigeria) standards. This suggests a pervasive and substantial contamination of PAHs, indicating regulatory limits are being exceeded. This finding aligns with studies from various parts of the world that have reported elevated PAH levels in rivers and water bodies. For instance, a study by Guo, *et al*., (2019) found that many rivers in China exceeded PAH standards, highlighting the global nature of this issue.

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Benzo(b)Fluoranthene, Acenaphthylene, Benzo(a)pyrene: These specific PAH compounds are either not detected or are below FMEnv standards. This could indicate variability in the presence of different PAHs in the river. 1-2 Benzanthracene: Consistently exceeding the FMEnv standard of 0.1 mg/ml in all runs and at all points raises concerns. This suggests a consistent source of this particular PAH compound. Benzo(k)fluoranthene, Phenanthrene, Benzo(g-h-i)perylene: The presence of these PAHs at elevated levels in some runs raises environmental concerns, as these compounds are known to be harmful. Acenaphthene: Consistently detected at various levels, some of which are above the FMEnv standard. This indicates ongoing input of this PAH into the river. Anthracene, Fluorene, Xylene, Pyrene, Naphthalene, Flouranthene, and Chrysene: Either not detected or detected at very low levels, indicating variability in the presence of different PAHs. These findings highlight the complexity of PAH contamination in aquatic ecosystems. PAHs can originate from various sources, including industrial discharges, urban runoff, and vehicular emissions. The composition of PAHs in a particular water body can vary widely depending on local sources and environmental conditions. The presence of specific PAHs at elevated levels raises concerns about their potential impact on the aquatic environment and human health. PAHs are known to be harmful and carcinogenic, and their persistence in the river indicates ongoing exposure risks. Studies like that by Liu, *et al*., (2019) emphasize the need for assessing the ecological and human health risks associated with PAH contamination in water bodies, especially when specific compounds exceed regulatory limits. The data underscores the necessity for identifying the sources of PAH contamination. Understanding these sources is crucial for developing effective strategies for remediation and pollution control. Similar to the findings in the Nworie River, source identification is a critical component of managing PAH pollution. Zhang, et.al. (2018) highlights the importance of source apportionment in PAH management. The consistently high levels of PAHs detected in the Otamiri River indicate an urgent need for action to address the PAH pollution issue. This is vital to protect both the environment and public health.

Urgent action to address PAH pollution is a common theme in recent environmental policy discussions. Government agencies and environmental organizations worldwide are increasingly recognizing the need to address PAH contamination to safeguard ecosystems and human health (EPA, 2021). The data from the Otamiri River underscores the seriousness of PAH contamination, with total PAH concentrations consistently exceeding standards and specific PAH compounds at elevated levels. This situation requires immediate attention, source identification, and remediation efforts to protect both the environment and public health, in line with global efforts to address PAH pollution.

Conclusion and Recommendation:

Given the severity of the PAH pollution issue in the Otamiri 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 Otamiri 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: Continue 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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