Evaluation of polycyclic aromatic hydrocarbons of some grandwater sources within the reclaimed Orji Auto repair workshops, Owrri, Imo State, Nigeria

Chukwu Fidelis Opia [1, *], Francis Chizoruo Ibe [2]

[1]*Department of Chemistry, Imo State University, Owerri, Imo State, Nigeria; chukwufidelis@gmail.com*
[2]*Department of Chemistry, Imo State University, Owerri, Imo State, Nigeria; francispavo@yahoo.com*

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ABSTRACT

The study determined the concentrations and assessed the risk of polycyclic aromatic hydrocarbons during wet and dry seasons of groundwater sources within the reclaimed Orji auto repair workshops, in Owerri, Nigeria. The amount of polycyclic aromatic hydrocarbons was determined in random samples from five locations within this vicinity using the liquid-liquid and soxhlet extraction procedures and gas chromatography in tandem with a flame ionization detector. A total of fourteen and twelve PAH congeners were detected for wet and dry seasons respectively with concentrations of total PAHs observed in water samples during wet season ranging from 0.0012mg/ml to 1.0352mg/ml, with Pyrene having the lowest concentration of 0.0012mg/ml and 1-2 Benzoanthracene having the highest concentration of 1.1143mg/ml, and from 0.0006mg/ml to 0.5839mg/ml for dry season with Fluorene having the lowest concentration and Flouranthene having the highest concentration. The ratios of low molecular weight polycyclic aromatic hydrocarbons to high molecular weight polycyclic aromatic hydrocarbons are less than 1 in all locations during the dry season but varied during the wet season indicating that the contamination was of pyrogenic and petrogenic sources which also highlights the significant contribution of rainfall in increasing the contamination, while diagnostic ratio of the data showed that the actions of craftsmen and artisans contribute significantly to the increased level of PAHs found in this vicinity. The carcinogenic potency major ecological concern because the cancer risks were above 1 x 10-6, indicating a higher risk of cancer and potential harm to the health of children and adults.

1. Introduction

Polycyclic Aromatic Hydrocarbons are petroleum products that are typically complex mixtures made up of hundreds to thousands of distinct hydrocarbon molecules, including aliphatic and aromatic hydrocarbons [1]. It is common for these petroleum products which consist of crude oil, lubricating oils, and a wide range of fuels, to contaminate the environment when indiscriminately disposed into the environment and can leach from the soil surface into underground water. Also, the amount of waste and pollutants produced globally has increased because of increasing rates of industrialization, urbanization, and population growth [2]. Polycyclic Aromatic Hydrocarbons ([PAHs) are organic compounds that comprise two or more fused benzene rings in diverse structural configurations that result from incomplete or partial combustion of organic substances such as coal, oil, gas, wood, waste, or other organic substances like tobacco [3].

Low molecular weight PAHs and high molecular weight PAHs are the two types of PAHs. LPAHs (such as naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene) have molecular structures with two to three

benzene rings (comprising of six-sided structured aromatic rings of carbon), and High-Molecular Weight PAHs (HPAHs) have four or above four aromatic benzene rings such as fluoranthene, pyrene, benzo(a)pyrene, and benzofluoranthenes [4]. With increasing molecular weight, the hydrophobicity, bioaccumulation propensity overall environmental persistence and biodegradation resistance of these chemicals rises as well [5]. PAHs in soil are hazardous to a variety of plants, microbes, and invertebrates. Some of these are harmful to human health as some PAH components are carcinogenic and mutagenic as well as endocrine disrupters [6]. They are pollutants of major concern that are common in various habitats because of their potentially harmful tendency. [7]. Due to the varied physiochemical properties of organic pollutants, polycyclic aromatic hydrocarbons interact to varying degrees with water, soil/sediments, and biota. The US Environmental Protection Agency (EPA) has designated 16 most common and/or harmful PAHs as priority pollutants, categorizing them as carcinogenic or non-carcinogenic. Among the human carcinogens are: Chrysene (Chr), benzo(b)fluoranthene (B(b)Flu), benzo(a)anthracene (BaA), benzo(k)fluoranthene (B(k)Flu), dibenzo(a,h)anthracene (DbA) and indeno(123cd)pyrene (IcdP). The International Agency for Research on Cancer recently categorized Benzo(a)pyrene (B(a)Pyr), one of the high molecular weight PAHs, as one of the most carcinogenic substances [USEPA, 2002; WHO 2003].

Leaching of PAHs from soil resources into groundwater or movement of particulate soil PAHs in the atmosphere are examples of PAH transfer between air, water, and terrestrial systems [8]. In the subterranean environment, PAHs are frequently persistent, that is, they may remain in the subsurface for a long time after contamination or pollution has occurred and cannot be removed from the subsurface in a reasonable amount of time using treatment techniques [9]. Because of their limited solubility, they frequently accumulate in sediments, soils, and underground water.

Digenetic processes produce alkylated PAHs, which are more hazardous than the parent molecules. In environmental matrices, they frequently coexist with their parent chemicals. Incomplete combustion of most organic substances like fossil fuels comprising of coal, gasoline, diesel, etc., and biomass fuels like straw and firewood, waste, petroleum product spillage, and various industrial, commercial, domestic, and agricultural activities are the primary sources of PAHs in the environment and PAHs can be found in a variety of environments, including soils, sediments, groundwater, and the atmosphere due to their ubiquitous nature. [10].

Excessive anthropogenic activities (such as fossil fuel combustion, gas flaring, oil spills, and improper industrial waste disposal) are some forms of environmental pollution that have been observed to cause significant harm to the environment, including poor water quality, adverse soil degradation, and a polluted atmosphere from an aesthetic standpoint [11].

Groundwater is frequently less expensive, more convenient, and contains fewer pollutants than surface water. As a result, it is extensively employed in public water systems. Groundwater accounts for around 20% of the world's freshwater supply, or about 0.61% of all water, including oceans [11]. Many municipal water supplies are completely sourced from groundwater. Measurement of water levels in locally dug wells and examination of geological records from well-drilling to establish the extent, depth, and thickness of water-bearing sediments and rocks can be used to estimate the volume of groundwater in an aquifer. Polluted groundwater is less obvious than pollution in rivers and lakes, but it is more difficult to clean up. The most common cause of groundwater pollution is improper waste disposal on land. Industrial chemicals and waste landfills, industrial wastes, automobile workshops, processed wastewater from mines, oil field brine pits, leaky underground oil storage tanks and pipelines, sewage sludge, and septic systems. [12]. Automobiles are the world's most fundamental modes of human and material transportation but the convenience of this mode of transportation comes with a cost, which includes pollution of varied magnitudes. Pollution caused by the dumping of used lubricating oil is more common than pollution caused by crude oil [5].

In Nigeria, the desire to establish and implement a long-term waste management plan based on public health principles has resulted in a huge number of open dumpsites that are not well managed, resulting in the discharge of hazardous chemicals and pollutants into the environment. Poor waste dumpsite management is well known to harm groundwater supplies, as chemical leachates from dumpsites infiltrate the soil and water aquifers, posing a threat to human health as well as the environment [13]. This is a major environmental issue that requires immediate action. Mishandling, intentional dumping, spillage, and leaking of petroleum products including gasoline, lubricating oils, diesel fuel, heating oils, and old motor oil can all result in pollution. As a result of these haphazard disposal techniques, the pace at which used motor oils spread and pollute the land and water near municipal areas has increased. [8].

Imo State being a commercial center in South East Nigeria has witnessed an incremental surge in the number of vehicles used for commercial and private purposes. Vehicles are prone to breakdown and hence require repairs and maintenance. Individuals or groups of people use portions of the property for small and big-scale vehicle workshops that provide public services. This approach is anticipated to pose environmental risks. This has posed serious effects on human health. As a result, this investigation is aimed at looking into the contamination levels of underground water in the reclaimed sections of Orji Automechanic Village now converted into a residential area.

The Orji auto mechanic village in Owerri was the biggest auto mechanic village in the Owerri metropolis before its evacuation and in recent times, concerns have been raised regarding the activities of automobile mechanics in Owerri with several automobile workshops scattered across the town where engine oil, lubricating oil and other organic solvents containing hazardous contents are spilled or disposed of indiscriminately after use on every available space by craftsmen and artisans involved in automobile repair, maintenance, and services. An increase in the number of vehicles leads to a corresponding increase in the demand for the services of these local artisans who deal in activities that utilize solvents that contain polycyclic aromatic hydrocarbons which are hazardous to humans even at low concentrations. Polycyclic aromatic hydrocarbons are major organic pollutants inherent in organic solvents like petrol, diesel, lubricating oil, used oil, etc., which are some of the numerous products used and disposed of during maintenance of automobiles, and with these indiscriminate disposals it is only natural to believe that the environment is polluted with different pollutants among which polycyclic aromatic hydrocarbons are believed to be involved, coupled with the fact the research carried out by Ibe et al., 2021 revealed concentrations of PAHs at different soil depths within this location were of great concern owing to values greater than the allowable limit for carcinogenic potency. With the reclaimed sections of Orji auto mechanic village now converted to residential areas it is important to determine the concentrations of polycyclic aromatic hydrocarbons as well as carry out human risk assessment in the groundwater sources in this area as increased exposure could be detrimental to human health. With the authorization of the Imo State Government that auto mechanics and others who carry out automobile repairs within the Orji auto mechanic village to leave the area after about thirty years of occupational activities in this area, it is therefore imperative for the investigative study of PAHs with few researches on underground water contamination in this area that are well-documented, however, researches that are reported found heavy metals in the surface soil and groundwater sources [14,15] as well we as concerned contaminated values of PAHs in soil samples of different depths discovered in this area [16]. Also, due to the skeletal operations of car mechanics and other artisans still going on in this vicinity, it is necessary to constantly monitor the level of pollutants in the area as exposure to these contaminants may cause serious issues like brain damage, cancer, tumors, nervous system diseases, and reproductive issues in both humans and animals. Ibe et al. 2021 revealed the presence of PAHs in soil samples of various depths within this vicinity as well as carcinogenic potency in some sample locations coupled with substantial health threats posed to both humans and the environment due to their persistent, mutagenic, and carcinogenic properties [17], leading to the suggestion that research be carried out on water samples within this vicinity [16]. This necessitates monitoring PAH concentration in water samples at different locations within the reclaimed section of the mechanic villages where it is believed that mechanics and inhabitants come into contact with organic solvents and that these products may be spilled or disposed of and eventually leached into the underground water source, giving rise to the justification of this study. Therefore, it is necessary to examine the ecological impact of auto mechanics operations in the reclaimed section of the mechanic village by determining the amounts of seasonal polycyclic aromatic hydrocarbons [PAHs] in the groundwater sources in the reclaimed sections of Orji auto mechanic village now converted to a residential area in Owerri, Southeast Nigeria and also to create awareness on the need for remediation process to be carried out before consumption of water from these boreholes and the area at large.

The study aims to determine the amount of Polycyclic Aromatic Hydrocarbons in different groundwater samples during wet and dry seasons in the reclaimed sections of Orji Auto Mechanic Village now converted into a residential area.

2. Materials and Methods
2.1 Study location
The reclaimed section of Orji auto mechanic village is Situated between longitude 7° 3′ 50″ and latitude 5° 31′ 39″, at around 125.8 m above sea level, and covers an area of roughly 0.41 km^2 in Owerri North Local Government Area, the Imo State's capital. Activities in the reclaimed section of the mechanic village
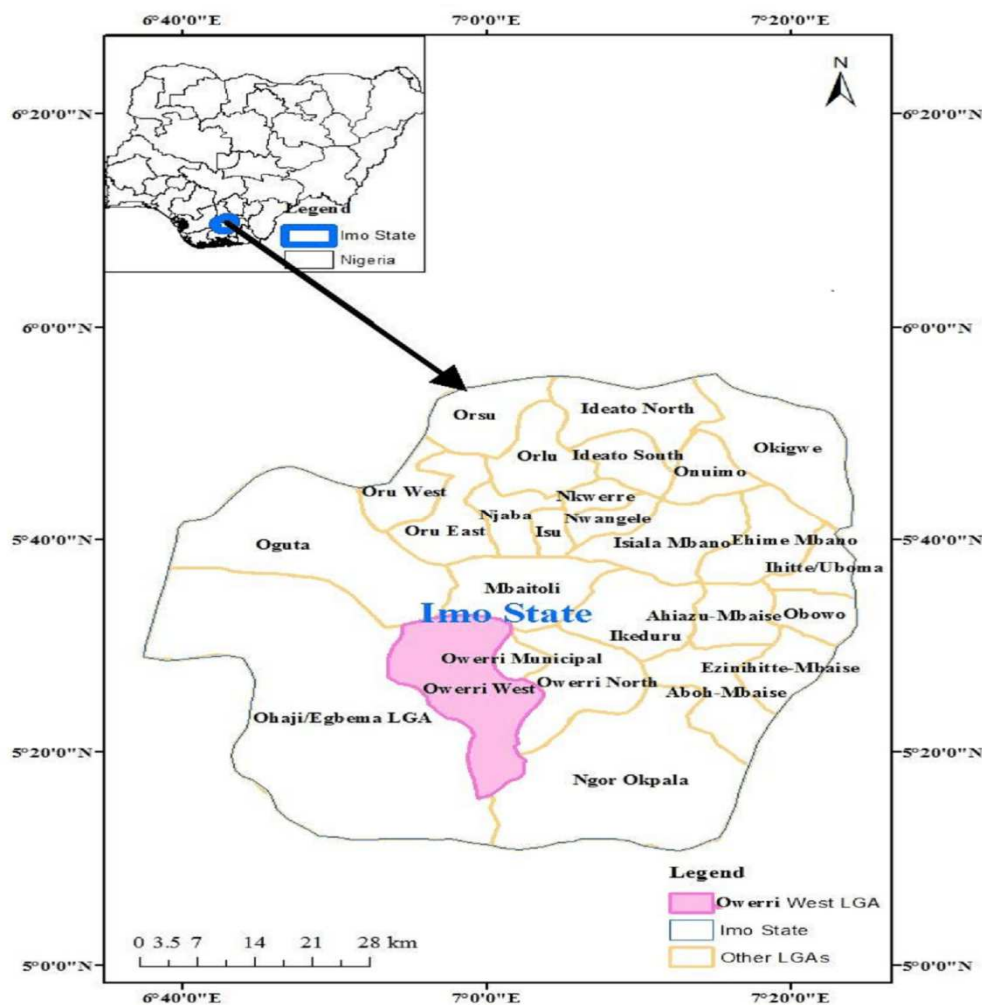
Figure: 1. Study location

Table 1. Description of study location

Sampling points	Latitude	Longitude	Description
Sample1	N5^{o}31'5.1978''	E7^{o}2'42.33336''	Hotel/Guest House
Sample 2	N5^{o}31'9.01812''	E7^{o}2'39.408''	Residential Apartment
Sample 3	N5^{o}31'10.0632''	E7^{o}2'39.01812''	Residential Apartment
Sample 4	N5^{o}30'31.32612''	E7^{o}2'34.96823''	Residential Apartment
Sample 5	N5^{o}30'34.02648''	E7^{o}2'33.756''	Residential Apartment

commenced in 1987 which include auto mechanics and other craftspeople who work on automobile maintenance.

2.2. Water sample collection

Water samples for polycyclic hydrocarbon analyses were collected using a broad mouth 500ml glass bottles fitted tightly with aluminum foil to prevent contamination of the samples. Glass bottles were used for the collection of samples since hydrocarbons interact with plastic containers, the collected water samples were properly labelled, and preserved in cool boxes before taken for analyses.

2.3. Physicochemical analyses

According to the protocols outlined in the Standard Method for the analysis of contaminated water, some physiochemical characteristics were evaluated amongst which are electrical conductivity, pH, Total Dissolved Solid (TDS), and turbidity.

Figure 2. Hotel/Guest House

Figure 3. Residential Apartment

Figure 4. Residential Apartment

2.3.1. Electrical conductivity

On the same day that the samples were collected, the electrical conductivity of the water samples was determined using a Lasany Microprocessor

Meter by dipping the electrode into 100 of each water sample, and the displayed readings were recorded.

2.3.2. pH test

To determine the pH of the water samples, a digital pH meter (Labman Scientific Instruments PVT Limited) was employed. The pH meter was first calibrated using Buffer 7.0 and Buffer 4.0, then 100ml of the water samples each were measured then the pH was determined by dipping the pH electrode into each of the water samples and the displayed readings were recorded.

2.3.3. Total Dissolved Solid Test

Materials dissolved in water are referred to as total dissolved solids. The Total Dissolved Solid of the water samples was determined using a Lasany Microprocessor Meter by dipping the electrode into 100ml of each water sample and the displayed readings were recorded.

2.3.4. Turbidity

The Turbidity of the water samples was determined using a hand-held portable turbidity Meter measuring 10ml of each water sample into the turbidity measuring bottle and placed in the detectable slot of the turbidity portable device and the displayed readings were recorded.

2.4. Determination of Polycyclic Aromatic Hydrocarbon in water

This was analyzed according to AOAC 1995

2.4.1. Extraction of PAHs from water samples

The extraction technique employed in this work was the United States Environmental Protection Agency (USEPA Method 3510 for aqueous matrix for the analysis of semi-volatile and non-volatile organics. After filtering, 100ml of the water sample was put into a glass-separating funnel with a capacity of 2L. To create a salt-out effect, 30 ml of saturated sodium chloride (NaCl) was then added. By turning the flask upside down three to four times, it was well-mixed. Dichloromethane, used as the extraction solvent, was added, and 100ml of it was violently agitated by hand for two to three minutes while periodically releasing the pressure. The phases were then allowed to separate for 5 minutes, and the Dichloromethane extract (organic layer) was separated or collected from the aqueous layer. The organic layers were combined and dried over anhydrous magnesium sulphate after the extraction was carried out once more using 100 ml of dichloromethane.

After being concentrated to a volume of roughly 2 ml using a rotary vacuum evaporator, the water sample extracts were cleaned [55].

2.4.2. Clean-up of extract (purification using Silica SPE cartridge)

To condition the cartridge, 6ml of dichloromethane was utilized after 1g of silica gel that had previously been activated at 130oC for 10 hours and was carefully packed into a 10ml polypropylene cartridge column. The column was then loaded with the concentrated extract, and a 50ml pear-shaped flask was positioned underneath the column to catch the eluate. The column was subsequently eluted with 10 ml of dichloromethane, and the whole filtrate obtained was concentrated using a rotary evaporator set to 38°C to just dryness. Before being quantified by gas chromatography, the residue was dissolved in 1 ml of methanol and placed into a 2 ml standard vial [56, 57].

2.4.3. Gas Chromatographic conditions for PAH determination

The final extracts were analyzed using gas chromatograph-Buck M910 scientific gas chromatography equipped with a combiPal autosampler and flame ionization detector that allowed the detection of contaminants even at trace levels of the matrix's concentrations (in the lower μg/g and μg/kg range) to which conventional detectors are insensitive. The GC conditions used for the analysis were capillary column coated with VF-5 (30m + 10m E guard column x 0.25mm internal diameter, 0.25 μm film thickness). The injector and detector temperatures were set at 270°C and 300°C respectively. The oven temperature was programmed as follows: 70°C held for 2 min, ramp at 25°C/ min to 180°C, held for 1 min, and finally ramp at 5°C/ min to 300°C. Nitrogen was used as a carrier gas at a flow rate of 1.0 ml/ min and detector make-up gas of 29 MLX min^{-1}. The GC's injection volume was 1L. Each sample ran for a total of 31.4 minutes.

2.4.4. Quantification of PAH residues.

The residue levels of PAHs were quantitatively determined using peak area. The detector's linear range was used for each of the measurements. The peak areas whose retention times correspond with the standards were extrapolated on their corresponding calibration curves to obtain the concentration.

2.5. DATA ANALYSIS: Principal Component Analysis (PCA)

This is a technique used to reduce the number of dimensions in data while minimizing the loss of information. It enables the condensation of the amount of data included in enormous data Tables into a manageable number of "summary indices" for easier visualization and analysis. This analysis works by rotating the axes uniquely so that there is more variance along them thereby transforming the data into principal component values, which are also referred to as scores. These principal components serve as the new axes, and the PC scores represent the projections of the original dimensions onto the new axes.

2.6. RISK ASSESSMENT

Guidelines from the United States Environmental Protection Agency [US EPA] were used to evaluate the ecological risk assessment.

2.6.1. Carcinogenic potency of the study area

The PAHs have been divided into two classes of carcinogenic chemicals and are thought to be among the most serious environmental pollutants. The PAHs may be Group1 carcinogenic to humans, probably human carcinogens (2A) and a source of possible human carcinogens (2B), and Group 3 not classifiable as to its carcinogenicity to humans according to the International Agency for Research on Cancer (IARC). Therefore, by calculating the benzo (a) pyrene equivalent (B(a)Pyreq) of each particular PAH,

$$B(a)Pyreq(mgkg^{-1}) = \sum (TEQF \times PAH_c) \quad (1)$$

Where B(a)Pyreq is benzo(a) pyrene equivalent.

TEQF is the toxic equivalent factor of the individual PAH,

PAH$_c$ is the concentration of the PAHs (mg/kg) [18].

2.6.2. Cancer health risk assessment

A cancer health risk assessment could be used to illustrate how unintentional interaction with substances that are carcinogenic or mutagenic increases one's risk of developing cancer. Dermal absorption and ingestion are two possible routes via which exposure to contaminated water could result in an increased risk of developing cancer. Health risk assessment as a result of exposure to PAH-containing compounds in the study region was carried out using the US EPA guidelines.

The formulas Chronic Daily Intake by Dermal (CDI der) and Chronic Daily Intake by Ingestion (CDI ing), respectively, were used to determine HHRA for the various water samples under study.

The formulas Chronic Daily Intake by Dermal (CDI der) and Chronic Daily Intake by Ingestion (CDI ing), respectively, were used to determine HHRA for the various water samples under study.

$$CDI\ ing = \frac{Cw \times IR \times EF \times ED \times CF}{BW \times AT} \quad (2)$$

$$CDI\ der = \frac{Cw \times kp \times ET \times EF \times ED \times CF \times SA}{BW \times AT} \quad (3)$$

According to the Integrated Risk Information system of the USEPA, the cancer slope factor (SF) of B(a)Pyr is 7.3(mg/kg/day)-1, Therefore, the SF value for dermal exposure was adjusted with the gastrointestinal absorption adjustment factor (AAF) [USEPA]. B(a)Pyr exposure is equal to 7.3 (mg/kg/day)-1/92%=7.9(mg/kg/day)-1. The carcinogen risk (CRs) of ingestion and dermal exposure was calculated using the equations: CR ing = CDI ing X SF (4)

$$CR\ der = CDI\ ing \times SF\ dermal \quad (5)$$

The total carcinogenic risk for the population was calculated.

A carcinogenic number of more than 10^6 is considered hazardous.

The carcinogenic risk assessment is given in by: CR = CR ing + CR der (6)

Where CR is carcinogen risk (CRs)

CR ing is of carcinogenic risk through ingestion and CR der is carcinogenic risk through dermal exposure were calculated using the equation. [50][51]

3.0 Results and Discussion
3.1 Physiochemical analyses

The mean values of the physical and chemical properties of water samples during wet and dry seasons within the reclaimed section of Orji auto mechanic village in Owerri North Local Government Area are presented in Figures 5 and 6 below. The results of mean pH values were 4.99, 4.7, 4.69, 4.59, and 4.33 for samples 1, 2, 3, 4, and 5, respectively during the wet season and 3.89, 3.75, 3.73, 3.97 and 3.94, and for samples 1, 2, 3, 4 and 5, respectively during the dry season. In all water samples, the highest pH value of 4.99 from sample 1 was obtained for the wet season and 3.97 was obtained in sample 4 for the dry season while the lowest value of 4.33 was obtained from sample 5 for the wet season and 3.73 was obtained at sample 2 for the dry season, all samples indicated that the water in this region is acidic with higher acidic values obtained during dry season, this is expected as the acidic values is

diluted during wet season due to excessive rainfall. The values obtained for Electrical Conductivity in µS/cm were 46.4, 56.6, 102, 51.3, and 172.9 for samples 1, 2, 3, 4, and 5, respectively during the wet season and 138.9, 245, 175.2, 111, and 106.1 for samples 1, 2, 3, 4 and 5, respectively for the dry season. The highest TDS values in the present study were obtained from sample 3 for the wet season which is 50.9ppm and for dry season sample 2 which was 120.3ppm while sample 1 showed the least value of 23.3ppm for the wet season and dry season samples 4 and 5 showed lesser values 54.1ppm and 53.7ppm respectively. Values range between 2.08NTU and 2. 48NTU for the wet season while the range of 7.08NTU and 8.98NTU were obtained for Turbidity for the dry season in various water samples with these variations attributed to seasonal variation and dilution due to the different amounts of rainfall during wet and dry seasons.

WHO's maximum contamination threshold of 1,000 µS/cm was not exceeded by the EC values obtained in the current investigation. EC measures a substance's or solution's ability to conduct an electric current and is based on the amount of dissolved solids in the water. High EC values signify the presence of rising amounts of inorganic ions in the water, including calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), nitrate (NO_3^-), and phosphate (PO_4^{3-}), while Total dissolved solids (TDS) is a measurement of the total amount of all molecules, ions, or microscopic granular colloidal suspended materials in a liquid. The TDS levels recorded in this investigation were lesser than the 600 mgL-1 maximum contaminant limit recommended by the WHO. The values obtained for pH showed that all water samples are acidic with slight variation amongst all. A trend of modest acidity was visible in the pH value, in all the samples analyzed and are below the requirement for potable drinking water as stipulated to be acceptable by the World Health Organization (WHO) It is impossible to overstate the significance of water pH because it controls metal solubility, water hardness, and acts as a sign of water pollution. The anthropogenic activities in the area may be responsible for the pH of the water samples, and the water may act as a sink for different contaminants.

3.2 Composition of PAHs

A total of fourteen and twelve PAH congeners were detected in the water samples for wet and dry seasons respectively, as presented in Figures 7 and 8.

Table 2. Parameters for estimating Human Cancer

Definition	Unit	Child	Adult
Body Weight (BW)	kg	15	70
Average Time (AT)	day		
Dermal permeability coefficient (kp)		1.2	1.2
Exposure Duration (ED)	years		70
Exposure Frequency (EF)	days/year	365	365
Exposure Time (ET)	(h/day)	0.33	0.25
Ingestion Rate (IR)	liters/day	1.8	2.2
Average Time for Carcinogens (ED X365)	(ED x 365)		25550
Exposed Skin Area (SA)	cm^2	6600	18000
Conversion Factor		10^{-3}	10^{-3}
Slope Factor (SF)		7.3	7.3
Slope Factor (SF) for dermal		7.9	7.9

Source: [53, 54]

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
pH	4/99	4/7	4/69	4/59	4/33
Electrical Conductivity (µs/cm)	46/4	56/6	102	51/3	172/9
Total Dissovled Solid (ppm)	23/3	28/1	50/9	25/8	85/7
Turbidity (NTU)	2/08	2/65	2/84	2/16	2/24
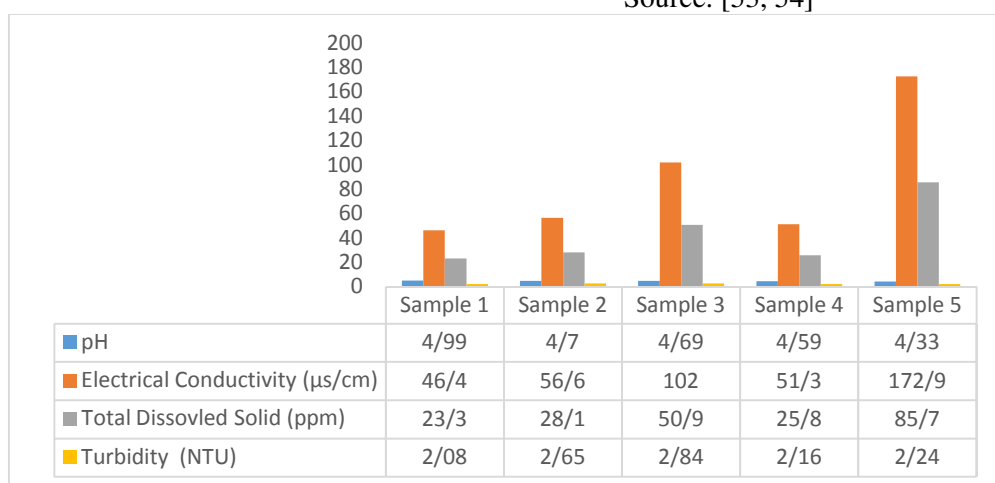
Fig. 5. Physical parameters for wet season

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
pH	3/89	3/75	3/73	3/97	3/94
Electrical Conductivity (µs/cm)	138/9	245	175/2	111	106/1
Total Dissovled Solid (ppm)	78/5	120/3	87/1	54/1	53/7
Turbidity (NTU)	7/08	8/85	8/98	8/28	8/82

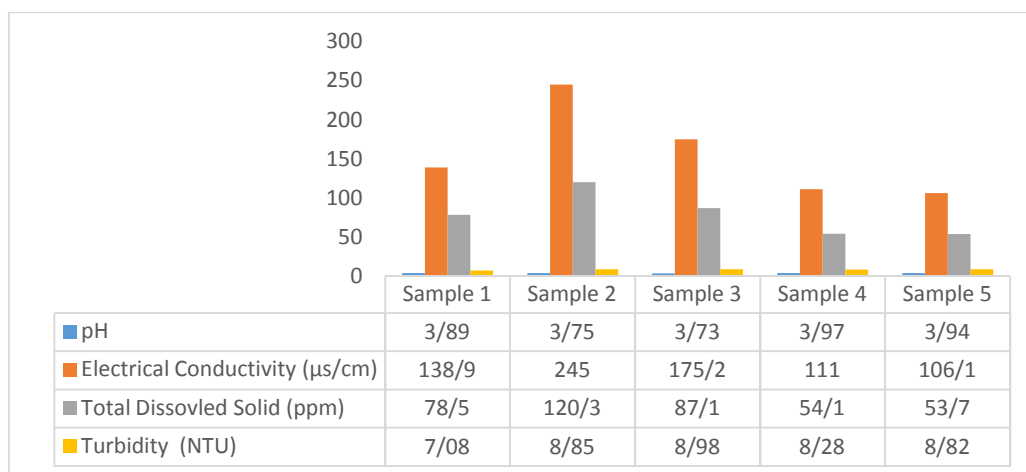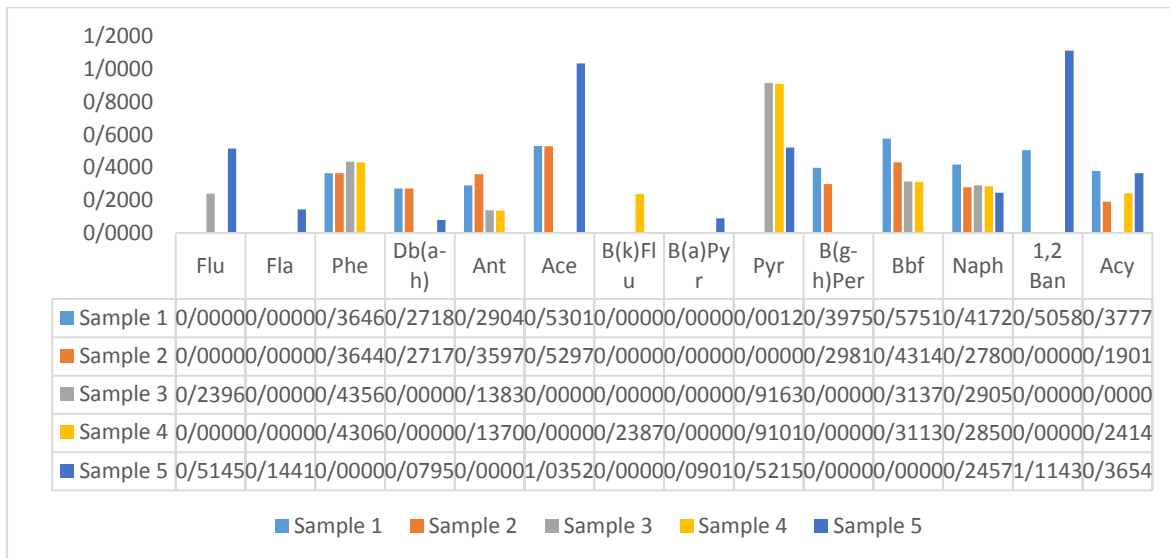**Fig. 6.** Physical parameters for dry season

Figure 7. PAHs Concentration during wet season
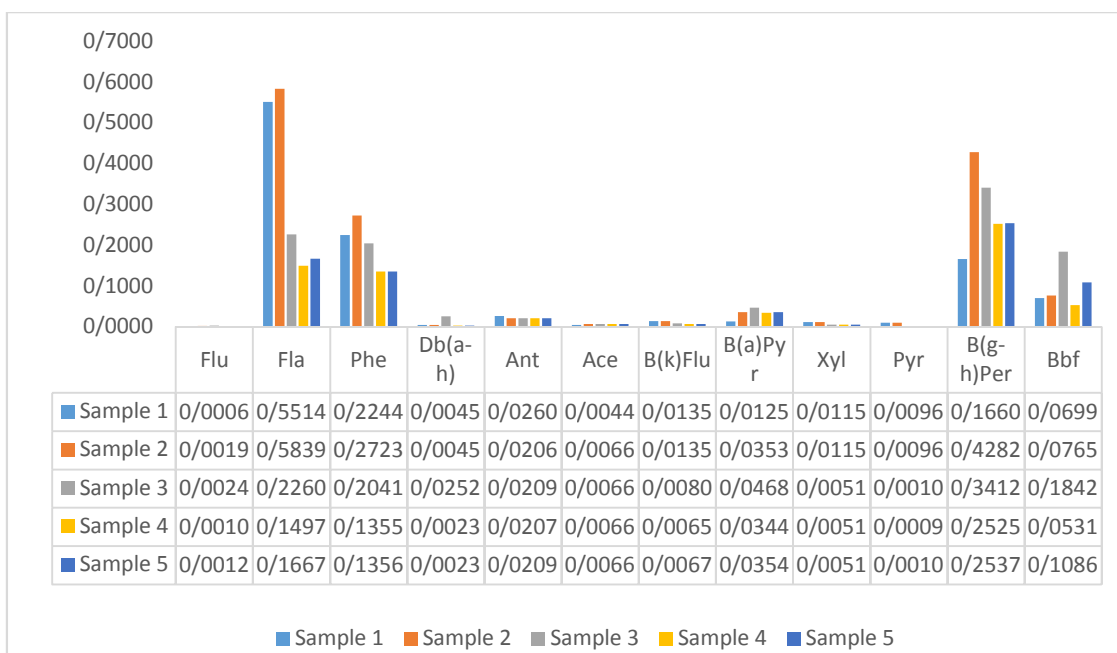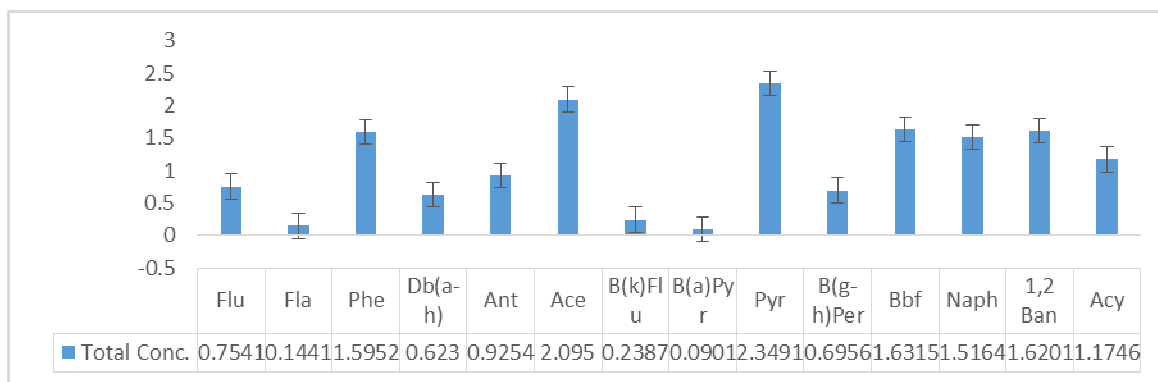

Figure 8. PAHs Concentration during Dry Season

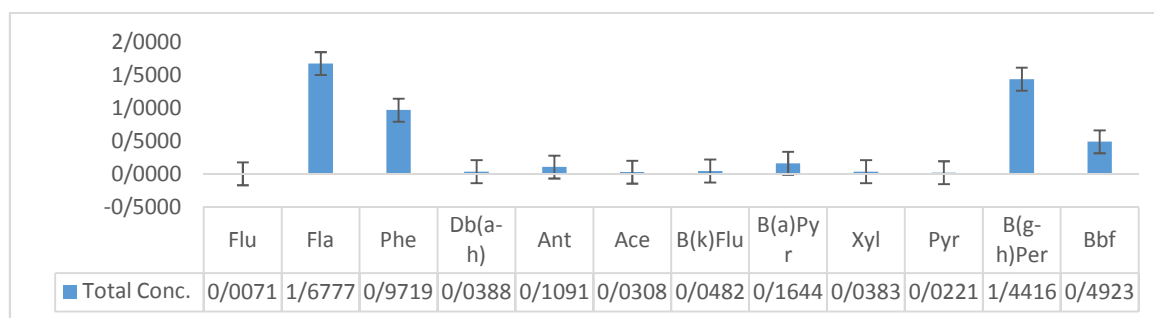**Figure 9.** Total Concentrations of PAHs during wet season

	Flu	Fla	Phe	Db(a-h)	Ant	Ace	B(k)Flu	B(a)Pyr	Pyr	B(g-h)Per	Bbf	Naph	1,2 Ban	Acy
Total Conc.	0.7541	0.1441	1.5952	0.623	0.9254	2.095	0.2387	0.0901	2.3491	0.6956	1.6315	1.5164	1.6201	1.1746

Figure 10. Total Concentrations of PAHs during dry season

	Flu	Fla	Phe	Db(a-h)	Ant	Ace	B(k)Flu	B(a)Pyr	Xyl	Pyr	B(g-h)Per	Bbf
Total Conc.	0/0071	1/6777	0/9719	0/0388	0/1091	0/0308	0/0482	0/1644	0/0383	0/0221	1/4416	0/4923

Table 3. Molecular weights, No of Carbon rings and TEF of PAHs

Wet season														
PAH	Flu	Fla	Phe	Db[a-h]	Ant	Ace	B[k]Flu	B[a]Pyr	Pyr	B[g-h]Per	B[b]Flu	Naph	1,2 Ban	Acy
Molecular formula	$C_{13}H_{10}$	$C_{16}H_{10}$	$C_{14}H_{10}$	$C_{22}H_{14}$	$C_{14}H_{10}$	$C_{12}H_8$	$C_{20}H_{12}$	$C_{20}H_{12}$	$C_{16}H_{10}$	$C_{22}H_{12}$	$C_{20}H_{12}$	$C_{10}H_8$	$C_{18}H_{12}$	$C_{12}H_8$
No. of Carbon Rings	3	4	3	5	3	3	5	5	4	6	5	2	4	3
Molecular mass g/mol	166.22	202.26	178.23	278	178.23	154.21	252	252	202.25	226.272	252	128.17	228.29	152.196
Toxic equivalency factor [TEF]	0.001	0.1	0.001	1	0.01	0.001	0.01	0.1	0.001	0.01	0.1	0.001	0.1	0.001
Dry season														
PAH	Flu	Fla	Phe	Db[a-h]	Ant	Ace	B[k]Flu	B[a]Pyr	Xyl	Pyr	B[ghi]Per	B[b]Flu		
Molecular formula	$C_{13}H_{10}$	$C_{16}H_{10}$	$C_{14}H_{10}$	$C_{22}H_{14}$	$C_{14}H_{10}$	$C_{12}H_8$	$C_{20}H_{12}$	$C_{20}H_{12}$	C_8H_{20}	$C_{16}H_{10}$	$C_{22}H_{12}$	$C_{20}H_{12}$		
No. of Carbon Rings	3	4	3	5	3	3	5	5	2	4	6	5		
Molecular mass g/mol	166.22	202.26	178.23	278	178.23	154.21	252	252	106.116	202.25	226.272	252		
Toxic equivalency factor [TEF]	0.001	0.1	0.001	1	0.01	0.001	0.01	0.1	0.001	0.001	0.01	0.1		

The concentrations of total PAHs observed in water samples during wet season ranged from 0.0012 to 1.1143mg/ml for samples collected during dry season with Pyrene having the lowest concentration of 0.0012mg/ml and 1-2 Benzoanthracene having the highest concentration of 1.1143mg/ml while for a dry season, the concentrations of total PAHs observed in water samples ranged from 0.0006 to 0.5839mg/ml with Fluorene having the lowest concentration and Flouranthene having the highest concentration. Of the 16 USEPA's priority polycyclic aromatic, Indeno(1,2,3-cd)pyrene and Chrysene were not discovered in the water samples collected and analyzed during the wet

season while Naphthalene. Indeno(1,2,3-cd)pyrene, Chrysene, Benzo(a)anthracene, and Acenaphthylene were not discovered in the samples collected and analyzed during the dry season and Xylene which is not one of the 16 priority polycyclic aromatics was discovered in the samples analyzed for the dry season.

Figures 7 to10 show the total concentration of PAHs in all locations with Pyr having the highest total concentration of 2.3491mg/ml for samples in the wet season and B(a)Pyr having the lowest concentration of 0.0901mg/ml while for dry season the highest total concentration of PAHs is Benzo(ghi)Per having a concentration of 1.4416mg/ml while the lowest was obtained in Flu with a concentration of 0.0071 during dry season. The mean concentrations in this order for the wet season are sample 3 < sample 4 < sample 2 < sample 1 < sample 5 for the wet season and sample 2 < sample 1< sample 3 < sample 5 < sample 4 for the dry season. A significant number of total PAHs recorded in various sample locations during the wet season and dry season can be attributed to factors like biomass combustion and other anthropogenic activities [16], as accumulated PAHs in the atmosphere which combined with rainwater during rainfall during the wet season as well as flooding due to heavy rainfall and leaching of contaminated rainwater could have contributed to such elevated concentrations [19].

According to Tables 3 to 6, and Figures 11 and 12, it was observed that for Low Molecular Weight (LMW) PAHs, comprising of 2 to 3 rings PAHs are found in close percentage in all the sample locations, 53.07%. ,63.23%, 47.30%, 42.83%, and 49.33%, in samples 1,2,3,4 and 5 respectively for samples analyzed during the wet season while High Molecular Weight (HMW) PAHs comprising of 4 to 6 rings accounted for 46.95%, 36.77%, 52.70%, 57.17%, and 44.51%, for PAHs analyzed in samples 1,2,3,4 and 5 respectively for a dry season while Low Molecular Weight (LMW) PAHs were found in varied percentage in all the sample locations, 24.39%, 21.37%, 22.31%, 25.27% and 22.77% in samples 1,2,3,4 and 5 respectively for samples analyzed and High Molecular Weight (HMW) PAHs accounted for 75.61%, 78.63%, 77.69%, 74.73%, and 77.23%, for PAHs analyzed in samples 1,2,3,4 and 5 respectively for the dry season.

3.3 DIAGNOSTIC RATIO
According to [20] [21], PAHs from petrogenic sources are distinguished by the prevalence of Low Molecular Weight PAHs (2 or 3-rings) whereas PAHs from pyrogenic sources are characterized by High Molecular Weight PAHs [22]. This is because LMW PAHs are

created at low to moderate temperatures, such as during the burning of biomass, but HMW PAHs are produced at high temperatures, such as during the emissions of automobiles [23]. Low Molecular Weight PAHs discovered in the groundwater samples of the study areas are less hazardous and carcinogenic than High Molecular Weight PAHs which unfortunately are less compared to HMWPAH in this study.

The low molecular weight, as well as High molecular weight PAHs, can leach easily through the soil to the groundwater after rainfall and flooding, and this could be the reason why samples contained both PAHs in the groundwater samples analyzed. Also, runoff brings certain dissolved PAHs from diverse areas close to the sample locations. Anthropogenic activities in the vicinity will be responsible for the presence of High molecular weight PAHs in the samples under investigation, as well as, vehicle emissions, burning of carbon-containing waste in auto mechanic workshops in this location after significant rainfall or runoff, the released PAHs settle in the soil and surface water before being leached into the groundwater. As a result of biochemical transformations and chemical interactions in water, it has been discovered that PAHs cause biological changes in organisms [24] and are often teratogenic, carcinogenic, and mutagenic and may cause lung, bladder, and skin cancer. High Naph concentrations can lead to hereditary conditions such as glucose-6-phosphate dehydrogenase deficiency (G6PD), which affects 400 million people globally. High Naph concentrations also have a deleterious effect on red blood cell formation in the bones [25].

3.4 SOURCE IDENTIFICATION OF PAHs
It has been established that diagnostic ratio can be used in the analysis of PAH concentrations to identify intra-source differences among polluting sources. It is frequently used to determine the level of anthropogenic influence on the concentrations of PAHs. Due to several ambiguities, there is a small disparity in the application of the diagnostic ratio in the PAH proficiency analysis [26]. However, using the PAH diagnostic ratio, it has been possible to distinguish between emissions from the burning of gasoline and diesel [27]. Environmental deterioration is brought on by a variety of pollutants from the processing of crude oil as well as biomass combustion activities like cooking and bushfires. It is a highly helpful tool for identifying the sources of PAH emissions in various contexts [28], [29]. PAHs come from both anthropogenic (pyrogenic) and natural (petrogenic) sources as well as oil leakages, oil spills, and combustion of fossil fuels. PAHs found in the

Table 4. Concentration of low molecular weight PAH

Wet season						
	Flu	**Phe**	**Ant**	**Ace**	**Naph**	**Acy**
Sample 1	0	0.3646	0.2904	0.5301	0.4172	0.3777
Sample 2	0	0.3644	0.3597	0.5297	0.278	0.1901
Sample 3	0.2396	0.4356	0.1383	0	0.2905	0
Sample 4	0	0.4306	0.137	0	0.285	0.2414
Sample 5	0.5145	0	0	1.0352	0.2457	0.3654
Total	0.7541	1.5952	0.9254	2.095	1.5164	1.1746
Dry season						
	Flu	**Phe**	**Ant**	**Ace**	**Xyl**	
Sample 1	0.0006	0.2244	0.026	0.0044	0.0115	
Sample 2	0.0019	0.2723	0.0206	0.0066	0.0115	
Sample 3	0.0024	0.2041	0.0209	0.0066	0.0051	
Sample 4	0.001	0.1355	0.0207	0.0066	0.0051	
Sample 5	0.0012	0.1356	0.0209	0.0066	0.0051	
Total	0.0071	0.9719	0.1091	0.0308	0.0383	

Table 5. Concentration of high molecular weight PAH

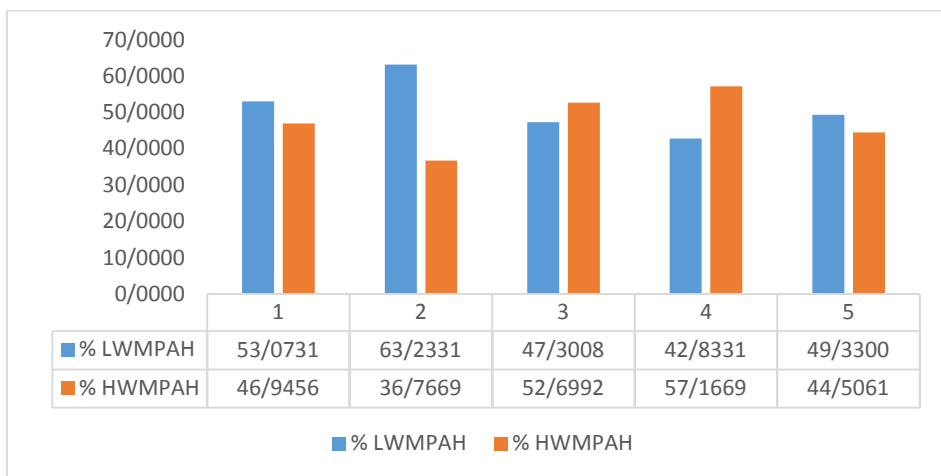| Wet season							
	Fla	**Db[a-h]**	**B[k]Flu**	**B[a]Pyr**	**Pyr**	**B[g-h] Per**	**B[b]Flu**	**1,2 Ban**
Sample 1	0	0.2718	0	0	0.0012	0.3975	0.5751	0.5058
Sample 2	0	0.2717	0	0	0	0.2981	0.4314	0
Sample 3	0	0	0	0	0.9163	0	0.3137	0
Sample 4	0	0	0.2387	0	0.9101	0	0.3113	0
Sample 5	0.1441	0.0795	0	0.0901	0.5215	0	0	1.1143
Total	0.1441	0.623	0.2387	0.0901	2.3491	0.6956	1.6315	1.6201
Dry season							
	Fla	**Db[a-h]**	**B[k]Flu**	**B[a]Pry**	**Pyr**	**B[ghi]Per**	**B[b]Flu**	
Sample 1	0.5514	0.0045	0.0135	0.0125	0.0096	0.166	0.0699	
Sample 2	0.5839	0.0045	0.0135	0.0353	0.0096	0.4282	0.0765	
Sample 3	0.226	0.0252	0.008	0.0468	0.001	0.3412	0.1842	
Sample 4	0.1497	0.0023	0.0065	0.0344	0.0009	0.2525	0.0531	
Sample 5	0.1667	0.0023	0.0067	0.0354	0.001	0.2537	0.1086	
Total	1.6777	0.0388	0.0482	0.1644	0.0221	1.4416	0.4923	

Figure 11. Percentage of Low Molecular Weight PAH and High Molecular Weight PAH for wet season
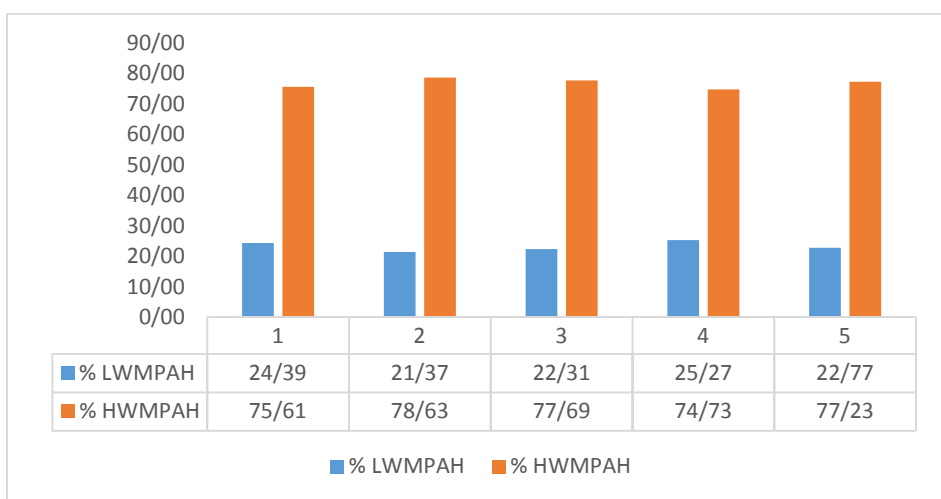

Figure 12. Percentage of Low Molecular Weight PAH and High Molecular Weight PAH for dry season

Table 6. PAHs used for Diagnostic Ratio

Wet season				
	LMWPAH	**HMWPAH**	**COMBUSTIBLE PAH**	**CARCINOGENIC PAH**
Sample 1	1.9793	1.7514	1.8968	0.8469
Sample 2	1.7219	1.0012	1.0075	0.7031
Sample 3	1.104	1.23	1.5205	0.3137
Sample 4	1.094	1.4601	1.7451	0.55
Sample 5	2.4308	1.9495	2.1157	0.1696
TOTAL	1.9793	1.7514	8.2856	2.5833
Dry season				
	LMWPAH	**HMWPAH**	**COMBUSTIBLE PAH**	**CARCINOGENIC PAH**
Sample 1	0.2669	0.8274	0.8229	0.1004
Sample 2	0.3129	1.1515	1.147	0.1298
Sample 3	0.2391	0.8324	0.8072	0.2642
Sample 4	0.1689	0.4994	0.4971	0.0963
Sample 5	0.1694	0.5744	0.5721	0.153
TOTAL	1.1572	3.8851	3.8463	0.1004

the research area were both petrogenic and pyrogenic in origin. Pyrogenic contribution is primarily caused by incomplete combustion of organic matter at carbonation temperatures which might originate in residential areas, agricultural regions, and gas stations, from the burning of fuel, coal, and wood, as well as indiscriminate disposal of petroleum products and used lubricating oil among other things. High molecular weight PAHs are typically linked with pyrogenic sources, whereas lower molecular weight PAHs are typically associated with petrogenic sources. Nonetheless, certain LMWPAHs that were observed in the current investigation were discovered to be petrogenic. This is because PAHs with 2 to 4 rings are extremely volatile and thus easily transferred from one point of impact to another [30]. Children who are exposed to carcinogenic High Molecular Weight PAHs run the risk of developing hemolytic anemia, which manifests as high fatigue, low appetite, restlessness, pale complexion, and jaundice as well as nausea, vomiting, diarrhea, blood in the urine, and jaundice which are more severe compared to adults because of their lesser weight [31]. B(a)Pyr has been utilized as a reference PAH molecule to evaluate the carcinogenesis of other PAH components because Chy is thought to have 1% biological toxicity with B(a)Pyr [32]. However, it has been demonstrated that over time, B(a)Pyr can cause both short-term (such as anemia and red blood cell destruction) and long-term (such as immunological suppression and disturbance of the neurological and reproductive systems) health issues [33]. The recognized carcinogens B(b)Flu and B(k)Flu, which are present in pyrogenic emissions and bioaccumulation in organisms before being deposited in soil and getting into groundwater sources, are present in pyrogenic emissions. Organ tumors have been connected to the cancer-causing compound BaA. Although BghiP, which is produced when petroleum products are burned insufficiently, has no known dangers for cancer, it can combine with B(a)Pyr over time to cause skin tumors and organ failure [16].

The ratio of identified PAHs mean concentrations were used to evaluate the sources of PAHs in this study presented in Table 7. In general, the ratios of Ant/ (Ant+Phe), Ant/Phe, Fla/ (Fla +Pyr), B(b)Flu/ (B(b)Flu +B(k)Flu), Total Comb. PAHs /Total PAHs and Total LMW/ Total HMW were used. It shows the composition for both wet and dry season of all the samples locations of combustible PAHs, carcinogenic PAHs, high molecular weight PAH compounds (HPAHs), which typically contain 4-6 rings of PAH, typically come from pyrogenic sources and low molecular weight PAH compounds (LPAHs), which contain 2-3 rings of PAH, may be the consequence of pyrogenic processes or petrogenic origin [49]. The ratio of (LPAHs) to (HPAHs) was less than 1 for samples 3 and 4 for samples collected during wet season, indicating that most of the PAHs contamination in those locations were of the pyrogenic source while those of samples 1, 2, and 5 are greater than 1 indicating petrogenic source as the contributory factor for PAHs contamination, however for the dry season the ratio of (LPAHs) to (HPAHs) were all less than 1 for all the sample location which implies pyrogenic source for this contamination. Also, a ratio of less than one was obtained in all sample locations for the ratio of total combustible PAHs to total PAHs for both wet and dry seasons while the ratio of Phe to Ant were all found to be less than ten [10] for both wet and dry seasons apart from sample 2 for dry season with a value of 13.22, an indication of pyrogenic origins for samples all samples in both seasons, apart from sample 2 for the dry season which could have petrogenic contribution in the location of that sample. This further suggests that the combustion of hydrocarbons could have led to an increase in the PAH concentrations. The Fla/(Fla+Pyr) ratio all less than 1 in all locations in both seasons suggesting that the levels of these PAHs may have been influenced by both pyrogenic and petrogenic sources as well as the burning of grass, wood, and coal [16]. Also, the ratio of B(b)Flu/(B(b)Flu B(k)Flu) data in all locations for both seasons indicates that the quantities of PAHs in the examined mechanic village were influenced by petrogenic sources and vehicle emissions. Moreover, the ratio of Ant/ (Ant+Phe) was all less than one (1), which indicated that the PAH emission was coming from a petrogenic source [34, 35, 36].

3.5 ECOLOGICAL HEALTH RISK ASSESSMENT
3.5.1 Carcinogenicity of PAH
B(a)Pyr is the PAH considered to be of most concern in terms of potential cancer risk. This substance is known to be a proven human carcinogen and is known to have significant carcinogenic activity in humans [37]. B(a)Pyr was found in all the sample locations in the dry season with 0.0125 mg/ml, 0.0353mg/ml, 0.0047mg/ml, 0.0034mg/ml, and 0.0035mg/ml for samples 1,2,3,4 and 5 respectively while surprisingly B(a)Pyr was found in only sample 5 during the wet season as shown in Table 8. Each PAH's carcinogenic potential was obtained by multiplying their respective concentration by the relevant TEF, [38] which gave the toxicity equivalent concentration (TEQ). Toxic equivalency factor (TEF) and B(a)Pyreq (mg/kg/day) values of the various PAHs

values for the four carcinogenic PAHs employed in this study are Benzo(k)Flu (0.01), Benzo(a)Pyr (0.1), Benzo(b)flu (0.1) and Dib(a-h).[39]

According to the 16 USEPA priority pollutants, pollution levels are divided into four categories: unpolluted (200 g/kg), mildly contaminated (200–600 g/kg), polluted (600–1000 g/kg), and severely polluted (1000 g/kg). According to this categorization, the area is unpolluted because the levels of PAHs at all the locations in the area were still under 200 g/kg. It is important to remember that despite the low overall concentration of carcinogenic B(a)Pyr in the region, the health risk evaluation of carcinogenicity cannot be based solely on this, but rather on the overall concentration of all carcinogenic PAHs in this area because other carcinogenic PAHs has a varied potential for cancer [47]. The B(a)Pyr concentrations are frequently used to determine health risks associated with PAH absorption. B(a)Pyr is cited as the primary cause of cancer in almost all studies [31]. The Toxicity Equivalency Factors (TEFs) developed by, adapted, and used to calculate the benzo(a)pyrene-equivalent (B(a)Pyreq) concentration and measure the carcinogenic potential of additional PAHs in comparison to B(a)Pyr. In comparison to previous investigations in polluted areas, the average benzo(a)pyrene equivalent concentration (B(a)Pyreq) of the discovered PAHs in the study during the investigation ranged from 0.3293 mg/kg/day, 0.3148 mg/kg/day, 0.0314 mg/kg/day, 0.0335 mg/kg/day and 0.0885 mg/kg/day for samples 1 to 5 respectively for the wet season and 0.0241 mg/kg/day, 0.0476 mg/kg/day, 0.0484 mg/kg/day, 0.0111 mg/kg/day and 0.0168 mg/kg/day for samples 1 to 5 respectively for dry season indicating a low carcinogenic potential. As a result, this study describes water samples as having concerned values of B(a)Pyr across all the sample locations. The results of this indicate that cancer-related illness is presumed to manifest in the exposed population (adults and children) over time based on age, sex, body weight, exposure period, and location and proximity to exposure points [40].

3.6 CORRELATION STUDY
3.6.1 Principal Component Analysis

By highlighting the similarities, differences, trends, and patterns in high-dimensional data, principal component analysis (PCA), a statistical technique is used to reduce it into simpler dimensions sets of data known as principal components or extracts. To have the first principal component account for as much of the variation in the original data as feasible, the extracts are generated in decreasing order of importance. A collection of data must pass the sample adequacy measures from a given PCA, which is always 100%.

For wet season the most important components (PC-PC-1, PC-2, etc.), are indicated by the eigenvalues as indicated in the PCA plot in Figure 13. In this study, the sampling adequacy measure for the wet season is presented in Table 9, principal component-1 (PC-1) explained 52.5% of the overall variation and was more heavily loaded with HMW PAHs (B(k)Flu, B(b)Flu, B(ghi)Per and B(a)Pyr) than LMW PAHs (Ace, Ant Phe, and Fla). This suggests that the sources of these groups of PAHs are similar to those that produced the diagnostic ratios that we previously noticed. This conclusion is consistent with observations reported by [6] for LMW PAH in their first PCA extract (PC1). The low-temperature pyrogenic processes, such as biomass combustion, produce the LMW PAHs [48]. Diesel and gasoline are primarily made up of PAH Molecules, which can result from insufficient fuel combustion, wood combustion, and car emissions, [40, 41], [42] and could also be the source of some of the PAHs obtained in this study. As a result, PC-1 depicts the sources of PAHs from incomplete fuel combustions, which is a major occurrence in the region as well as the anthropogenic disposal of fuel products, used engine oil, lubricating, and a lot of other substances that contain PAHs without considering the impact on the environment. Principal component-2 (PC-2) analysis explained 34% of the overall variance, whereas principal component-3 (PC-3) analysis only explained 8.58%. The main PAHs present in PC-2 are Pyr. B(b)Flu, B(a)Pyr, Fla, and B(ghi)Per are found in high concentrations in both PC-1 and PC-2, which shows that these PAHs derive from a variety of sources [Ibe et al., 2021]. B(k)Flu and Fla are the PAHs that are most strongly loaded for PC-3. Table 11 shows that PC-2 and PC-3 have negative loadings such as Ant and B(k)Flu, for PC-2 and B(k)Flu, DahA, B(ghi)Per, etc. for PC-3; this suggests that these PAHs are negatively associated or correlated with the other PAHs from which they were derived.

However, for the dry season, principal component-1 (PC-1) explained 55.6% of the overall variation while principal component-2 (PC-2) analysis explained 30.4% of the overall variance, and principal component-3 (PC-3) analysis only explained 13.4%. Like the wet season, the main PAHs present in PC-2 are B(a)Pyr, B(b)Flu, Fla, and Phe are found in high concentrations in both PC-1 and PC-2, which shows that these PAHs derive from a variety of sources as presented in Table 10 and Figure 13. [43-45].

Table 7. Diagnostic Ratio

	Ant/ [Ant+Phe]	Phe/Ant	Fla/ [Fla+Pyr]	B[b]Flu/ [B[b]Flu+B[k]Flu]	∑Comb ∑PAH	∑LPAH ∑ HPAH
Wet season						
Sample 1	0.443	1.256	0.000	0.000	0.508	1.130
Sample 2	0.497	1.013	0.000	0.000	0.370	1.720
Sample 3	0.241	3.150	0.000	0.000	0.651	0.898
Sample 4	0.241	3.143	0.000	1.304	0.683	0.749
Sample 5	0.000	0.000	0.216	0.000	0.483	1.247
Dry season						
Sample 1	0.104	8.63	0.983	0.838	0.752	0.323
Sample 2	0.070	13.22	0.984	0.850	0.783	0.272
Sample 3	0.093	9.77	0.996	0.958	0.753	0.287
Sample 4	0.133	6.55	0.994	0.891	0.744	0.338
Sample 5	0.134	6.49	0.994	0.942	0.769	0.295

Table 8. Toxic equivalency factor (TEF) and B(a)Pyreq (mg/kg/day) values for the total carcinogenic PAHs

Carcinogenic PAH	No. of Carbon Rings	Toxic equivalency factor [TEF]	Sample 1 PAH Conc. X TEF	Sample 2 PAH Conc. X TEF	Sample 3 PAH Conc. X TEF	Sample 4 PAH Conc. X TEF	Sample 5 PAH Conc. X TEF
Wet season							
Db[a-h]	5	1	0.2718	0.2717	0	0	0.0795
B[k]Flu	5	0.01	0	0	0	0.0024	0
B[a]Pyr	5	0.1	0	0	0	0	0.009
B[b]Flu	5	0.1	0.0575	0.0431	0.0314	0.0311	0
B(a)Pyreq (mg/kg/day)			0.3293	0.3148	0.0314	0.0335	0.0885
Dry season							
Dib[a-h]ant	5	1	0.0045	0.0045	0.0252	0.0023	0.0023
Benzo[k]Flu	5	0.01	0.0001	0.0001	0.0001	0.0001	0.0001
Benzo[a]Pyr	5	0.1	0.0125	0.0353	0.0047	0.0034	0.0035
Benzo[b]flu	5	0.1	0.007	0.0077	0.0184	0.0053	0.0109
B[a]Pyreq [mg/kg/ day]			0.0241	0.0476	0.0484	0.0111	0.0168

Table 9. PCA for wet season.

Parameter	Eigenvalue	% of Variance	Cumulative (%)
PC☐	7.3553	52.5378	52.5378
PC☐	4.7613	34.0095	86.5473
PC☐	1.2014	8.5814	95.1287
PC☐	0.682	4.8713	100
PC☐	-2.87E-16	-2.05E-15	100

PC□	-2.82E-16	-2.02E-15	100
PC□	-2.25E-16	-1.61E-15	100
PC□	-1.59E-16	-1.14E-15	100
PC□	-8.34E-17	-5.96E-16	100
PC□□	6.94E-17	4.95E-16	100
PC□□	3.12E-17	2.23E-16	100
PC□□	2.78E-17	1.99E-16	100
PC□□	-2.61E-17	-1.86E-16	100
PC□□	0	0	100
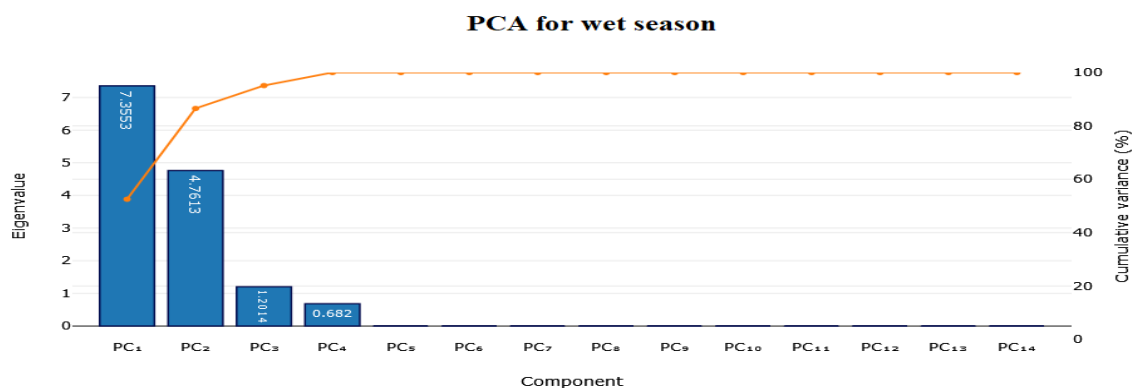
Figure 13. PCA for wet season

Table 10. Covariance for PAHs for wet season

Group\Group	Flu	Fla	Phe	Db[a-h]	Ant	Ace	B[k]Flu	B[a]Pyr	Pyr	B[g-h]Per	B[b]Flu	Naph	1,2 Ban	Acy
Flu	1	0.8907	-0.8215	-0.4205	-0.8226	0.546	-0.3694	0.8907	0.32	-0.5932	-0.8829	-0.5424	0.7307	0.07722
Fla	0.8907	1	-0.982	-0.1824	-0.73	0.7927	-0.25	1	0.06319	-0.4015	-0.8603	-0.4876	0.8959	0.4742
Phe	-0.8215	-0.982	1	-0.006536	0.592	-0.8935	0.3434	-0.982	0.1265	0.2248	0.76	0.3938	-0.9281	-0.571
Db[a-h]	-0.4205	-0.1824	-0.006536	1	0.7832	0.4548	-0.504	-0.1824	-0.9928	0.9559	0.5993	0.5349	0.08878	0.4352
Ant	-0.8226	-0.73	0.592	0.7832	1	-0.1756	-0.1897	-0.73	-0.7061	0.8553	0.8841	0.5269	-0.5472	-0.07179
Ace	0.546	0.7927	-0.8935	0.4548	-0.1756	1	-0.539	0.7927	-0.5584	0.2292	-0.4076	-0.1099	0.8666	0.6994
B[k]Flu	-0.3694	-0.25	0.3434	-0.504	-0.1897	-0.539	1	-0.25	0.5383	-0.4015	-0.03955	-0.1548	-0.3673	0.02355
B[a]Pyr	0.8907	1	-0.982	-0.1824	-0.73	0.7927	-0.25	1	0.06319	-0.4015	-0.8603	-0.4876	0.8959	0.4742
Pyr	0.32	0.06319	0.1265	-0.9928	-0.7061	-0.5584	0.5383	0.06319	1	-0.9211	-0.5031	-0.4824	-0.199	-0.5017
B[g-h]Per	-0.5932	-0.4015	0.2248	0.9559	0.8553	0.2292	-0.4015	-0.4015	-0.9211	1	0.7927	0.738	-0.06369	0.3641
B[b]Flu	-0.8829	-0.8603	0.76	0.5993	0.8841	-0.4076	-0.03955	-0.8603	-0.5031	0.7927	1	0.8022	-0.5686	-0.06822
Naph	-0.5424	-0.4876	0.3938	0.5349	0.5269	-0.1099	-0.1548	-0.4876	-0.4824	0.738	0.8022	1	-0.05024	0.3144
1,2 Ban	0.7307	0.8959	-0.9281	0.08878	-0.5472	0.8666	-0.3673	0.8959	-0.199	-0.06369	-0.5686	-0.05024	1	0.7172
Acy	0.07722	0.4742	-0.571	0.4352	-0.07179	0.6994	0.02355	0.4742	-0.5017	0.3641	-0.06822	0.3144	0.7172	1

The correlation matrices of the analyzed PAH components, which assessed the strength and direction of a linear relationship, are provided in Table 10. (PAHs variables of interest). ($\geq$0.70 PC$\leq$ 1.00) indicates Strong correlation, ($\geq$0.30 PC $\leq$ 0.69) medium correlation, and ($\geq$0.00 PC $\leq$0.29) weak correlations were used to conduct the correlation at significance p$\leq$ 0.05 with mostly positive correlation over negative correlation to derive salient information [16] [45]. A negative correlation existed between Flu and Phe (- 0.8215), Ant (- 0.8226) and B(b)Flu (- 0.883), almost perfect negative correlation existed between Fla and Phe (- 0.982), Fla exhibited a strong negative correlation with B(b)Flu (- 0.86). Phe had a strong negative correlation (- 0.893) with Ace, Db(a-h) showed an almost perfect negative correlation with Pyr (- 0.993), while B(g-h)Per showed a strong negative correlation with Pyr (- 0.9211), all presented in Table 10.

Table 11. PCA for dry season

Parameter	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚	PC⬚⬚	PC⬚⬚	PC⬚⬚
Eigenvalue	6.668	3.643	1.605	0.085	-2.013E-16	1.663E-16	1.064E-16	9.563E-17	9.448E-17	7.354E-17	4.114E-17	1.514E-17
% of Variance	55.564	30.359	13.371	0.706	-1.677E-15	1.386E-15	8.869E-16	7.970E-16	7.873E-16	6.128E-16	3.428E-16	1.261E-16
Cumulative [%]	55.5635	85.9228	99.2939	100	100	100	100	100	100	100	100	100
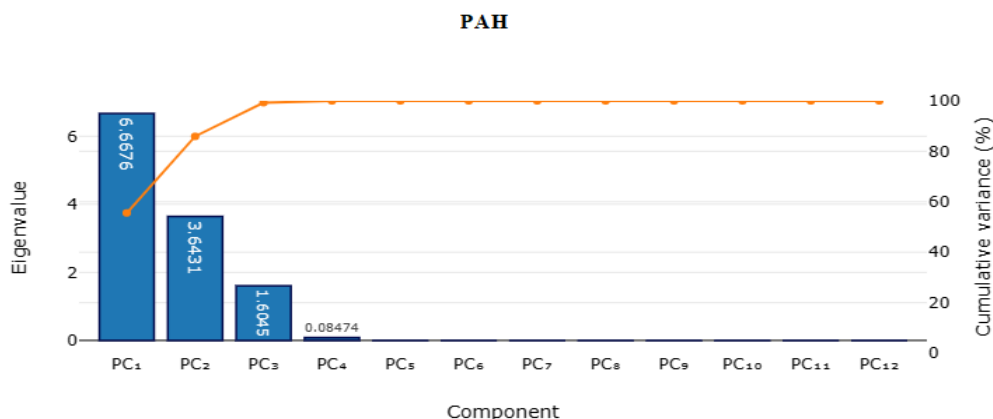
Figure 14. PCA for dry season

Table 12. Covariance for PAHs for dry season

Group	Flu	Fla	Phe	Db(a-h)	Ant	Aph	B(k)Flu	B(a)Pyr	Xyl	Pyr	B(g-h)Per	Bbf
Flu	1	-0.081	0.351	0.765	-0.627	0.635	-0.092	0.840	-0.215	-0.211	0.839	0.757
Fla	-0.081	1	0.901	-0.177	0.531	-0.564	0.998	-0.564	0.990	0.991	0.176	-0.322
Phe	0.351	0.901	1	0.198	0.256	-0.284	0.898	-0.178	0.833	0.835	0.504	0.027
Db(a-h)	0.765	-0.177	0.198	1	-0.159	0.186	-0.147	0.570	-0.303	-0.299	0.319	0.908
Ant	-0.627	0.531	0.256	-0.159	1	-0.999	0.573	-0.898	0.577	0.578	-0.705	-0.268
Aph	0.635	-0.564	-0.284	0.186	-0.999	1	-0.604	0.912	-0.612	-0.612	0.685	0.308
B(k)Flu	-0.092	0.998	0.898	-0.147	0.573	-0.604	1	-0.585	0.987	0.988	0.137	-0.302
B(a)Pyr	0.840	-0.564	-0.178	0.570	-0.898	0.912	-0.585	1	-0.657	-0.655	0.688	0.647
Xyl	-0.21	0.99	0.83	-0.30	0.58	-0.61	0.99	-0.66	1	1	0.080	-0.445
Pyr	-0.211	0.991	0.835	-0.299	0.578	-0.612	0.988	-0.655	1	1	0.082	-0.438
B(g-h)Per	0.839	0.176	0.504	0.319	-0.705	0.685	0.137	0.688	0.080	0.082	1	0.300
Bbf	0.757	-0.322	0.027	0.908	-0.268	0.308	-0.302	0.647	-0.445	-0.438	0.300	1

Due to the leaching processes correlation performed on all samples produced a mix of weak medium and strong correlation, indicating that the PAHs component was from a similar source but that its interactions were weak, medium, and strong [47]. For the dry season, Strong correlations were found between Flu and B(a)Pyr (0.84) and B(gh)Per (0.839), respectively. The connection between Fla and Phe, B(k)Flu, Xyl, and Pyr showed an excellent correlation of 0.9.1, 0.998. 0.99 and 0.991 respectively. Phe also correlated strongly with B(k), Flu, Xyl, and Pyr (0.898, 0.833, 0.0.835). Db(a-h) has a very strong correlation with B(b)Flu (0.908). B(b)Flu also exhibited a substantial correlation (0.998, 0.987, and 0.988) with Fla, Xyl, and Pyr. It is clear from all the locations that there was a strong correlation between B(a)Pyr, B(k)Flu, Fla, and Phe which suggests that there was a strong indication that B(a)Pyr, B(k)Flu, Fla and Phe contaminants were significant across all locations. Also observed are medium and weak medium correlations in the correlation matrices as presented in

Table 12. Evaluating these data showed a perfect negative correlation between Ant and Ace (-1), Ant and B(a)Pyr (-0.9) respectively, and a medium negative correlation between Fla and Ace (-0.56) and Fla and B(a)Pyr (-0.56). A negative correlation indicates that different biochemical interactions were occurring in various sample sources. With these positive correlations, we can assume that all of these PAHs analyzed came from the same source of pollution and had migratory tendencies with adverse effects on human exposure [46-48]. Also, for the dry season, Strong correlations found Flu showed a strong correlation with Fla (0.89) and B(a)Pyr (0.89), respectively. Also, Db (a-h) has a very strong correlation with B(ghi)Per (0.956) as Ant showed a moderately strong correlation (0.855) with B(ghi)Per, 1,2 Ban showed a strong correlation with Fla (0.896), Ace (0.866) B(a)Pyr (0.896) while Naph showed a strong correlation with B(b)Flu (-0.8022).

Table 13. CR in all sample locations

Wet season					
Adults					
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Carcinogenic PAHs	Total CR	Total CR	Total CR	Total CR	Total CR
Dib[a-h] ant	1.6571	1.6564	0.0000	0.0000	0.4847
Benzo[k]Flu	0.0610	0.0000	0.0000	0.0000	0.0146
Benzo[a]Pyr	0.6097	0.0000	0.0000	0.0000	0.5487
Benzo[b]flu	0.6097	0.3506	0.2628	0.1914	0.1896
Children					
Carcinogenic PAHs	Total CR	Total CR	Total CR	Total CR	Total CR
Dib[a-h]ant	3.7418	3.7404	0.0000	0.0000	1.0945
Benzo[k]Flu	0.1377	0.0000	0.0000	0.0000	0.0330
Benzo[a]Pyr	1.3767	0.0000	0.0000	0.0000	1.2390
Benzo[b]flu	1.3767	0.7916	0.5934	0.4323	0.4281
Carcinogenic PAHs	Total CR	Total CR	Total CR	Total CR	Total CR
Dry season					
Adults					
Dib[a-h] ant	2.7435E-02	2.7435E-02	1.5363E-01	1.4022E-02	1.4022E-02
Benzo[k]Flu	8.2304E-04	8.2304E-04	4.8773E-04	3.9628E-04	4.0847E-04
Benzo[a]Pyr	7.6207E-02	2.1521E-01	2.8532E-02	2.0972E-02	2.1582E-02
Benzo[b]flu	4.2615E-01	4.6639E-	1.1230E-01	3.2501E-	6.6209E-02

		02		02	
Children					
Dib[a-h] ant	6.1951E-02	6.1951E-02	1.5363E-01	3.1664E-02	3.1664E-02
Benzo[k]Flu	1.8585E-03	1.8585E-03	4.8773E-04	8.9484E-04	9.2238E-04
Benzo[a]Pyr	1.7209E-01	4.8597E-01	2.8532E-02	4.7358E-02	4.8735E-02
Benzo[b]flu	9.6230E-01	1.0532E-01	1.1230E-01	7.3391E-02	1.4951E-01

Table 13 displays the cancer risk in water for both adults and children. The chronic daily intake of B(a)Pyreq exposure from ingesting and dermal absorption as well as the likelihood that they will cause cancer were estimated. The chronic daily intake through different carcinogenic PAH routes is all captured in this table. The New York State Department of Health (NYSDOH) describes the lifetime health cancer risk using numerical values as very low cancer risk: ≤ 10-6 to <10-4, moderate cancer risk: ≤ 10-4 to <10-3, high cancer risk: ≤ 10-3 to <10-1 and very high cancer risk: ≥10-1. [16]. Also, carcinogen risk for both adults and children followed the same trend as the chronic daily intake concerning the carcinogenic PAHs routes of exposure. Children may be more susceptible to cancer through ingestion, although the carcinogenic risk calculated for both adults and children was higher than the USEPA tolerable cancer risk. The estimated carcinogenic risks for adults and children for water samples collected during the wet season are presented in Table 13 revealing high-risk exposure concerning exposure through ingestion and dermal, the chronic daily intake B(a)Pyreq concerning the following carcinogenic PAHs routes for adults are in the following order samples 1, Dib(a-h)ant <Benzo(b)flu = Benzo(a)Pyr < Benzo(k)Flu, sample 2, Dib(a-h)ant < Benzo(b)flu, sample 3 and 4 Benzo(b)flu alone, sample 5 Benzo(a)Pyr < Dib(a-h) < Benzo(b)flu < Benzo(k)Flu< while for children for samples during wet season followed the same trend as adults for all sample locations[49-51]. Whereas for samples collected during the dry season (table 13) concerning exposure through ingestion and dermal, the chronic daily intake B(a)Pyreq concerning the following carcinogenic PAHs routes are the same for adults and children in the following order samples 1, Benzo(b)flu < Benzo(a)Pyr < Dib(a-h)ant < Benzo(k)Flu, for sample 2, Benzo(a)Pyr< Benzo(b)flu< Dib(a-h)ant < Benzo(k)Flu, for sample 3, Dib(a-h)ant < Benzo(b)flu < Benzo(a)Pyr < Benzo(k)Flu while sample 4 and 5 are in the same order of Benzo(b)Flu < Benzo(a)Pyr < Dib(a-

h)ant < Benzo(k)Flu while in children the following trend was observed.

4. Conclusions

The current study evaluated the polycyclic aromatic hydrocarbons (PAHs) in different groundwater in the reclaimed sections within Orji auto mechanic village, Imo State, Nigeria now converted to residential area. The results of this investigation revealed the presence of pollution above the specified drinking water criteria including fluoranthene, pyrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h) anthracene, and benzo(ghi)perylene The concentration found in samples 4 and 5 were slightly lower than other samples locations in the dry season, while the concentrations were higher in samples 1 and 5 collected during dry season suggesting that the impact of rainfall, runoff, and leaching significantly contributes to the variations in groundwater pollution in the areas under study. For the wet season levels of PAHs found demonstrated a slight prevalence for low molecular weight polycyclic aromatic hydrocarbons (less than four fused rings) over high molecular weight polycyclic aromatic hydrocarbons in samples 1 and 2 and less in samples 3, 4, and 5 whereas, in the dry season, high molecular weight polycyclic aromatic hydrocarbons concentrations were consistently more than the low molecular weight PAHs in all the sample locations. Diagnostic ratios revealed both Pyrogenic and Petrogenic sources were the likely origin of the PAHs in this study location. However, the PAH concentration levels determined revealed that the groundwater sources are contaminated and unsafe for human consumption due to the contamination level and risks associated with their consumption. The build-up of PAHs can have a detrimental effect on the health of humans and can result in fatal conditions such as cancer, long-term gastrointestinal tract irritation, headaches, lethargy nausea, and diarrhea. PAHs are also linked to adverse health effects such as interstitial and digestive

disturbances, and renal disorders as well as dermatitis, blisters, eye irritation, and skin inflammation

After evaluating these potential health impacts, it is of great concern that children are particularly exposed to more danger from prolonged ingestion and dermal exposure to PAHs in groundwater, according to their pollution levels detected. Government organizations should set up monitoring stations for water contamination to help establish a practical strategy and remedial action plan to avoid potential health problems in the future. This study serves as the foundation for an appeal to Nigerian policymakers about the need to provide potable water to its citizens as non-communicable diseases (NCDs) such as cardiovascular disease, diabetes, cancer, renal disorders, and liver failure and so on may be connected with PAH pollution. Thus, it is advised that comprehensive remediation be done there. Also, the general population in that region needs to be made aware of the dangers of these contaminants.

Abbreviations
PAHs: Polycyclic aromatic hydrocarbons; Nap: Naphthalene; Apt: Acenaphthylene; Aph: Acenaphthene; Flu: Fluorene; Phe: Phenanthrene; Ant: Anthracene; Fla: Fluoranthene; Pyr: Pyrene; Ban: Benzo(a)anthracene; Chy: Chrysene; Bbf: Benzo(b)fluoranthene; Bkf: Benzo(k)fluoranthene; Idp: Indeno(1,2,3-cd)pyrene; Dib(a-h)ant: Dibenzo(a,h)anthracene; ∑PAHs: The sum of all the PAHs determined;∑HPAHs: The sum of high molecular weight (4–6 rings) PAHs; ∑LPAHs: The sum of low molecular weight (2–3 rings) PAHs); ∑Comb-PAHs: The sum of combustible PAHs; STD: Standard deviation; Min: Minimum; Max: Maximum; PCA: Principal component analysis; IARC: International Agency for Research on Cancer; GC: Gas chromatography; USEPA: United State Environmental Protection Agency; BePeq: Benzo(a) pyrene equivalent; TEQF: Toxic equivalent factor; RI: Rate of ingestion; ESA: Exposed skin area; SAF: Skin adherence factor; SAF: Skin adherence factor; DE: Duration of exposure; ET: Time of exposure; AT: Averaging time; OSF: Oral slope factor; GIAF: Gastrointestinal absorption factor; DAF: Dermal absorption factor; IUR: Inhalation unit risk; mg: milligram; ug: microgram.

Author's contribution
CFO: Investigation, Writing-Original Draft Preparation, Resources. Methodology, Statistical Treatment; IFC: Conceptualization, Supervision, Methodology, Visualization, Reviewing and Editing.

Conflicts of interest
The authors declare no conflict of interest concerning the publication of this manuscript

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