

Research Article
Journal of Research and Review in Science
1-12, Volume 10, December 2023.
DOI: 10.36108/jrrslasu/3202.01.0170

ORIGINAL RESEARCH



Determination of Polycyclic Aromatic Hydrocarbons in the Water of Ijegun-Egba Community of Lagos State, Nigeria

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Funding information

No funding was received for this work

Abstract:

Introduction: Polycyclic Aromatic Hydrocarbons (PAHs) are common pollutants in water that have been reported to cause severe health effects in humans and harm the ecosystem.

Aims: This study examined the concentrations of PAHs in different water sources used for domestic purposes in Ijegun- Egba community.

Materials and Methods: Twenty-four (24) groundwater samples were collected from four sites in Ijegun-Egba. The Physicochemical parameters were determined using standard methods and PAHs were determined through Gas chromatography-flame – Flame ionization detector.

Results: The appearance, odour, and temperature were within the limits of World Health Organisation (WHO). Conductivity levels were within the WHO limit (2,500 μ S/cm) in well water (1,400 μ S/cm) and borehole water (1,470 μ S/cm) except for river water (4,432.5 μ S/cm) which was above WHO recommended limit (2,500 μ S/cm). pH was within limits in all sites studied except for borehole water (pH =4.0). Among the 16 PAHs, Naphthalene (NAPH) was generally the most abundant PAH (23.89% to Σ 16PAHs). There was a significant difference (at < 0.005) in the level of PAHs in the four sources of water.

Conclusion: River water has the highest level of PAHs. This points to the activities of the tank farms and suggests that petrol and oil deposits find themselves either through percolation, soil runoffs, or erosion into the water bodies. The Lagos State Environmental Protection Agency should continue to monitor the activities of oil tankers in Ijegun community oil depots. Truck stations should be built outside the community and the residents should avoid the use of water from rivers in Ijegun community.

To Keywords: Polycyclic aromatic hydrocarbons, Oil depots, Groundwater, Pollutants

All co-authors agreed to have their names listed as authors.

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thors. *Journal of Research and Reviews in Science – JRRS, A Publication of Lagos State University*

1. INTRODUCTION

Water is an invaluable natural resource that is essential to human survival and the ecosystem's health. No life is without water [1]. Water is abundant on Earth in the form of rivers, oceans, seas, wells, lakes, and ice caps. However, a large proportion of this water is not in a state suitable for human or animal consumption [2]. Water comprises coastal water bodies and freshwater bodies e.g. lakes, rivers and groundwater, wetlands, and underground water [3]. Rainfall can also be grouped under freshwater resources – although man has little or no influence over its availability.

The survival of man and other living things on earth depends on the wise and safe use of water. Freshwater resources serve as the main source of safe drinking water for the human population and support agricultural activities through natural feeding and irrigation practices, and it is far cheaper to use freshwater for industrial purposes. For centuries humans have been depositing waste products by burning, carelessly placing them in streams, storing them in the ground, or placing them in the ground. Human-induced influences on surface water quality reflect waste discharged directly into a stream and contaminated surface runoff. The quality of groundwater is most affected by surface waste disposal and land use [4]. Indiscriminate disposal of waste materials is a major source of pollution of water in most places. Such waste materials that pollute water sources include manure, sludge, garbage, and industrial waste. The waste may occur as individual mounds or may be spread all over the land. If the waste material contains soluble substances, they may infiltrate similar problems that occur in the vicinity of various types of stockpiles [5, 6].

Polycyclic Aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms [7]. PAHs occur naturally in most cases in the form of crude oil, gasoline and coal. PAHs are produced when coal, gas oil, wood, garbage, and sometimes tobacco are exposed to high temperatures. They usually bind to small particles in the air. Exposure of meat and other foods to high temperatures could result in the formation of PAHs [8]. Cigarette smoke contains many PAHs. [9].

[10] argued that Polycyclic aromatic hydrocarbons are among the most widespread persistent organic pollutants in the water environment. Polycyclic Aromatic Hydrocarbon solubility in water decreases with increasing molecular weight. This results in low concentrations of PAHs in water [11]. PAHs are usually found in water in significant concentrations due to their characterized low solubility and high affinity for particulate matter [12]. Their presence in surface water or groundwater is an indication of a source of pollution [13]. In most cases under aerobic conditions, PAHs are only slowly biodegradable but are stable for hydrolysis [14]. The relative concentrations of PAHs in air, water, and food are usually the same, although this can change depending on certain sources of pollution [13].

PAHs are emitted mainly into the atmosphere and have been detected long distances from their source [15]. Usually, PAHs, compounds with five or more aromatic rings under low vapour pressures will exist mainly adsorbed to airborne particulate matter while those with four or fewer rings will occur both in the vapour phase and adsorbed to particles [16]. PAHs in the hydrosphere are mainly through dry and wet deposition of oil and road runoff. In addition, industrial wastes containing PAHs and equally the leaching from creosote-impregnated wood do find their way into the atmosphere [17]. The compounds are very slowly biodegradable under aerobic conditions in the aqueous compartment. The biodegradation rates decrease drastically with an increasing number of aromatic rings.

PAHs are stable towards hydrolysis. Under laboratory conditions, the reaction of the compounds with airborne hydroxyl radicals shows maximum half-lives between about 3 and 11 hours. For pure water, the photo-degradation half-lives appear to be in the range of hours, whereas the half-lives increase drastically

when sediment/water partitioning is considered [18]. Measured bio-concentration factors (BCFs) for the compounds in the aquatic environment vary widely owing to different measurement techniques and are especially high for some algae (BCF = 2398–55 800), crustaceans (BCF = 180–63 000), and mollusks (BCF = 58– 8297). Bio-concentration factors in fish appear to be much lower than in these organisms because of rapid biotransformation processes (BCF = 10–4700) [19].

The purpose of the research was to investigate groundwater quality (physicochemical parameters) as well as check for the presence and concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) of some selected functional borehole water, table water, well water, and water from the river in Jetty Ijegan-Egba community especially those closer to the depot, Oriade LGA, Lagos State, Nigeria.

2. MATERIAL AND METHODS

2.1 Study Area

The study was carried out in the Ijegan- Egba community of Oriade Local Government Area of Lagos state. Lagos state is situated in the Southwestern region of Nigeria (Figure 2.1).

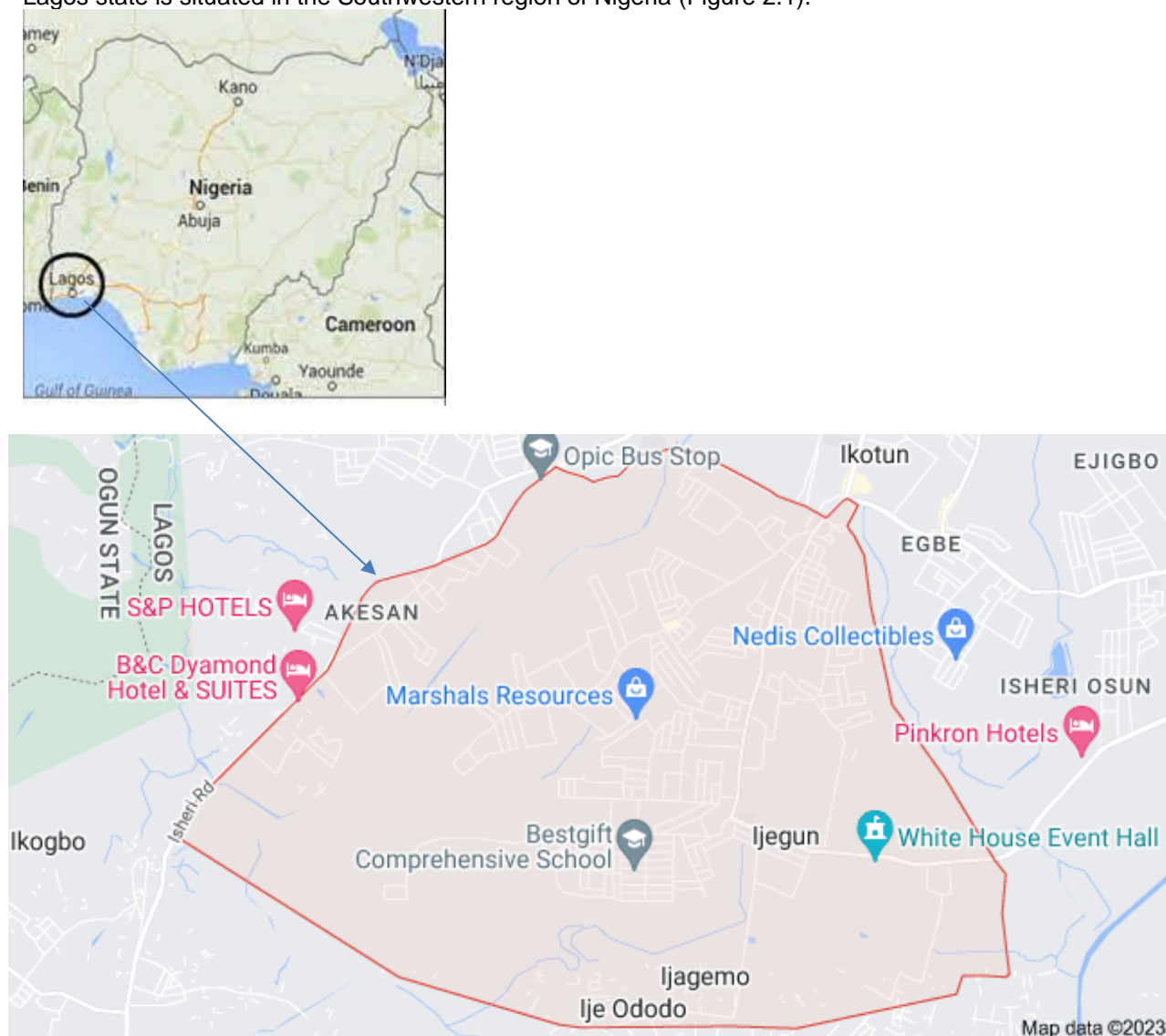


Figure 2.1: Map showing Ijegan Lagos Nigeria. Source: Google Map 2023

2.2 Procedure for Sample Collection

The water sample was collected from Ijegan Community in 2021. Groundwater sample was collected from the study area shown in Figure 2.1 above. 5 sub-sampling sites each within the representative area of the single sampling Ijegan Egba river water, Well water, and Tap water while purified laboratory water was used as control. Having multiple subsamples does provide a more accurate picture of the entire study area and prevents an irregular area from skewing the results of the findings. Sampling was done twice from 4

different sources (sampling Ijegun Egba river water, well water, and Tap water while purified laboratory water was used as control) in the community, with 3-week intervals to compare and look out for any significant changes. Sub-sampling sites are selected at 5m from each other, and the subsamples collected were put into one representative sample. Groundwater samples were collected with new 1.5-litre-sized bottles from the different sampling locations within the Ijegun-Egba community. The physical parameters (Odour, pH, temperature, conductivity) were determined in-situ.

2.3 Procedure for Determination of pH, TDS, EC and temperature: Hanah Multi-parameter meter was calibrated with pH buffers 4, 7 and 10 respectively. An Aliquot of water sample was used to rinse the 100ml beaker that was used for this exercise. 50ml of the sample was poured into a 100ml beaker immediately after collection. A calibrated probe of Hannah's multi-parameter meter was inserted into the water sample to measure the pH, TDS, EC and temperature. The readings were documented as appropriate. The probe of the multi-parameter meter was rinsed with distilled water while the meter was switched off.

2.4 Determination of the physiochemical Quality parameters

2.4.1 Procedure for Determination of Acidity: Titrimetry was used to determine acidity in the sample. 25 ml of the water sample was pipetted into a conical flask. 2 drops of phenolphthalein indicator were added into the flask. The solution was titrated with 0.1 M NaOH solution to a pink-colored endpoint. The process was repeated so the analysis will be performed in duplicate.

$$\text{Acidity (mg/l)} = \frac{\text{ATV} \times \text{F} \times 1000}{\text{Volume of sample used}}$$

ATV = Average titer value

F = Factor of titrant

2.4.2 Procedure for Determination of Alkalinity: The alkalinity of the sample was also determined using the titrimetry method. 25 ml pipette/measuring cylinder, conical flask, Methyl orange indicator, 0.02 M sulphuric acid (H₂SO₄) solution. 25 ml of the water sample was pipette into a conical flask. Then 2 drops of methyl orange indicator were added to the water sample. The sample was then titrated with 0.02 M H₂SO₄ to a red colour endpoint. The analysis was also performed in duplicate.

$$\text{Alkalinity (mg/l)} = \frac{\text{ATV} \times \text{F} \times 1000}{\text{Volume of sample used}}$$

ATV = Average titer value,

F = Factor of titrant

2.4.3: Determination of Chloride: 25 ml of water sample was transferred into a conical flask, then 1.0 ml of 5% K₂CrO₄ and titrate with standard 0.0141 M AgNO₃ was added to a pinkish yellow endpoint to determine Chloride.

The analysis was conducted in duplicates.

Calculation:

Equation 3.3

$$\text{Cl}^- \text{ (mg/l)} = \frac{(\text{A}-\text{B}) \times \text{M} \times 35450}{\text{Volume of Sample}}$$

Where, A = Average titer value of the sample

B = Average titer value of the blank

M = Morality of AgNO₃

2.4.3 Procedure for Determination of Chemical Oxygen Demand: The Chemical Oxygen Demand (COD) reactor was turned and allowed to settle for few minutes. The temperature was now then to be $150\text{ }^{\circ}\text{C} \pm 2$ and pre heat to the set temperature. Desired number of COD reagent vials was added the homogenized sample the required volume based on reagent range specifications to the vials held in $45\text{ }^{\circ}\text{C}$ angles. (For: low range 0-150: (2 ml) medium range 0-1,500: (2 mls) and high range 0-15,000: 0.2 mls). Capped the vial tightly and mix gently the sample with the reagent by inversion, rinsed the outside of the tube with water and wiped the droplet on the vials with soft tissue paper. Repeated steps 2 through 5 using the required volume of distilled water (this is the reagent blank). Placed the vials (tubes) in preheated block heater (COD reactor) and maintained temperature at $150\text{ }^{\circ}\text{C} \pm 2$ for 2 hours.

After 2 hours, the block heater was switched off and inverted several times. The spectrophotometer was turned, scrolled to, and selected COD ranges from the menu (chose the range of my reagent vials). Wiped the tube with tissue paper to remove fingerprints, then inserted the reagent blank into the chamber and selected scan blank. The blank tube was removed and the digested sample tube into the chamber, then the selected scan sample recorded the results. For the most accurate results, three readings on each sample and averaged the results after which the spectrophotometer was turned off.

2.4.4 Procedure for Determination of Biochemical Oxygen Demand: Determination of 5 days of Biochemical Oxygen Demand (BOD) in water using a BOD Meter. DO of the aerated water to be used was tested and ensured it is $\geq 7.5\text{ mg/l}$ DO, then 500 ml aerated water into 1 L volumetric flask. 1 ml each of phosphate buffer, MgSO_4 , CaCl_2 and FeCl_3 were added to the aerated water in the volumetric flask. Then mixed thoroughly and made up to mark in 1 L volumetric flask and tagged it dilution water. The temperature was checked and adjusted to $20 \pm 30\text{ }^{\circ}\text{C}$. 200 ml of dilution water was added to a 300 ml BOD bottle. Then appropriate sample volume was added based on the specifications in Table 1 below.

Table 1: Sample Volumes of Water

	0.1% - 1% Strong industrial Waste	1% - 5% Raw and settled wastewater	5%- 25% Biologically treated effluent	25% - 100% Polluted river water
Lower % range	0.1 % - 0.03 mls	1% - 3 mls	5% - 15 mls	25% - 75 ml
Medium % range	0.9% - 2.7 mls	5% - 15 mls	25% - 75 mls	100% - 300 mls
Higher % range	1.0% - 3 mls	5% - 15 mls	25% - 75 mls	100% - 300 mls

The bottle was filled to the brim with dilution water and sealed. The sealed bottle was inverted in water and taped with foil paper to reduce the evaporation of sealed water during incubation. A duplicate sample by repeating steps 6 - 9 above was made. Measured and recorded the DO₁ of the sample and blank with calibrated DO meter. The samples and blank were incubated for 5 days at $20 \pm 1\text{ }^{\circ}\text{C}$ in the absence of light. Measured and recorded the DO₅ of the incubated samples and blank on the 5th day with calibrated DO meter.

$$\text{BOD}_5 \text{ mg/l} = \frac{\text{DO}_1 - \text{DO}_5 (\text{sample}) - \text{DO}_1 - \text{DO}_5 (\text{blank})}{D_F}$$

$$D_F = \frac{\text{Sample volume used for DO (ml)}}{\text{Volume of BOD bottle (ml)}}$$

BOD₅ = Biochemical oxygen demand after 5 days

DO₁ = Initial Dissolved oxygen @ day1

DO₅ = Final dissolved oxygen after incubation @ day 5

2.5 Determination of Polycyclic Aromatic Hydrocarbons (PAH):

2.5.1 Water Sample

The samples were carefully taken and emptied into a 500 ml extraction bottle of borosilicate material and 30 ml of the ratio 3:1 redistilled hexane: dichloromethane was added. The bottle and its contents were placed in the sonicator to extract the hydrocarbon for about 2 hours. The extraction was repeated with the same amount of the extracting reagent and filtered the organic layer into a borosilicate beaker (250 ml). The organic layer of the liquid sample was obtained by separating the liquid mixture with a 1-litre capacity separation funnel.

2.5.2 PAH Separation

The concentrated oil was separated into the aliphatic profiles and Polycyclic Aromatic Hydrocarbons profiles by packing the glass column with activated alumina, neutral and activity/grade 1.10 ml of the treated alumina were packed into the column and cleaned properly with redistilled hexane before the aromatic fraction was recovered.

2.5.3 Gas Chromatography Analysis

The extract was analyzed by whole oil-gas chromatography analysis by concentrating the extract to 1.0 ml by the stream of nitrogen gas before the gas chromatography analysis. 1-2 microliter was injected into the Gas Chromatography column through the injection port.

Simple descriptive statistics (mean) and Analysis of Variance were used to analyze the data.

3. RESULTS AND DISCUSSION

Table 2 shows the results of the physicochemical characteristics of samples collected from the four different sources in the Ijegan-Egba community. The appearance of all the water samples collected was mostly clear and without particles except for the one collected from the river itself which had some tiny particles. The temperatures ranged from 25.4 °C to 26.55 °C with the lowest value observed in Well water and the highest value in Table water (control) followed by the Ijegan-Egba river water. The temperatures of the water were within the acceptable regulation which requires ambient levels.

The Samples from the River recorded the highest Conductivity (4,453.5 µs/c). The lowest value was recorded for the control (55 µs/c), but every one of the parameters was within the acceptable limit set by WHO. The other samples had high conductivity records well above the WHO Standards. Though some fell within the acceptable range of WHO standards. The high levels of electrical conductivity indicate the presence of ions within the waters. This is usually due to saline water. The levels of pH were within an acceptable range apart from samples collected from borehole/Tap with a mean pH of about 4.0.

The river water sample recorded the highest values for TDS (total dissolved solids) {4,432.5 mg/l} as compared to others with 1,071 mg/l and 1,018 mg/l respectively. They all showed high levels of TDS which were way above the acceptable values. The Alkalinity was lowest in Tap water (13.125 mg/l) and highest in Well water (116.55 mg/l). Nevertheless, the recorded values complied with the applicable standards. The borehole water has the highest levels of acidity (11.2 mg/l), which could be caused by the treatment or treating agent used for the water treatment process in the facility, it indicates the presence of a weak or strong acid. The water sample from the river has the lowest levels of acidity (6.6 mg/l)

The values/levels of Chloride (Salinity) are highest in the river water (3,746 mg/l). The lowest is seen in the well water (83.44 mg/l). Chloride for the Tap water is a bit higher than the acceptable value; this can also be attributed to the water treatment in the facility. The unusual and ridiculous spike noticed in the Salinity/chloride levels of the river water is due to the salty nature of the water in that river. The levels of dissolved oxygen (DO) and biochemical oxygen demand (BOD) recorded were well within the range of acceptable standards. This indicates that the waters are good enough to sustain aquatic life. The recorded values of chemical oxygen demand (COD) in the samples revealed the lowest concentration (15 mg/l) in tap/borehole water, and the maximum concentration (191.5 mg/l) in river water Fluorene (Flu) has the second-highest concentrations (giving about 20.23%) followed by Acenaphthene (Ace), Pyrene (Pyr), Acenaphthalene (Acy), Phenanthrene (Phen), Anthracene (Ant), Flouranthene (Fit), Benzo (a) Pyrene (BaP), Dibenzo (a, h) anthracene (DbA) etc. Benzo (a) anthracene (BaA) has the lowest concentrations in all the samples. Its values in Well water and Tap water (2.92 µg/l and 4.79 µg/l respectively) fell within the permissible limits of NSDWQ of 7.0 µg/l, except for its value in the river water (9.2 µg/l) which was a bit above the acceptable limits. All the 16 PAHs detected gave values or levels way above the WHO and Nigerian Standard Drinking Water Quality (NSDWQ) recommendations of 0.7 µg/l and 7.0 µg/l respectively.

The highest values of individual PAH compounds detected belong to the low molecular weight (LMW) categories (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene) which are often classified to be of petrogenic sources (like crude oil spills or seepages) (Table 3). A significant difference was observed in the level of Polycyclic Aromatic Hydrocarbons in the four sources of water (Table 4). PATHs level in the control water source was the lowest followed by well water and tap water. River water has the highest level of Polycyclic Aromatic Hydrocarbons (Table 3).

Table 2: Mean values of Physicochemical parameters of samples

S/ N	PARAMETER	UNITS	SAMPLE 1 (Control)	SAMPLE 2 (Ijegun Egba River Water)	SAMPLE 3 (Well water)	SAMPLE 4 (Tap water)	WHO/EPA	NESREA
1	Appearance	N.A	Clear Colourless liquid	Colourless liquid with particles	Clear Colourless liquid	Clear Colourless liquid	NS	NS
2	Odour	N.A	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable	Unobjectionable
3	Temperature	°C	26.55	26.2	25.4	25.7	25	NS
4	Conductivity	µS/cm	55	4,432.5	1,400	1,470	2,500	1,000
5	pH	N.A	7.05	7.0	7.0	4.0	6.5-8.5	6.5-8.5
6	TDS	Mg/l	45	5,836.5	1,018	1,071		500
7	Alkalinity	Mg/l	22.58	38.85	116.55	13.125	200	NS
8	Acidity	Mg/l	8.2	6.6	9.6	11.2	NS	NS
9	Chloride	Mg/l	1.0	3,746	83.44	377.5	250	≤350
10	DO	Mg/l	8.60	8.205	7.82	8.805	≥9.00	≥4.0
11	BOD	Mg/l	0.95	2.575	2.335	0.285	≤5.0	≤6.0
12	COD	Mg/l	19	191.5	33.5	15		≤30.0

N.A – Not Available

NS – Not Specified

Sample 1: Control (Purified Laboratory Water}, Sample 2: Ijegun Egba river water, Sample 3: Well water Sample 4: Tap water.

Table 3: Mean values of the 16 PAHs detected.

PAH Compounds	River water (µg/l)	Well Water (µg/l)	Tap Water (µg/l)	Table water (Control) (µg/l)
Naphthalene (Naph)	2221.58	1302.61	1608.95	0.26
Acenaphthylene (Acy)	930.03	286.57	214.80	0.07
Acenaphthene (Ace)	1586.93	1078.32	1410.92	0.38
Fluorene (Flu)	1602.52	1362.34	1382.6	0.72
Phenanthrene (Phen)	609.28	332.64	348.64	0.21
Anthracene (Ant)	308.00	184.91	216.73	0.13
Flouranthene (Fit)	306.92	123.57	145.70	0.09
Pyrene (Pyr)	1573.61	648.61	788.21	0.60
Benzo (a) anthracene (BaA)	9.20	2.92	4.79	0.01
Chrysene (Chry)	31.16	11.12	13.93	0.01
Benzo (b) fluoranthene (BbF)	36.17	11.40	14.29	0.01
Benzo (k) fluoranthene (BkF)	14.08	7.13	12.45	0.01
Benzo (a) pyrene (BaP)	237.72	127.64	162.47	0.05
Indeno (1,2,3-cd) pyrene (IP)	11.46	4.32	7.39	0.01
Dibenzo (a,h) anthracene (DbA)	41.74	24.77	35.03	0.03
Benzo (ghi) perylene (BgP)	69.16	9.60	11.09	0.01

Table 4 Analysis of Variance of Polycyclic Aromatic Hydrocarbon s in the Various Sources of Water

Metals

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	0.558	3	0.186	136.813	0.000
Within Groups	0.011	8	0.001		
Total	0.569	11			
Source	Mean Value of PAHs				
River	0.5990c				
Well	0.3450b				
Tap	0.3990b				
Control	0.0001a				

Generally, the physicochemical characteristics of the waters in the Ijegun-Egba Community are varied and were comparable with the results obtained from similar studies across Nigeria. Higher conductivity was recorded in other studies (20; 21). All these changes are due to temporal, spatial and environmental dynamics. All the water samples tested showed the occurrence of one or more individual PAHs, suggesting that PAHs were ubiquitous in the waters of the Ijegun-Egba community. Among the 16 PAHs, Naphthalene (NAPH) was generally the most abundant individual PAH (averagely contributing 23.89% to Σ 16PAHs). This was consistent with the previous national-scale investigation of drinking water in China (22). The PAH levels were highest in the river water even though the river is a free flowing one which could have suggested lower concentrations. This shows that the Petrol is being transported to the Depots via the river to be loaded in the tank farms, one way another gets exposed to the river. The Values were compared with World Health Organization (WHO), Nigerian Standard for Drinking Water Quality (NSDWQ), and the Irish Environmental Protection Agency (IEPA). PAHs are of major concern in drinking water as they pose serious health problems including mutagenic, toxic, and carcinogenic effects among others (23).

4. CONCLUSION

From the analysis of the samples for physicochemical parameters and polycyclic aromatic hydrocarbons (PAHs), it was evident that the activities of the oil depot cum tank farm were wreaking havoc in the environment. The 16 priority PAHs appeared in all the water samples analyzed though some in very small quantities (i.e the high molecular weight) while others in large quantities (the low molecular weight). The level of PAHs in the river water of this environment points to the activities of the tank farms and suggests that petrol and oil deposits find themselves either through percolation, soil runoffs or erosion into the rivers in Ijegun community of Lagos State Nigeria.

It is essential that the Lagos state government through its water corporation should extend its services to the Ijegun community and provide potable water for the community. The Lagos Waste Management Agency (LAWMA) should ensure proper and subsequent cleaning of the environment to eliminate dirt from the surroundings and clean the stagnant gutters which have turned into a breeding ground for mosquitoes thereby helping to curb the highly increases rate of malaria infection. The Lagos State Environmental Protection Agency (LASEPA) should increase its monitoring activities and testing to check and balance the activities of the oil deportation and make sure all guidelines are strictly followed. They should also trace where the leakages are (if any), to know how these pollutants are getting to contaminate the waters. LASEPA in collaboration with the state government, should take it upon themselves to create awareness and educate the people about the hazards in the area and how they can protect themselves from them. Moreover, truck stations should be built outside the community so that trucks can stay and come into the tank farm only when called upon to avoid heavy traffic on the already dilapidated road network. Also, the monitoring of levels of individual indicator PAHs (including FA and BaP) and not just total PAHs in drinking water should continue with the objective of detecting the major source(s) and levels of contamination in the area. Following the high level of PAHs observed in rivers around Ijegun community, residents are advised to avoid the use of water from rivers in the Ijegun community.

COMPETING INTERESTS

The corresponding author states that there is no conflict of interest.

AUTHORS' CONTRIBUTIONS

Oluwakemi Tovide and Obaro Bernard Eterigho contributed to the study's conception and design. Obaro Bernard Eterigho performed experiments and Sanjo Peter Adewale was responsible for data analysis. The

first draft of the manuscript was written by Obaro Bernard Eterigho and revised by Oluwakemi Tovide and Peter Sanjo Adewale. All authors read and approved the manuscript.

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