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Impact Assessment of Petrol Filling Stations on Groundwater Quality in Akure Metropolis, Ondo State

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Abstract: The presence of PFSs in urban areas has increased significantly, leading to conflicts with existing land use planning and violations of the minimum environmental safety requirements set by the Department of Petroleum Resources (DPR) and have adverse social and environmental impacts despite their socioeconomic importance. This paper aims to investigate the spatial distribution of petrol filling stations and their impact on groundwater quality in Akure Metropolis of Ondo State. A total of 147 PFSs and 140 water wells were identified and recorded. Laboratory analysis was done purposefully on wells near PFSs that were both 26 years or older and still functional, as older underground storage tanks (USTs) pose a potential threat to groundwater safety. Findings revealed 119 functional filling stations, 28% located within residential area and 68% domiciled in commercial areas, 2% in outskirts of town and 1% in standalone environment. Findings showed all mapped filling stations were found to be within 50m from built up (residential) area, 104 mapped stations within residential and commercial areas violate the DPR standard. Using spatial analysis, it was also found that 116 of the 147 (78.9%) mapped filling stations were within 400m away from the next. 108 of the 147 (73.47%) mapped PFSs violated the standard of distance not less than 15meters from the edge of the road to the nearest pump. The findings also showed that groundwater system is contaminated by PAHs, which comprises; naphthalene.F, pyrene and acenaphthylene.F. Low mean concentrations of PAHs recorded in this study suggest that there is no major compromise in the quality of groundwater due to the operation of PFSs in Akure metropolis Hand-dug Wells in the study area. It is recommended that spatial compliance for siting PFSs should be strictly adhered to in order to avoid disaster that may occur due to the hazard they pose

Keywords: Groundwater; Health Impact; Polycyclic aromatic hydrocarbons; Seasonal variation; Water quality

I. INTRODUCTION

Nigeria, an oil-rich country, is continually facing social and environmental impacts associated with the storage, transportation and retailing of refined petroleum products [1, 2, 3], namely diesel oil, gasoline and kerosene. The downstream sector of her oil and gas industry teems with an overwhelming number of petrol filling stations (PFSs) mostly around residential areas [2, 4]. This phenomenon is a result of the rapid urban development and increased usage of automobiles, generator sets, and agricultural machineries. It is further exacerbated by the pathetic situation of power supply in the country, raising the demand for petroleum products as fuels for powering households. The presence of PFSs in urban areas has increased significantly, leading to conflicts with existing land use planning [3] and violations of the minimum environmental safety requirements set by the Department of Petroleum Resources (DPR) [5, 6, 7]. Among the social issues surrounding the concentration of PFSs in an area are traffic congestion, accidents and risk of fire outbreak [6, 8].

Several studies have explored the question of the spatial conformity of PFSs to standards set by regulatory bodies, such as DPR in Nigeria, in attempts to ascertain the level of compliance and conjecture the degree of hazards they pose on the population and the environment [3, 4, 5, 9]. Others have identified and investigated the environmental effects of the operation of PFSs through sampling of environmental media (air, soil, and water) [10, 11, 12, 13]. Hydrocarbon pollutants in a PFS come from a number of different places, including the storage tank's vent pipe, the vehicle's tank during refueling, leaking dispensing hoses, liquid spills during refueling, and vapour emissions from the evaporation of spilled fuel [14], operational errors, pipe failure, tank leakages, improper installations, overfills, loose fittings, corroded underground storage tanks (USTs), etc. [13, 15]. Corroded/leaking USTs stand out as a significant source by which groundwater can be polluted [13, 16].

Groundwater is the most widely valuable natural resource in the world. It is commonly found below the Earth's surface, typically at depths less than 750 metres [17]. Past research has investigated the groundwater quality near PFSs, specifically focusing on physico-chemical properties and heavy metals [13, 18, 19]. Studies have examined the levels and potential harmful effects of polycyclic aromatic hydrocarbons (PAHs) in soils and groundwater near chemical waste generating industrial layouts, such as PFSs. These investigations have been conducted by researchers including [20], [21], [22], [23] and [24]. Polycyclic aromatic hydrocarbons (PAHs) are a class of contaminants characterized by their elevated melting and boiling points, minimal vapour pressure, and limited solubility in water. PAHs, or polycyclic aromatic hydrocarbons, are persistent organic pollutants that are frequently found in the environment. They are recognized as one of the most challenging organic contaminants to remediate [25]. Some PAHs are carcinogenic, while others are mutagenic to mammals, according to studies conducted by the [26], [27] and [28]. The present study seeks to investigate the quality of groundwater in the vicinity of PFSs (with PAHs as contaminants of interest) and determine the role of spatial conformity and other geological and hydrogeological factors in the protection of groundwater resource.

Petrol stations serve as important socioeconomic hubs. Despite their significance in meeting our daily energy needs, they have adverse social and environmental impacts. Previous research has placed less importance on quantifying the levels of hydrocarbon contaminants in groundwater caused by the operations of filling stations. Previous studies have primarily focused on the geographical distribution of filling stations in relation to compliance with DPR criteria. However, there has been limited attention given to assessing the levels of hydrocarbon contaminants in groundwater resulting from the activities of these filling stations [4, 5, 13]. Additional studies by [3], [5], [29] have also been conducted in this area. The study area lacks a comprehensive spatial data repository that considers parameters such as the year of operation, functionality status, number of underground storage tanks, and type and volumes of stored products. This study aims to address the existing knowledge gap by expanding the geographical scope and using a more comprehensive data collection method. The objective is to determine if there is a spatial relationship between the age of underground storage tanks (UST) and the contamination levels of PAHs in water samples from nearby hand-dug wells.

The aim of this study is to investigate the spatial distribution of petrol filling stations and their impact on groundwater quality in Akure Metropolis of Ondo State. Also, the study tends to identify location of filling stations and wells within the study area and assess compliance to National standard and analyse the physico-chemical properties and polycyclic aromatic hydrocarbon constituent of water samples from selected wells in the study area.

II. STUDY AREA

The study area, Akure Metropolis, lies within latitudes $07^{\circ} 7'$ and $07^{\circ} 19' N$ and longitudes $005^{\circ} 6'$ and $005^{\circ} 20' E$ (Figure 1.1). The landmass extends over an area of 331 square kilometres and has an elevation of around 250 metres above sea level. The highest altitude is about 430m. It shares a border with Akure North Local Government Area to the north-east, Ifedore Local Government Area to the northwest, and Idanre Local Government Area in the south

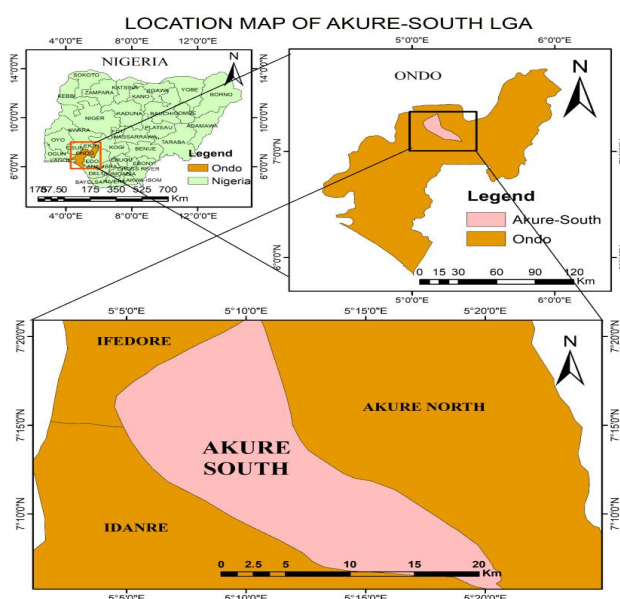


Fig 1 Location map of Akure-South L.G.A

III. LITERATURE REVIEW

A. *The Distribution of Petrol Filling Stations in Nigeria*

The high demand for petrol, diesel and other petroleum products has led to an explosion in the number of fuel stations in Nigeria. These products are primarily sold at stations located near residential areas. Petrol, diesel, and kerosene are essential products for various daily activities. Petrol and diesel are commonly used as fuels in automobiles and machines, as well as for electricity generation in businesses. Kerosene is primarily used as a cooking fuel [9]. Consequently, substantial growth has been observed in the number of filling stations located in close proximity to consumers throughout the country. These stations typically have a maximum of three underground storage tanks (USTs) per station, which are used to store petroleum products such as petrol, diesel and kerosene. According to the Petroleum Product Pricing Regulatory Agency (PPPRA) in 2016, there were 31,220 operational stations with a total estimated storage capacity of 4,800,470,724 Litres for petroleum products. This necessitates the establishment of a more rigorous regulatory body with a primary focus on monitoring underground storage tanks (USTs), preventing leaks, conducting routine inspections, and facilitating prompt cleanup efforts. The Department of Petroleum Resources (DPR) is responsible for regulating the downstream oil and gas industry, including the establishment and operations of filling stations. The activities of filling stations have significant environmental impacts, particularly in terms of soil and underground water contamination. These impacts are associated with health problems, environmental damage, and negative social consequences. Multiple causes and sources of groundwater contamination have been identified. One significant hazard is the contamination resulting from leaks in underground fuel storage tanks. This hazard is particularly severe due to the high concentration of toxic substances with mutagenic and carcinogenic properties in the fuels. Additionally, the increased probability of soil movement and the probable delay in finding a leak can increase the danger. Over time, tanks may experience leakage caused by corrosion, cracks, defective piping, and spills during refilling and maintenance procedures. Leaking underground storage tanks, such as those containing petroleum and other fuels, can result in pollution that seeps into the surrounding soil and groundwater. This pollution has the potential to contaminate nearby water bodies and ecological systems [15].

B. *DPR Procedure Guide for the Issuance of License, Establishment and/or Operations of Petrol Stations*

A range of requirements are stipulated in the act establishing the Department of Petroleum Resources to guide the licensing of petroleum products retail outlets (PFSs). However, for the purpose of this study, partly the assessment of spatial conformity of existing PFSs, four of those guidelines will be considered basically because these four are measurable using geospatial techniques/technology. They are:

- 1) A petrol station should be sited 400 meters away from the next petrol station.
- 2) A petrol station should be located at a minimum distance of 50 metres from every direction of built-up areas.
- 3) The closest pump should be not be less than 15 metres from the road's edge.
- 4) Petrol stations should be situated at a minimum distance of 100 metres from public and semi-public buildings.

The focus of the regulations for filling stations has been on their locational compliance to the standards mentioned above; however, the integrity of underground storage tanks (USTs) used in filling stations poses a significant risk to the safety of groundwater resources. According to [30], an Underground Storage Tank (UST) is a tank and its associated underground piping that has a minimum of 10 percent of its total volume located underground. USTs are used as the major storage facilities for these petroleum products in the filling stations, and reports showed that leaking tanks from these stations are possible sources of release for pollutant like benzene, toluene, ethylbenzene, BTEX, PAHs and other toxic substances into the environment [31].

C. *Water Quality Problems in Nigeria*

It can be dangerous for people to drink or bathe in water that has been contaminated with organic and inorganic chemicals, radionuclides or microorganisms. There have been several cases of contamination and pollution caused by petroleum hydrocarbons that have not been properly recorded over the years [32]. In big cities that use a lot of petroleum products, data on how much petroleum hydrocarbons have made their way into the surface and groundwater are not available. Trying to do research like this takes a lot of time and money, so it could be years before we know how much petroleum hydrocarbons are in our drinking waters and how they affect our health. It would not be worthwhile to attempt a regional estimate of petroleum hydrocarbon contamination, and the information needed to predict how petroleum hydrocarbons will affect controlled water sources in the future isn't easy to find, so it's not worth it.

D. Occurrence of Polycyclic Aromatic Hydrocarbons in Nigeria's Water Resources

Petroleum pollutants in tropical regions, such as Nigeria, comprise intricate combinations of aliphatic and aromatic hydrocarbons [33, 34]. Polycyclic aromatic hydrocarbon (PAH) contamination of water sources is a problem in oil-producing areas in the Niger Delta because of the existence, processing, and usage of fossil fuels and their byproducts.

Nine key polycyclic aromatic hydrocarbons (PAHs) were detected in water samples taken from the Ubeji River in Warri, Delta State, Nigeria, by [35]. According to the results, PAHs with lower molecular weights predominated. Naphthalene was found to have the greatest concentration of the detected polycyclic aromatic hydrocarbons (PAHs), with an average concentration of 34 ng/ml. High molecular weight PAHs were confirmed to be present in samples of three coastal waters collected from oil-producing regions of Nigeria by [36].

At most, eleven different polycyclic aromatic hydrocarbons (PAHs) were identified in the water of Woji Creeks, as reported by [37]. Over the course of three months, the PAH concentrations in the water samples ranged from 6.029 to 29.257 ppm, whereas the sediment samples ranged from 1809.08 to 1809.08 ppm. According to [38], [39], and [40], petrogenic and pyrogenic processes are the most common PAH producers in oil-rich locations.

The presence of polycyclic aromatic hydrocarbons (PAHs) has been confirmed in the waters of non-oil producing communities in Nigeria, in addition to oil producing communities. [41] investigated the presence of polycyclic aromatic hydrocarbons (PAHs) in groundwater in the rural Ife-North Local Government Area of Osun State, Nigeria. The researchers found that light PAHs were the most prevalent, and their concentrations exceeded the World Health Organization's recommended limit of 10 µg/L during both dry and wet seasons.

According to a study conducted by [42], the consumption of water in the Atlas Cove area of Lagos State was found to have carcinogenic risks that exceeded the acceptable limit set by the USEPA. Lighter PAHs were found to be more prevalent in the water samples, with values ranging from 46 to 507 µg/L. [43] conducted a study on the water of Egbe Dam in Ekiti State, Nigeria, and found carcinogenic polycyclic aromatic hydrocarbons (PAHs). [44] analysed water samples from the Rivers Niger and Benue in Nigeria's North Central region and detected many polycyclic aromatic hydrocarbons (PAHs), including the recognised carcinogen Benzo[a]pyrene. There is concern for human and animal health due to the quantities of benzo[a]pyrene found.

PAHs can be found in non-oil producing areas due to various sources such as agricultural bush burning, open burning waste disposal, the use of herbicides, pesticides, and fertilisers in agriculture, industrial production methods, transportation networks, vehicle repair facilities and petrol filling stations. Atmospheric deposition, surface water run-off, and groundwater leaching are all pathways via which PAHs can reach aquatic systems. Volatile organic chemicals (VOCs) like benzene, toluene, ethylbenzene, and xylenes (BTEX) are frequently detected alongside polycyclic aromatic hydrocarbons (PAHs) [45, 46]. BTEX compounds are commonly detected in water sources due to the extensive use of petroleum hydrocarbons, which have a relatively high solubility in water (130 – 1780 mg/L at 20°C) [45]. However, it should be noted that BTEX can be present in sources other than groundwater. Two- to five-ringed aromatic polycyclic hydrocarbons (PAHs) are of particular significance to [47]. Because of their lipophilic characteristics and electrochemical stability, these PAHs can linger in the environment for a long time, which is cause for concern. There is evidence that PAHs can remain in soils for long periods of time [48], and some PAHs have been identified as carcinogens, mutagens, or teratogens.

E. Human Toxicology and Exposure to PAHs in Nigeria

The presence of PAHs in human body has been confirmed. Numerous studies have linked polycyclic aromatic hydrocarbons (PAHs) to a wide range of diseases and health problems.

However, there is a scarcity of such studies conducted in Nigeria. [42] investigated the effects of drinking water containing polycyclic aromatic hydrocarbons (PAHs) on the health of both children and adults. The researchers specifically investigated the effects of ingestion and skin contact on health outcomes. The US Environmental Protection Agency reported that the carcinogenic hazards for this group, especially for children, were higher than what was deemed acceptable. This implies a potential risk of cancer development in children through ingestion. [49] conducted a study on 36 children in Imo State, Nigeria. Elevated levels of carcinogenic PAHs were detected in their blood and urine. In their study, [50] identified 14 different types of PAHs in the blood samples of individuals with neurological conditions. The blood plasma contained pyrene in the range of 2.96-236.86 ng/ml, fluoranthene in the range of 1.96-11.55 ng/ml, and acenaphthene in the range of 11.08-1.81 ng/ml. The significance of the results was attributed to the patient's medical condition.

IV. EMPIRICAL REVIEW

[51] identified some of the sources of possible release of pollutants from underground storage tanks (USTs) into the environment. They include operational errors, pipes failure, tank leakages, improper installations, overfills, loose fittings, corroded USTs etc. [13] noted that corroded USTs stands out as a major source in Nigeria because of the failure of regulatory agencies in monitoring activities of vendors and enforcement of periodic assessment of the integrity of underground filling stations tanks. The present study is a step in the right direction in creating awareness of the probable environment damage the phenomenon of USTs leakage is causing.

[52] looked at water samples from four wells that were dug by hand and one that was a control. The water was analysed for its microbiological, chemical, and physical characteristics. Each of these parameters, as well as total dissolved solids, chloride concentration, and calcium hardness, are reported in milligrammes per millilitre (mg/L). They used standard analytical procedures to figure out the values in mg/L for each one. According to the WHO, USEPA, and the Nigerian Industrial Standard, the average physicochemical properties of all of the wells were in line with the maximum permissible limits (MPLs) set by these three groups. Wells near filling stations had different levels of contamination, but the control well didn't have as much contamination compared to those near filling stations. The study is very detailed in the number of factors that were looked at, but there isn't a spatial component that can help us figure out how to keep contamination at bay.

Water samples were collected from hand-dug wells near gas stations in three different LGAs of Ilorin metropolis and analysed for their physicochemical and heavy metal contents in a study by [13]. Standard methods were employed for the analysis. The analysis revealed anomalies in the concentration of several parameters, including Turbidity, Conductivity, total dissolved solids, Total Hardness, Lead, Cadmium, Chromium, and Nickel. These results point to the filling stations in the vicinity as a possible source of groundwater contamination. This study is robust in the number of physico-chemical parameters under consideration, but did not include contamination by organics which may have resulted from leaking of USTs. The present study seeks to incorporate this component and also analyze the spatial attributes of the phenomenon of environmental effect of irresponsible operation of petrol/diesel filling stations.

[5] assessed the spatial distribution of fuel filling stations in Akure metropolis; they wanted to see how well they met planning standards set by the Department of Petroleum Resources. They used simple GIS operations like query, buffering, and Z-ratio analysis to look at how far the petrol filling stations were from each other and from the road, and how close they were to each other and to the road. Most of the filling stations that they looked at were at least 400 meters apart, and 95.5 percent were at least 100 meters away from a school and 100% were at least 100 meters away from a health care facility. The spatial pattern of these analyzed data showed a tendency toward a clustering pattern. This study is useful in its consideration of a spatial perspective in analyzing the siting of filling station in accordance to set regulations.

[53] carried out a geospatial analysis and assessment of the distribution of 168 petrol filling stations in Uyo for compliance to development regulations laid out by DPR. The studied employed field mapping and spatial statistics (Nearest Neighbor Analysis) in ArcGIS environment to uncover the spatial pattern of the distribution. The analysis resulted in a clustered pattern of filling station distribution in Uyo. Also, only 5 out of 168 petrol stations complied with all the development standards namely: distance from edge of road to nearest pump; distances from Residential Buildings/Areas; distance between a Petrol Station and the one nearest to it (400m); distance of Petrol Stations from Public Buildings (100m). The study revealed the high level of incompliance with set regulations. The geospatial method employed for this study is useful in analyzing the spatial dependence of the potential hazard of indiscriminate siting of petrol filling stations in urban centers.

In their study, [9] employed GIS technology to analyse the attributes of fuel filling stations within the Ilorin metropolitan area. A study found that 112 out of the 297 retail petrol stations in Ilorin, representing 38 percent, were more than 15 years old. Additionally, 224 petrol stations, accounting for 75 percent, were operational during the research period, while 73 petrol stations, or 25 percent, were either abandoned or under construction. Interestingly, most stations were situated in close proximity to public amenities. Specifically, 10 stations (3%) were located near schools, 226 stations (76%) were near stores, 192 stations (65%) were near residential areas, and 11 stations (4%) were near hospitals. This study utilized the spatial analytical capabilities of GIS to determine the amount of hazard to the public as a result of filling station non-compliance with guidelines.

[3] investigated the location and impact of petrol stations on people's perceptions of environmental health in Ede, Osun state, Nigeria. This study examined the spatial distribution of PFSs in the historic Nigerian city of Ede, and also assessed the public's perception of the health and environmental impacts associated with PFSs. The data collection method employed in this study was a cross-sectional survey utilising a basic random sampling technique. A standardised questionnaire was used to survey the residents.

The PFS coordinates were acquired through GPS, and the distances between the PFSs and residential land use were measured using a speedometer. In total, 15 PFSs were located and sampled throughout the city. The information was gathered via a questionnaire distributed to PFSs' management. In addition, inhabitants of villages surrounding the PFSs were randomly given one of 150 pretested structured questions. Using descriptive statistics (frequency and percentages), they surveyed locals to learn what they think about the negative effects of PFSs on the environment and human health. The spatial distribution of PFSs was assessed using ARCGIS 10.2 and Nearest Neighbour Analysis. The public had a limited understanding of the impacts of the PFS. The PFSs exhibited a linear concentration pattern along the main routes of the town, as indicated by a closest neighbour index of 0.71. The majority of PFSs did not meet the specified planning criteria. Promoting public participation in awareness campaigns and implementing stricter enforcement of planning regulations in existing Planned Food Service Facilities (PFSs) and other land uses can effectively address concerns related to negative perceptions and non-adherence to planning standards.

V. METHODOLOGY

A. Data Preparation

Data on the location of PFSs and water wells were collected during field surveys with the aid of a handheld GPS. A total of 147 filling stations and 140 water wells were mapped in study area, and prepared as an excel spreadsheet. The water wells were sampled for the purpose of laboratory analysis. The sampling of the groundwater from wells was purposively done to be from around the mapped PFSs which met the age criterion of PFSs that are 26 years and older and functionality criterion of being functional. The age criterion limited the scope of the sampling since PFSs with UST that are older than the 26-30 year usable life span represent a threat to groundwater safety (<https://epa.gov/ust/>). The database of mapped PFSs was queried by selecting stations with an age attribute (≥ 26 years) in order to achieve this. Fourteen wells located near PFSs that met the specified criteria were sampled for laboratory analysis of Polycyclic Aromatic Hydrocarbons (PAHs). The selection of wells did not take into account any specific distance from the filling station. The closest well meeting the criteria was selected for each filling station. The distances to the filling stations of all the selected wells were recorded. [13] and [54] have both utilised this sampling method. In addition, three wells located outside of the initially sampled locations were selected as control sites. These control sites were chosen from three distinct clusters of the PFSs in the study area. The Google Earth image was downloaded to use as a base map for the research. The road system was digitalized from a Google Earth image. USGS Earth Explorer (earthexplorer.usgs.gov) provided the SRTM data used to create the DEM for the research area.

B. Locational Compliance

The prepared data sheet of the locations and attributes of PFSs was imported into ArcGIS to be displayed in X and Y coordinates. Sentinel-2 data of the study area was utilized to generate a color infra-red raster through band combination (8 4 3). Supervised image classification of the color infra-red raster was done with the aid of the Google Earth image of the area to classify it into different land use types. The classified image (raster) was then converted to vector for the purpose of spatial analysis. To assess the spatial conformity of mapped PFSs to DPR standards, we initially analysed the distance to residential area standard. This involved using the selection by location method to identify PFSs located within a 50m radius of residential areas. The PFSs point layer and the raster to vector layer of the land use land cover image were employed for this purpose. The second standard examined is the proximity of the nearest filling station pump to the road. The PFSs were selected based on the attribute of the nearest pump's distance to the road being less than 15m. The third standard requires a minimum separation distance of 400m between each PFS. The ArcGIS query function was employed to identify PFSs that were within a 400m proximity of another PFS.

C. Physico-Chemical Properties And Polycyclic Aromatic Hydrocarbon Constituent Of Water Samples

On-site, at the time of sample collection, a portable water testing instrument measured the PH and temperature of the water samples. The presence of petroleum hydrocarbons, in particular PAHs, in the medium was investigated by collecting water samples from a total of 17 wells. Within 48 hours of collection, the water samples were sent to Sustainable Laboratory Services Limited for chemical analysis in sterile glass bottles containing 1 litres of water and preserved with a drop of Hydrochloric acid. The chemical purity of the water samples was not compromised in any way, and every effort was made to assure this. The water samples were examined using the standard laboratory process outlined in EPA 5030C, which includes the steps listed below.

The procedure began with organic extraction, moved on to cleaning, and culminated in a Gas Chromatography test, where the fume ionisation detector examined the likely pollutants. The water samples underwent organic extraction and cleaning procedures prior to analytical evaluation.

To get a high rate of analyte recovery, we used a liquid-liquid extraction (LLE) procedure with several extractions of the sample using an organic solvent and a separating funnel. The extraction procedure is as follows:

- 1) 50 ml of water sample was measured using graduated measuring cylinder into separating funnel graduated with 250 ml;
- 2) 50 ml of organic solvent Dichloromethane (DCM) was measured and added into the funnel to make a 1:1 ratio of water and solvent;
- 3) The sample mixture was then thoroughly shaken using electronic shaker for one hour;
- 4) The separating funnel was then erected and allowed to stand with the aid of the retort and stand for 10-15 minutes until there is a clear demarcation (a thin layer) between the water and the solvent;
- 5) The solvent on top was thereafter decanted into pre-weighed beaker and passed through rotary evaporator until the volume was concentrated into very low volume.
- 6) Steps 1-5 were repeated for the other water samples that were labelled accordingly.

The clean-up procedure followed for the extracted samples is as follows:

- a) A glass wool of about 5 ml was inserted into a graduated packing column syringe with the aid of a glass rod;
- b) 5 g of silica gel of 200-400 mesh size was weighed and added to the packing;
- c) Another 3 g of Sodium Sulphate anhydrous was weighed and also added into the packing column;
- d) The column was then erected on a retort and stand setup;
- e) 200 ml of N-hexane was measured and added to the column in order to activate the column as well as determine the rate of drop;
- f) The solvent N-hexane was collected with a fresh beaker and discarded;
- g) 10 ml iso-octane was pour into the beaker containing the dried sample to reconstitute the dry extracted samples;
- h) The dissolved/reconstituted sample was poured into the packing column and collected in a pre-weighed clean beaker;
- i) 50 ml of DCM was added into the column to make sure all the samples in the column are fully eluted;
- j) The collected sample from the column is then dried in a rotary evaporator to concentrate its volume into little volume;
- k) The concentrated sample was then transferred into a 2 ml graduated Gas Chromatography (GC) vial bottle for gas chromatography test.

The samples contained in vials were thereafter introduced into a gas chromatograph and subjected to analysis in order to detect and quantify Polycyclic Aromatic Hydrocarbons (PAHs). This analysis was performed using a flame ionisation detector (GC-FID), which is commonly favoured due to its advantageous sensitivity and specificity towards hydrocarbon compounds. The identification of analytes was accomplished through the comparison of the retention time of each individual chemical with that of a reference standard. Subsequently, calibration standards were employed to generate calibration curves, which were utilised for the quantification of the compounds of interest. The concentrations of the different polycyclic aromatic hydrocarbons (PAHs) were determined by analysing the data obtained from the gas chromatography (GC) output. The groundwater samples were subsequently assessed for the levels of PAHs and compared against the maximum allowable limits established by the World Health Organisation (WHO) and the Nigeria Standard for Drinking Water Quality (NSDWQ). This analysis aimed to ascertain whether the groundwater exhibited signs of pollution.

VI. RESULT

A. Spatial Distribution and Compliance Analysis

Analysis of the data gathered from field survey revealed that of the 119 functional filling stations (Table 1, Figure 1), 28% were located within residential area and 68% were domiciled in commercial areas, 2% in outskirts of town and 1% in standalone environment (Figure 2). All of the mapped filling stations were found to be within 50m from built up (residential) area. According to the DPR standard which stipulates that the nearest pump of a filling station should be up to 15m from the road, 104 mapped stations within residential and commercial areas were found to violate this set standard (Figure 3). Figure 4 and Figure 5 represents the count and percentages of filling stations that are 26 years and older within residential and commercial areas. Using spatial analysis, it was also found that 116 of the 147 (78.9%) mapped filling stations were within 400m away from the next (Fig 5). 108 of the 147 (73.47%) mapped PFSs violated the standard of distance not less than 15meters from the edge of the road to the nearest pump (Fig. 5). The result of the locational compliance analysis using the spatial analyst extension of ArcGIS with reference to DPR standards is presented in Figure 5. It is a superimposition map of the parameters of the standards analyzed. Analysis of the data gathered from field survey revealed that of the 147 Petrol filling stations, 57% has four (4) underground storage tanks (USTs), 18% have 5 USTs, 9% have 6 USTs, 5% have 3 USTs, 3% have dismantled USTs, 1% have 0 USTs, and those with 2 USTs accounts for 4% (Figure 6).

Table 1. Descriptive Summary of PFSs by Count

YEARS OF OPERATION	(All)
DISTANCE OF THE NEAREST PUMP TO ROAD	(All)
Description of PFSs	Count of PFSs
COMMERCIAL	101
FUNCTIONAL	81
NON-FUNCTIONAL	20
OUTSKIRTS OF TOWN	4
FUNCTIONAL	2
NON-FUNCTIONAL	2
RESIDENTIAL	40
FUNCTIONAL	34
NON-FUNCTIONAL	6
STANDALONE	2
FUNCTIONAL	2
Grand Total	147

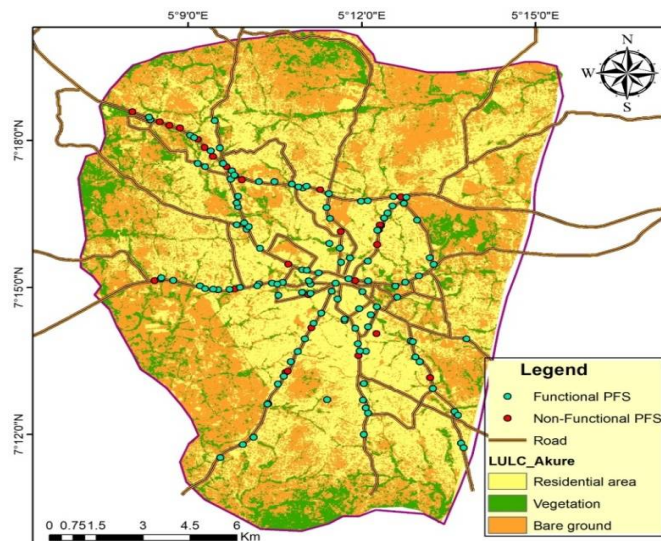


Fig.1 Land Use Land Cover Map of the Study Area with displayed locations of Mapped Petrol Filling Stations.

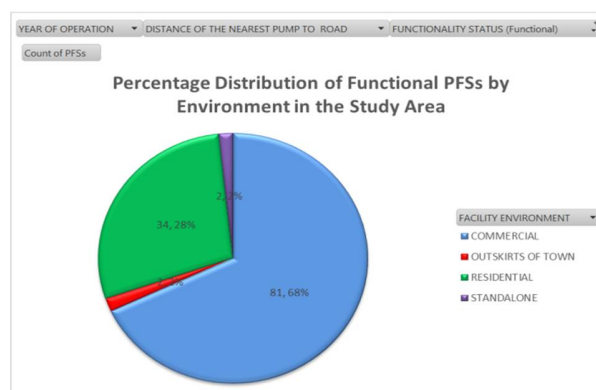


Fig. 2 Distribution of Petrol Filling Stations by Environment of Location.

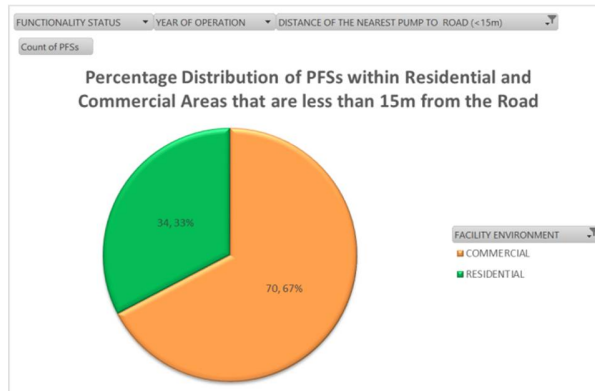


Fig. 3 Distribution of Petrol Filling Stations with Residential and Commercial Areas that are less than 15m from the Road.

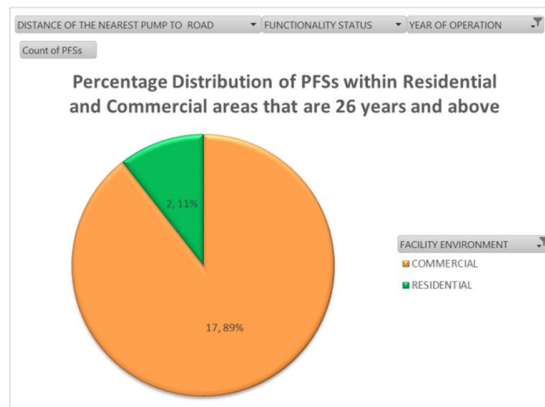


Fig. 4 Distribution of Filling Stations within Residential and Commercial Areas that are 26 years and older.

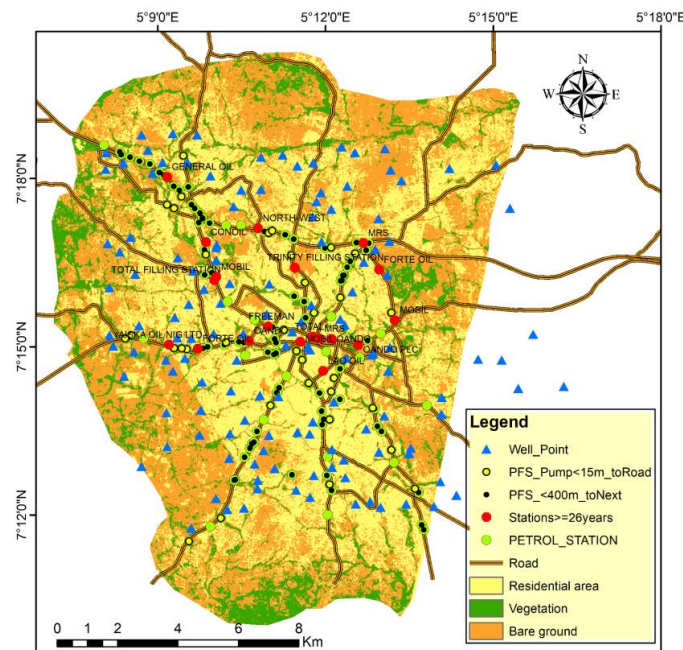


Fig. 5 Land use land cover map and locational compliance of petrol filling stations in Akure metropolis.

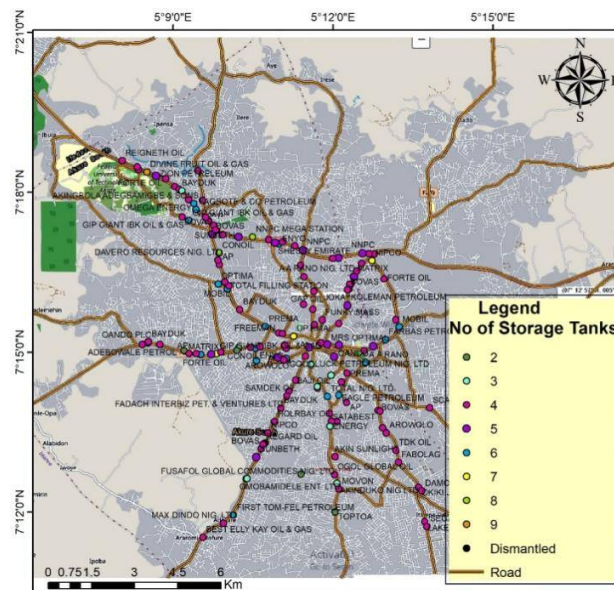


Fig. 6 Distributions of Underground Storage Tanks in the PFS

B. Data Analysis of Water Samples

The results of physico-chemical and organo-chemical analyses of water samples from selected hand-dug wells are presented in Table 2. Identification of PAHs compounds on chromatograms was done by comparing the retention time of an individual PAH to that of a reference standard.

1) Electrochemical Conductivity, Total Dissolved Solutes and Temperature of Water Samples from Selected Hand-dug Wells in the study area

The measurement of electrochemical conductivity, total dissolved solutes and temperature of water samples from selected hand-dug wells are shown on Table 2. The range of value of electrochemical conductivity (EC) of water samples from selected hand-dug wells in various selected sample sites ranged from 86 $\mu\text{S}/\text{cm}$ to 133 $\mu\text{S}/\text{cm}$, the value for total dissolved solutes (TDS) ranged from 43 mg/L to 67 mg/L and the temperature values from 24.57°C to 27.56°C. The maximum value of electrochemical conductivity and total dissolved solutes of water samples from selected hand-dug wells was obtained in the water sample from Sample10, followed by the water sample obtained from Sample4, while the minimum value for electrochemical conductivity and total dissolved solutes of water was obtained in the water sample from Sample6. Meanwhile, the electrochemical conductivity and total dissolved solutes of water samples obtained from Sample12 and Sample13 were the same. There was small variation (CV%=5.80) in the temperature of the water samples from selected hand-dug wells.

Table 2. Electrochemical Conductivity, Total Dissolved Solutes and Temperature of water samples from selected hand-dug wells in the study area

Petrol Station in Akure South-I	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	Temp (°C)
Sample1	119.00 ^g	59.00 ^g	26.14 ^l
Sample2	126.00 ^d	63.00 ^d	25.96 ^o
Sample3	99.00 ^l	50.00 ^k	25.90 ^p
Sample4	132.00 ^b	66.00 ^b	26.32 ^h
Sample5	102.00 ^j	51.00 ^j	26.30 ⁱ
Sample6	86.00 ^p	43.00 ^o	26.16 ^k
Sample7	115.00 ^h	58.00 ^h	25.85 ^q
Sample8	96.00 ^m	49.00 ^l	26.41 ^f

Sample9	89.00 ^o	45.00 ⁿ	26.17 ^j
Sample10	133.00 ^a	67.00 ^a	26.72 ^d
Sample11	129.00 ^c	64.00 ^c	26.10 ^m
Sample12	111.00 ⁱ	56.00 ⁱ	26.65 ^e
Sample13	111.00 ⁱ	56.00 ⁱ	27.56 ^a
Sample14	124.00 ^e	62.00 ^e	27.10 ^c
Control1	120.00 ^f	60.00 ^f	27.11 ^b
Control2	101.00 ^k	51.00 ^j	25.97 ⁿ
Control3	95.00 ⁿ	48.00 ^m	26.37 ^g
SE±	15.01	7.33	0.47
CV	0.00	1.47	5.80

Letters in superscript indicate order of increase of the values. CV= Coefficient of Variance

2) P^H and Dissolved Oxygen of Water Samples from Selected Hand-dug Wells in the study area

Figure 7 shows the pH and dissolved oxygen of water samples from selected hand-dug wells in the study area. The pH value for water samples from selected hand-dug wells ranged from 6.1 to 7.21, and dissolved oxygen in water samples from selected hand-dug wells ranged from 5.84 to 7.33 mg/L. The highest pH was obtained from water sample from Sample13, followed by those obtained from Control2 while the lowest pH was obtained from water sample from Sample12. The results from the analysis revealed that the pH value of the water sample obtained from Control1 and Sample2 were the same (6.48). The pH value of the water sample obtained from Control2, Sample6 and Sample13 was significantly different ($p \leq 0.05$) from those obtained from other filling stations. There was no significant difference ($p \leq 0.05$) in the pH value of the water sample obtained from Control3, Sample1, Sample2, Sample3, Sample4, Sample5, Sample7, Sample8, Sample9, Sample10, Sample11, Sample12 and Sample14 (Figure 4.10).

The dissolved oxygen of water samples from selected hand-dug wells was highest in the water samples obtained from Sample10, followed by those obtained from Sample6, and lowest in those obtained from Sample4. Dissolved oxygen of water samples from obtained from Sample12 and Sample13 were the same (6.56). There was no significant difference in the dissolved oxygen of water samples obtained from Sample6, Sample9, Sample10 and Sample11. Also, there was no significant difference in the dissolved oxygen of water samples obtained from Sample2, Sample4 and Sample8 (Figure 7).

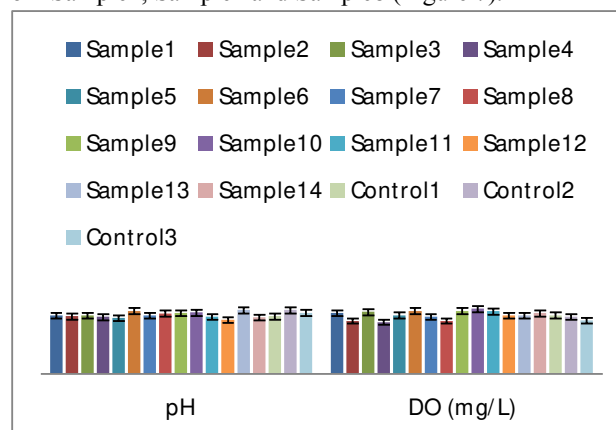


Fig.7 P^H and Dissolved Oxygen of water samples from selected hand-dug wells in study area.

3) Polycyclic Aromatic Hydrocarbon Concentrations of Water Samples

The results of the laboratory analysis for PAHs in the sampled wells revealed that three (3) PAH compounds were present namely; naphthalene.F, pyrene and acenaphthylene.F. Acenaphthylene.F was found in sample 5 as a lone contaminant with concentration of 0.0025 ppm (Plate 1), naphthalene.F was found as a lone contaminant in sample 13 with concentration of 0.0026 ppm (Plate 2). In sample 8 and 12, naphthalene.F and pyrene were found with total concentrations of 0.0086 ppm and 0.007 ppm respectively (Plate 3 and 4). There were no PAHs detected in the rest of the samples which suggest that the ratio of contaminated samples to uncontaminated samples is 2:5. The result from control wells show that there is no PAH contamination as no PAH compounds were detected in the water samples.

Lab name: Sustainable Laboratory Services Limited
 Client: Akinyosoye Olufemi
 Client ID: Sample 5
 Collected: 02/02/2023
 Method: Syringe Injection
 Lab ID: SLSL02312AL
 Description: PAH/February08/02/23
 Column: RESTEK 15METER MXT-2887
 Carrier: Nitrogen @ 10 PSI
 Integration: Peak sens=95.0 Base sens=60.0 Min area= 100.00 Standard= 1.000 Sample= 1.000 Tangents=off
 Sample: Sample 5
 Operator: Mr Idowu

Temperature program:

Init temp	Hold	Ramp	Final temp
80.00	5.000	12.000	350.00
350.00	35.000	0.000	350.00

Events:

Time	Event
0.000	ZERO
0.000	SOUND

Retention	Height	Area %	Carrier	Component	Units	External
3.870	5.947	0.9743	Nitrogen@ 10 PSI	acenaphthylene.F	ppm	0.0025
		100.0000				0.0025

Plate 1 Chromatographic result of sample 5 showing constituent PAHs

Lab name: Sustainable Laboratory Services Limited
 Client: Akinyosoye Olufemi
 Client ID: Sample 13
 Collected: 02/02/2023
 Method: Syringe Injection
 Lab ID: SLSL02312AL
 Description: PAH/February08/02/23
 Column: RESTEK 15METER MXT-2887
 Carrier: Nitrogen @ 10 PSI
 Integration: Peak sens=95.0 Base sens=60.0 Min area= 100.00 Standard= 1.000 Sample= 1.000 Tangents=off
 Sample: Sample 13
 Operator: Mr Idowu

Temperature program:

Init temp	Hold	Ramp	Final temp
80.00	5.000	12.000	350.00
350.00	35.000	0.000	350.00

Events:

Time	Event
0.000	ZERO
0.000	SOUND

Retention	Height	Area %	Carrier	Component	Units	External
1.210	7.695	0.9356	Nitrogen@ 10 PSI	Naphthalene.F	ppm	0.0026
		100.0000				0.0026

Plate 2 Chromatographic result of sample 13 showing constituent PAHs

Lab name: Sustainable Laboratory Services Limited
 Client: Valued Customer
 Client ID: Sample 8
 Collected: 02/02/2023
 Method: Syringe Injection
 Lab ID: SLSL02312AL
 Description: PAH/February08/02/23
 Column: RESTEK 15METER MXT-2887
 Carrier: Nitrogen @ 10 PSI
 Integration: Peak sens=95.0 Base sens=60.0 Min area= 100.00 Standard= 1.000 Sample= 1.000 Tangents=off
 Sample: Sample 8
 Operator: Mr Idowu

Temperature program:

Init temp	Hold	Ramp	Final temp
80.00	5.000	12.000	350.00
350.00	35.000	0.000	350.00

Events:

Time	Event
0.000	ZERO
0.000	SOUND

Retention	Height	Area %	Carrier	Component	Units	External
1.210	7.563	0.9396	Nitrogen@ 10 PSI	Naphthalene.F	ppm	0.0047
15.916	5.219	0.5238	Nitrogen@ 10 PSI	Pyrene	ppm	0.0039
		100.0000				0.0086

Plate 3 Chromatographic result of sample 8 showing constituent PAHs

Lab name: Sustainable Laboratory Services Limited
 Client: Akinyosoye Olufemi
 Client ID: Sample 12
 Collected: 02/02/2023
 Method: Syringe Injection
 Lab ID: SLSL02312AL
 Description: PAH/February08/02/23
 Column: RESTEK 15METER MXT-2887
 Carrier: Nitrogen @ 10 PSI
 Integration: Peak sens=95.0 Base sens=60.0 Min area= 100.00 Standard= 1.000 Sample= 1.000 Tangents=off
 Sample: Sample 12
 Operator: Mr Idowu

Temperature program:

Init temp	Hold	Ramp	Final temp
80.00	5.000	12.000	350.00
350.00	35.000	0.000	350.00

Events:

Time	Event
0.000	ZERO
0.000	SOUND

Retention	Height	Area %	Carrier	Component	Units	External
1.210	7.945	0.9569	Nitrogen@ 10 PSI	Naphthalene.F	ppm	0.0049
15.916	5.252	0.5375	Nitrogen@ 10 PSI	Pyrene	ppm	0.0021
		100.0000				0.007

Plate 4 Chromatographic result of sample 12 showing constituent PAHs

VII. DISCUSSION OF FINDINGS

The relatively low mean total PAHs concentrations of 0.026 ppm (or 26 ppb) recorded in the groundwater of the study area suggests that there is minimal introduction of PAH contaminants purportedly originating from the operation of PFSs in the study area. Although PAHs are known to be ubiquitous in nature, the recorded contamination input could be attributed to the non-compliance of the operation of the PFSs to standards, aging of PFSs and the probable loss of integrity of the USTs. There has not been proper monitoring of the operation of PFSs in residential and commercial areas in terms of their potential impact on groundwater which is a major source of municipal potable water. Hence, the possibility of constituent pollutants seeping and subsequently contaminating groundwater aquifer proximal to PFSs sites is not in doubt.

This research was conducted during the dry season, which may have an effect on the results. The lack of permeating rainwater to drain constituent PAH chemicals that are bound to soil may possibly contribute to the comparatively low concentration of PAHs. Also, higher temperatures during the dry season may cause more PAHs, particularly those with a low molecular weight, to evaporate, reducing the concentration of these pollutants. [55] findings provided support for the idea that the dry season when the study was conducted contributed to the low concentration of PAHs. A greater concentration of PAHs was found in groundwater during the wet season compared to the dry season in the study by [55] in the Ife North Local Government Area of Osun State, Nigeria. Since PAHs are lipophilic (soluble in lipids) but not readily soluble in water, the presence of PAHs at elevated concentrations in groundwater indicates an overexposure issue. Differential levels and close-by inputs of contaminants in the wells are mainly responsible for the observed spatial heterogeneity in PAH concentration in the research area. Areas with higher concentrations are likely closer to PFSs with leaking USTs or other undefined means of introduction which could be related to PFS or not. Sample point 8, which had the highest measured concentration of total PAHs is located close to Agbogbo oil station which appear to fall within the lower concentration zone of the PAHs concentration surface created from the populated PAHs concentration data across the study area in Fig. 4.12. The PAHs concentration surface reveals that the areas with the highest concentration are toward the west of the study area around Jipadola Petroleum and OANDO PLC.

Overall, the mean total PAHs levels exceeded the maximum permissible limit of 10 ppb recommended by WHO by only 10 units. This is negligible. This finding demonstrated that the groundwater in this location is still safe to drink because the concentrations are below the action level. The groundwater in the study area can be said to be contaminated but not polluted.

Total PAHs results from this investigation were found to be quite similar to those reported by [56], who analysed groundwater samples from the Okrika mainland and found concentrations ranging from 21.39 to 303.32 ppb. Water samples from the Agbabu bitumen field in Southwest Nigeria were found to have values ranging from 11.2 to 341.5 ppb in [33] study. The results of this investigation were significantly lower than the levels reported for Osogbo and Ile-Ife by [32], which ranged from 100 to 15810 ppb. This study's findings were far lower than the 119,800–450,000 ppb range reported by [57] in their ecotoxicological and epidemiological assessment of human exposure to polycyclic aromatic hydrocarbons in the Niger Delta region of Nigeria. The values of 0.033-0.733 ppb discovered in this study are significantly higher than the values reported by [58] for Tehran, Iran's drinking water. This variation could probably be due to differences in level and duration of exposure and/or differences in ecological area.

VIII. CONCLUSION / RECOMMENDATION

The investigation has found that the groundwater system in the study area is contaminated by PAHs, which comprises; naphthalene.F, pyrene and acenaphthylene.F. The low mean concentrations of PAHs recorded in this study suggest that there is no major compromise in the quality of groundwater due to the operation of PFSs in Akure metropolis.

It is recommended that spatial compliance for siting PFSs should be strictly adhered to in order to avoid disaster that may occur due to the hazard they pose. Although the study concluded based on analysed data that the groundwater is uncompromised, there is the need for further and more comprehensive research into the presence and levels of PAHs in unsampled locations.

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