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PRINCIPAL COMPONENT ANALYSIS OF GROUNDWATER CONTAMINATION AT IWOCHANG COMMUNITY OF AKWA–IBOM STATE, NIGERIA

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Abstract: About 22% of the freshwater on Earth comes from groundwater, making it the greatest source of drinkable water. However, frequent crude oil spills have caused serious petroleum hydrocarbon contamination of groundwater, which is detrimental to the environment and human health. Following an oil spill, this made it necessary to look into the presence, source, and concentration of petroleum hydrocarbons in groundwater in the Iwochang community in Akwa–Ibom State, Nigeria, in order to determine the cause of the pollution and any potential hazards. Soil samples were taken from three locations (L_1, L_2, L_3) and three depths (topsoil, subsoil, and aquifer) and examined petroleum hydrocarbons, such as Naphthalene, Acenaphthene, Fluorene, Pyrene, Anthracene, and Benzo(a)anthracene. Laboratory results found that Naphthalene had the highest concentration in all samples, particularly topsoil, whereas heavier petroleum hydrocarbons such as Pyrene and Anthracene had lower quantities, notably in aquifer samples. The Leach Pollution Index (LPI) ranged from 71,199.20 to 93,374.50, indicating a high level of contamination potential. Statistical analysis using ANOVA revealed significant variation in the concentrations of lighter petroleum hydrocarbon such as Naphthalene (P–value = 0.0006) and Fluorene (P–value = 0.0024) between soil layers, while heavier PAHs such as Pyrene (P–value = 0.9691), Anthracene (P–value = 0.9849), and Benzo(a)anthracene (P–value = 0.3582) showed no significant differences across the samples. Principal component analysis revealed that the source of the contaminants is the oil spill incident at Iwochang community of Akwa–Ibom State, Nigeria. The findings underline the necessity for focused remediation measures to mitigate groundwater contamination from crude–oil spill, while safeguarding public health and environmental quality.
Keywords: Principal component analysis, Contaminants, Groundwater, Crude Oil Spill, Leach Pollution Index

1. INTRODUCTION

Since water is a basic need and the most important resource for all of God's creations to survive, it must be made available as fresh, clean, and pure water in order to keep people alive and healthy when ingested. As a result, the availability of fresh and clean water is becoming increasingly important on a worldwide scale as the population grows (Ijaola, et al 2013; Oyinloye and Jegede, 2004; Sanda et al., 2022; Jackson et al., 2001). The largest supply of potable water is found in groundwater, which is less contaminated than surface water because of natural filtration. About 22% of the world's freshwater resources come from groundwater, which is an essential part of the global water cycle. (World Health Organization, 2018), Its lengthy retention period and aquifers' inherent filtration ability make it a vital source of water for ecosystems, agriculture, industry, and human consumption, promoting economic growth, human health, and environmental sustainability (National Research Council, 2015). However, a number of contaminants, both organic and inorganic, pose a threat to the quality of groundwater. According to Ijaola and Sangodoying (2020), the petroleum and pharmaceutical industries are among the sectors that contribute significantly to organic pollutants due to their ongoing use. The primary sources of pollutants produced by the petroleum industry are its effluents, specifically produced water and crude oil spills (Ijaola and Sangodoying, 2020; 2021). Polycyclic Aromatic Hydrocarbons (PAHs), one of the many organic toxins produced by the crude oil spill, are extremely dangerous to both human health and the environment (Agency for Toxic Substances and Disease Registry, 2019). A class of organic chemicals known as PAHs is created when organic materials including wood, tobacco, and fossil fuels burn incompletely. These molecules are made up of two or more fused aromatic rings (Smith, 2020). (PAHs) are ubiquitous environmental pollutants that pose significant risks to human health and the ecosystem (WHO, 2019; Ijaola and Sangodoying, 2020; 2021). PAHs can contaminate groundwater

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through various pathways, including industrial activities, agricultural runoff, and crude oil spills (Doe & Amadi, 2019). Because of their toxicity, persistence, and ability to cause cancer, PAHs stand out among the many pollutants of concern as being especially harmful (Osuji et al., 2015). They are extremely resistant to natural deterioration and easily accumulate in organisms, endangering aquatic life and possibly making their way into the food chain, which could have an indirect effect on human health (Ogwo et al., 2019; Ijaola and Sangodoying, 2020). They are known to have teratogenic, mutagenic, and carcinogenic properties, which can lead to detrimental health outcomes like cancer, problems with reproduction, and developmental disorders (World Health Organization, 2018, Boonpragob et al., 2019; Ijaola and Sangodoying, 2020). Groundwater pollution by PAHs can result from crude oil spills, which are frequent in oil–producing areas such as Ogbia, Nigeria (Osuji 2015). According to Adeniyi (2018), leached crude oil has the potential to permeate soil and aquifers, releasing PAHs and other harmful substances into groundwater.

Nigeria, with its rich oil reserves, faces severe environmental challenges due to oil spillage (NNPC, 2020). Iwochang in Ibeno LGA is situated in the Niger Delta Area of Nigeria, which has had numerous crude oil spills as a result of oil production and exploration (Nwankwoala et al., 2017). As a result, there is now extensive environmental deterioration and health issues, such as groundwater contamination (Amadi & Smith, 2017; Kumar , 2017). A persistent problem in the Niger Delta, frequent oil spills come from a variety of sources, such as pipelines, storage facilities, and exploration operations. A poisonous mixture of pollutants, including heavy metals, hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs), are released by these spills. Both plants and animals are impacted by the severe instant harm. But the real cost extends well beyond the first effects, leaving a legacy of contaminated groundwater and soil that endangers the environment and the long–term welfare of its inhabitants (Abdel–Shafy & Mansour, 2016). Although it doesn't affect people's health right away, contaminated water can eventually prove fatal (Sanda et al, 2022). Worldwide, drinking water, rivers, lakes, and oceans are impacted by water pollution, endangering both human health and the environment (Gambhir et al. 2012).

PAHs remain in the environment despite efforts to clean up oil spills, endangering ecosystems and human health in the long run (Doe and Amadi, 2019). Even with cleanup efforts, PAHs remain in the environment and pose long–term hazards to ecosystems and human health (Agency for Toxic Substances and Disease Registry, 2019). The persistence of PAHs is consistent with researchers who have shown that the main cause of recent issues in water treatment is the growing contamination of water by organic compounds that are hard for the body to break down because they thwart the rivers' natural purification processes and the breakdown of traditional wastewater treatment facilities (Ademiluyi et al., 2009; Olafadehan and Aribike, 2000; Ogunlowo and Sakwe, 2023). As a result, the persistent carcinogenic qualities of PAHs have sparked grave worries about the direct hazards of prolonged exposure through tainted groundwater sources (Boonpragob et al., 2019, Ogunlowo, 2022). Even while total prevention is still the ideal, cleanup measures are essential for minimizing damage from spills that have already occurred. Spilled oil and the pollutants it contains are removed or contained using a variety of ways, including pump–and–treat procedures and bioremediation. However, the type of spill, the surrounding environment, and the methods used for implementation all have a significant impact on how effective these interventions are (Osuji, 2015). It is essential to comprehend their actual influence on PAH leaching in order to maximize remediation tactics and protect groundwater quality.

Prior research has examined the presence of PAHs in soil and water, such as in the drinking water of China's Huai River counties, and has found a correlation between PAHs and a high risk of cancer (En chun et al , 2015 According to their epidemiological research, exposure to PAHs by professionals is linked to a variety of cancer types (Eom, et al., 2013, Mastrangelo et al., 1996; Tsay et al., 2013), and PAHs are listed as priority pollutants by the United States Environmental

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Protection Agency (US EPA) due to crude oil spillage in the Niger Delta region (Osuji, 2015; Nwankwoala et al., 2017). Despite the risks, limited studies have investigated PAHs contamination in groundwater with leached crude oil in Iwochang, Nigeria. So, understanding the extent and impact of PAHs contamination in groundwater is crucial for developing effective mitigation strategies, protecting human health, and preserving environmental quality. In order to assess the pathways, the presence, and concentration of leached Polycyclic Aromatic Hydrocarbons (PAHs), a contaminant from oil spills into the groundwater; the potential environmental and health impacts with PAHs by comparing with USEPA standards; and the risk level of samples taken from polluted sites with control using (a) statistical inferences such as ANOVA, Leached Pollution Index (LPI) and Principal Component Analysis, this study will add to the body of knowledge already available on groundwater contamination by PAHs.

2. MATERIALS AND METHODS

Study Area

The study was conducted in Iwochang community, Akwa–Ibom state. Ibeno is located in the South–South of Nigeria and is a Local Government Area of Akwa Ibom State. Ibeno lies on the eastern side of Qua Iboe River about 3km from the river and is one of the largest fishing settlements in the Nigerian coast. The global positioning system (GPS) coordinates of the site is (4°37'50"N–7°50'04"E) (Figure 1a and 1b).

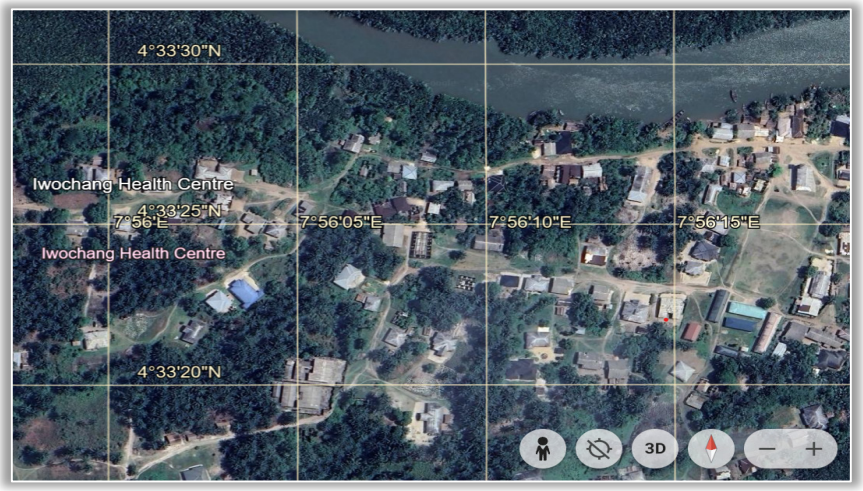

Figure 1a: Satellite image of Iwochang community of Akwa–Ibom State, Nigeria

Figure 1b: Sample area with Massive seaweed after crude–oil spilled.

Sampling Design and Soil Collection Sampling plots were erected at both the oil spill impacted site (Iwochang community in Ibeno Local Government Area of Akwa–Ibom State) and un–impacted (control) sites by grid system. An impacted area was delimited by reconnaissance with the area of

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heaviest spill as the epicenter. A sampling area of 200 by 200 m2 and of this was randomly selected. The community, like many others in Akwa–Ibom, has a rich cultural heritage tied to fishing, farming, and trading, with a strong reliance on the natural environment for sustenance. This led to environmental challenges, including oil spills and pollution, affecting the local ecosystem and traditional livelihoods. Despite these challenges, Iwochang remains a close–knit community with deep cultural roots, actively involved in preserving its traditions and seeking sustainable development amidst the complexities of modern industrial activities.

Sample collection

Samples were collected from a network of three bore holes located inside the research region. Three sites around the spill site were sampled for soil using a trowel and a hand shovel. The initial sample in the spill region was collected from locations 1 and 2, which are across the river and point toward latitude 4o37 N and longitude 6°20 E. The second sample was located in the spill region at latitude 4°54 N and longitude 6°27 E. With latitude 4°55N and longitude 6°25E, the control was conducted among the community's residents. Samples were taken at three different depths to understand the vertical distribution of pollutants. At each site, samples of three soil levels were taken. Using a hand trowel, the top dirt was collected at each site. Using a hand auger, a second sample was taken at each site at a depth of 0.3 meters. Using a hand auger, the third sample was collected at a distance of 0.9 meters from each site. Hand augers, shovels, trowels, polythene bags, amber bottles, PPE, coolers, and ice packs are among the materials used in this study. A sanitized extraction container was filled with 2g of the sample. The material was well combined with 20 milliliters of hexane, the extraction solvent, and then let to settle. Filter paper fitted onto Buchner funnels was used to carefully filter the mixture into extraction bottles that had been washed with solvent. After the extracts were concentrated to 2 ml, they were moved for separation and cleanup.

Laboratory Procedure for PAH Analysis

According to Ijaola and Sangodoyin (2020), the laboratory process for Polycyclic Aromatic Hydrocarbon (PAH) analysis entails extracting PAHs from soil and water samples, cleaning and separating them, and then using gas chromatographic analysis to identify and measure the PAH compounds.

Statistical Analysis

To further ascertain how the mean variation of assessed pollutants by PAHs differs from one another, and to ascertain whether there were statistically significant variations in the quantities of PAHs at various depths (S1, S2, and S3) between locations, an ANOVA analysis was performed for each PAH. Significant differences were found between sites for the majority of PAHs, although not consistently between soil layers, suggesting that spatial variability matters more than depth.

Leach Pollution Index (LPI)

The likelihood of leachate pollution at a given location is gauged by the LPI. According to Simeon and Ayotamuno (2022), a single figure between 5 and 100 gives important information about the soil's capacity to contaminate groundwater by releasing harmful compounds. The typical LPI value is 7.37, and it is an ascending scale index; a greater value indicates a bad environmental condition (Kumar and Alappat, 2003, Churchill and Ogunlowo, 2022). The WHO's Standard values for groundwater quality are used to generate the Leach Pollution Index (LPI).

$$\mathrm{LPI} = \frac{\sum(\mathrm{wi} \times \mathrm{pi})}{\sum \mathrm{wi}}$$

where Wi is the weight assigned to i–th parameter

$\mathbf{Pi}$ is the sub–index for the i–th parameter, calculated as:

$$\mathrm{Pi} = \frac{\textbf{observed value}}{\textbf{standard Value}} \times 100$$

The $\mathbf{Wi}$ should be Sum to 1.

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Principal Component Analysis

One method for reducing the size of high–dimensional data without significantly sacrificing information is principal components analysis (PCA), which uses the relationships between the variables to express the data in a more manageable, lower–dimensional format (Jolliffe, 1986). One of the most reliable and straightforward methods for reducing dimensionality is PCA. Known by several names, including the Hotelling transformation, the method of empirical orthogonal functions, the Karhunen–Loève transformation, and singular value decomposition, it is also among the oldest and has been rediscovered numerous times in other domains (Morrison, 1967). The number of factors extracted from the variables was determined by Kaiser's rule (Kaiser and Rice, 1974). This criterion retains only factors with Eigen–values that exceed one. According to Morrison (1967) principal component should account for approximately 75% of the total variance. Throughout the study SPSS 23 was used. Our intention was to perform data processing in the same way for all cases preferring such a way of the factors rotation to get as many as possible positive sample location to achieve a more meaningful interpretable solution. In order to interpret the significance retained principal components in terms of the original variables only those factors (coefficients) whose absolute value was greater than 60% of the maximum coefficients in absolute value in each principal component were considered (Jolliffe, 1986). The principal component analysis was used to provide an overview of groundwater contamination at Iwochang community of Akwa–Ibom State Nigeria.

3. RESULT AND DISCUSSION

Comparison of PAHs concentrations between sample Locations and Pathways

Naphthalene, Acenaphthene, Fluorene, Pyrene, Anthracene, and Benzo(a)anthracene concentrations in parts per million (PPM) are among the PAHs that are shown in Table 1 and Figs (1–3). In every sample, benzo(a)anthracene exhibited the lowest quantities, while naphthalene consistently displayed the greatest concentrations. All locations had the greatest levels of naphthalene in the topsoil, with Location 1 (L1S1) having 1.265 PPM and Location 2 (L2S1) having 1.342 PPM. While aquifer samples had the lowest concentrations of naphthalene (L1S3 at 1.0502 PPM), these amounts show significant pollution, most likely from surface oil spills. Similar patterns were seen in the levels of acenaphthene, which steadily decreased from topsoil to aquifer and had the maximum concentrations in topsoil (L1S1: 0.0543 PPM). The concentration of fluorene in the subsoil at Location 2 was higher than that of the other layers (0.0397 PPM), suggesting that there may be an accumulating effect in this layer. Although Pyrene and Benzo(a)anthracene were slightly more common in the subsoil, the concentrations of the other PAHs, Pyrene, Anthracene, and Benzo(a)anthracene, were generally lower. According to the research, the aquifer shows the least amount of PAH contamination, while the topsoil and subsoil are the most contaminated layers overall. The information gathered from the analysis of PAH concentrations in soil samples provides valuable insight into how these pollutants behave in different soil layers.

Table 1: PAHs concentration between soil samples (all in parts per million (ppm))

Location	Naphthalene	Acenaphthene	Fluorene	Pyrene	Anthracene	Benzo(a)anthracene
L_1S_1	1.270	0.054	0.037	0.041	0.033	0.003
L_1S_2	1.250	0.047	0.038	0.030	0.071	0.039
L_1S_3	1.050	0.037	0.005	0.006	0.004	0.005
L_2S_1	1.340	0.029	0.024	0.012	0.064	0.048
L_2S_2	1.290	0.039	0.040	0.045	0.034	0.028
L_2S_3	1.050	0.038	0.005	0.008	0.020	0.007
L_3S_1	1.260	0.038	0.040	0.024	0.062	0.061
L_3S_2	1.270	0.037	0.039	0.034	0.050	0.060
L_3S_3	1.060	0.018	0.0070	0.010	0.007	0.004

Note: L_1S_1 – Location A sample 1, L_1S_2 – Location A sample 2, L_1S_3 – Location A sample 3 L_2S_1 – Location B sample 1, L_2S_2 – Location B sample 2, L_2S_3– Location B sample 3, L_3S_1 – Location C sample 1, L_3S_2 – Location C sample 2, L_3S_3– Location C sample 3.: Where S1= TOP SOIL, S2 = SUB–SOIL, S3= WATER. L3= Control, L1= first site of pollution, L2= second site of pollution

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The quantities of PAHs were higher in topsoil (S1) than in subsoil (S2) and aquifer (S3) layers, indicating that PAHs are more likely to accumulate near the surface. This is explained by the fact that PAHs are hydrophobic, which frequently causes them to adhere to organic matter in the soil, especially in the upper layers where organic content is higher. This is consistent with the findings of Patel et al. (2020), who discovered that the deposition of PAHs is accelerated in soil/sediments due to their higher hydrophobicity and low aqueous solubility.

Additionally, Jesus et al. (2020) found that PAHs tend to accumulate in the sediment because of their higher hydrophobicity. According to Chen et al. (2022), this explains the reduced PAH concentrations in the aquifer layer and suggests that PAH migration to groundwater may be restricted because of the soil's high filtration capacity, even though some pollution is still present. The study's lightest PAH, naphthalene, had consistently greater quantities in all samples, especially the topsoil. Additionally, it demonstrates that the mobility increases with the lightness of the pollutants. This means that lighter PAHs, such as naphthalene, leach more readily than heavier PAHs, which explains why they are more prevalent in the samples Figures 2, 3 and 4.

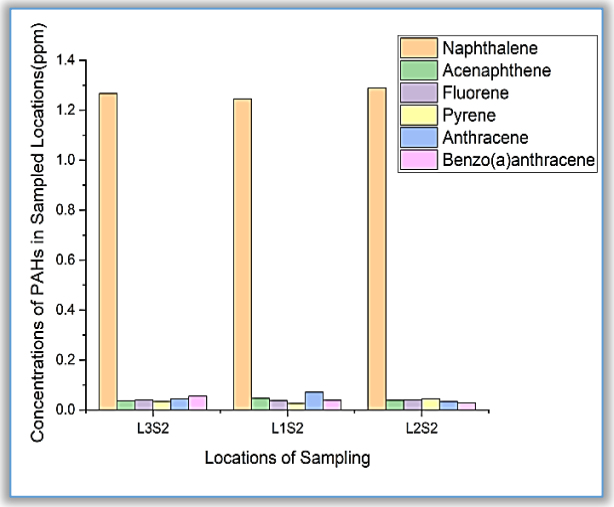

Figure 2: Comparison of PAHs Pollutant Between the Crude Oil Spills Polluted Area and Control at the Top-soil

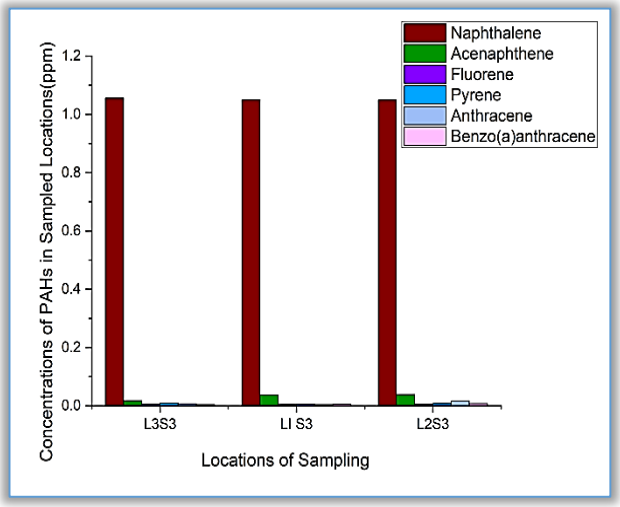

Figure 3: Comparison of PAHs Pollutant Between the Crude Oil Spills Polluted Area and Control at the Sub-soil

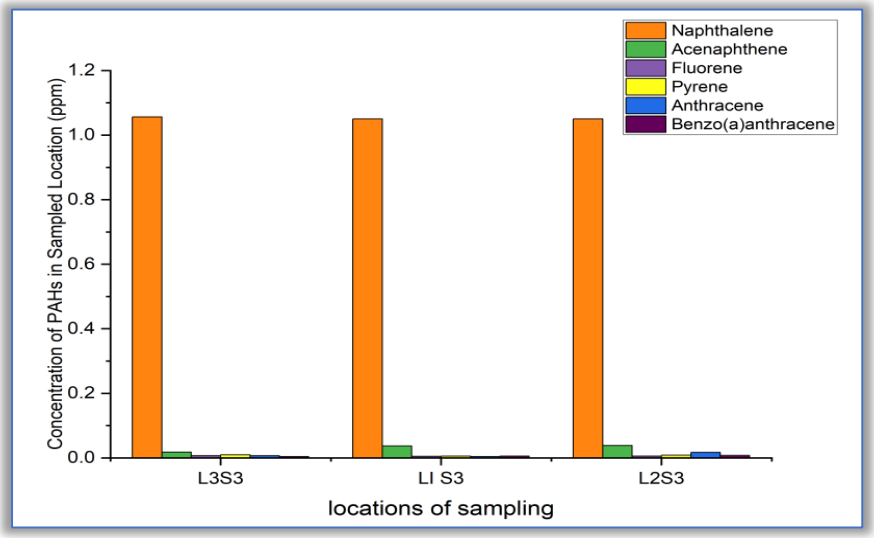

Figure 4: Comparison of PAHs Pollutant Between the Crude Oil Spills Polluted Area and Control at the aquifer

Statistical inferences and a comparison of the PAHs pathway in each sampled area with the USEPA

The mean concentrations of each PAH taken into account within each location's pathway are displayed in Table 2 along with a comparison to USEPA's groundwater PAH standards. Additionally,

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statistical inferences were used to compare the measured results. When compared to the other PAH compounds in Table 2, Naphthalene has the highest concentration levels (1.187–1.227) ppm, suggesting possible contamination from petroleum. All tested PAHs were compared to standards, revealing several acceptable limit violations.

Table 2: Mean Values of PAHs concentration within each sampled Locations compared with USEPA Standard and Statistical inferences

Contaminants	L1	L2	L3	USEPA	P–value (soils)	P–value (water)
Naphthalene	1.190	1.230	1.120	0.0001	0.2293	0.0006
Acenaphthene	0.046	0.036	0.031	0.0001	0.1967	0.3715
Fluorene	0.026	0.023	0.030	0.0002	0.4275	0.0024
Pyrene	0.024	0.022	0.023	0.0002	0.9691	0.1189
Anthracene	0.036	0.040	0.040	0.0002	0.9849	0.0810
Benzo(a)anthracene	0.016	0.028	0.040	0.0002	0.3582	0.1413

While anthracene and benzo(a)anthracene exhibit variable concentration levels across sampling locations, suggesting multiple contamination sources, acenaphthene, fluorene, and pyrene have relatively low concentration levels ranging from 0.046–0.031, 0.029–0.023, and 0.022–0.024 ppm, respectively, suggesting minimal impact from these compounds. Significant variations in naphthalene concentrations between soil layers are confirmed by the ANOVA results in table 2 (P–value = 0.2293, P–value > 0.05), with topsoil samples showing the highest amounts. All samples had significantly reduced quantities of higher PAHs, especially in the aquifer layers, such as pyrene, anthracene, and benzo(a)anthracene. These PAHs have limited vertical mobility because of their increased propensity for adsorption onto soil particles and poorer solubility. These substances are less likely to contaminate groundwater than lighter PAHs like naphthalene, as evidenced by their comparatively low quantities in the aquifer and subsurface. Additionally, the ANOVA results for these compounds showed a significant difference (P–value ≥ 0.05) between the samples: Pyrene (P–value = 0.9691, which is >0.05), Anthracene (P–value = 0.9849, which is >0.05), and Benzo(a)anthracene (P–value = 0.3582, which is >0.05). However, their concentrations showed consistently low levels in water samples but higher values across the various soil layers, as shown in Table 2. The ANOVA results for fluorene (P–value = 0.002376112, which is < 0.05) showed significant differences between the samples, indicating that fluorene concentrations vary significantly across soil layers. The subsoil in Location 2 had particularly high levels of fluorene. Once more, the topsoil had the highest levels of Acenaphthene. Acenaphthene levels are high, but the variance across layers is not statistically significant, according to the ANOVA results, which showed no significant changes between samples (P–value = 0.3715, P–value ≥ 0.05). Multiple PAH contamination levels varied significantly between locations, according to the ANOVA analysis, indicating significant geographical heterogeneity in contamination. Given that some regions have higher amounts of particular PAHs than others, this data suggests that the causes of contamination may be localized. The majority of PAHs, on the other hand, showed less significant change across soil layers, suggesting that soil depth had little effect on variations in PAH concentrations. This shows that although topsoil is typically more contaminated, soil depth alone may not have as much of an impact on PAH levels as other factors, such as past contamination episodes or local.

Leach Pollution Index and Contamination Assessment

An important source of information on the soil's capacity to contaminate groundwater with dangerous compounds is the Leach Pollution Index (LPI). According to Table 3, the samples' LPI values for the three locations varied from 81,199.25 to 83,374.10, with Location 1 having the greatest value and Location 3 having the lowest. The possible risk of PAH pollutants seeping into the aquifer from the soil and

Table 3: Leach pollution index

Location	Leach Pollution Index (LPI)
A	83374.10
B	81460.90
C (Control)	81199.30

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ultimately compromising groundwater quality is reflected in this index. The USEPA standard values for groundwater quality were used.

Comparing these LPI results to the typical threshold values used for soil contamination evaluations is crucial to determining their significance. Environmental guidelines state that hazardous leachates can have an LPI threshold of 7,500. According to Ogbozor et al. (2015), any value higher than this suggests a possible risk of pollutant migration into groundwater sources. All of the reported LPI values in this study, the lowest being 81,199.25 and the highest being 83,374.10, significantly surpass the conventional threshold. Since these numbers exceed the norm, there is a serious risk of contamination across all locations. The high LPI values imply that the topsoil and subsoil in particular, as well as the soil in the analyzed locations, have a significant potential for contaminant migration, which is mostly caused by the presence of PAHs. This presents a serious risk of groundwater contamination, particularly in regions where environmental damage from crude oil spills has been severe. Due to higher concentrations of PAHs in the topsoil and subsoil, which may be caused by the area's closer proximity to the spill site or other factors like soil type and permeability, Location 1 (83,374.10) has the highest LPI value, indicating that it has the largest leaching potential. In contrast, even though Location 3 has the lowest LPI (81,199.25), the value is still well above the typical threshold, making it a risky location.

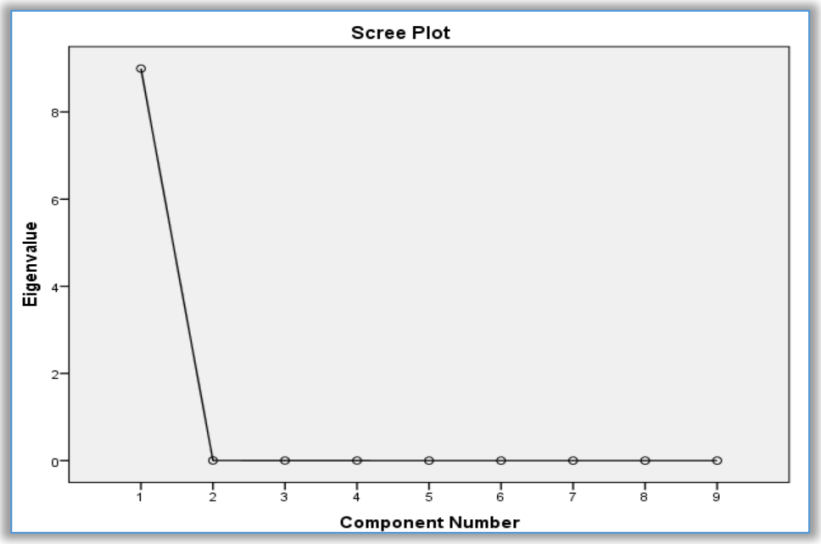

Figure 5: Scree plot of the factors (Sample location)

The scree plot test (Fig. 5) show that only the sample from the top–soil of location A is the significant factor or component contributing to groundwater contamination in Iwochang community of Akwa–Ibom State. The outliers as shown in Fig. 5 are the samples of the sub–soil and aquifer.

Effects on the Quality of Groundwater

Even at lower concentrations than in topsoil, the presence of PAHs in aquifer samples raises questions regarding the quality of the groundwater. The existence of PAHs in groundwater samples indicates that there is still a chance of PAH contamination in drinking water sources, even though the findings show minimal vertical migration. Over time, consuming such water will undoubtedly have a detrimental impact on human health. In order to stop further contamination, this highlights the necessity of continuous monitoring and potentially remediation efforts.

4. CONCLUSION

This study discovered that the topsoil (S1) had significant contamination from Polycyclic Aromatic Hydrocarbons (PAHs), whereas the subsoil (S2) and aquifer layers (S3) had moderate contamination. While heavier PAHs like pyrene and anthracene had lower concentrations because of their poor solubility and greater affinity for soil, naphthalene had the highest amounts, suggesting mobility. All areas had considerable pollution, according to the Leach Pollution Index.

The soil sample from the topsoil in the oil spill area is a contributing factor to groundwater contamination in Iwochang community, according to the main component analysis. Even though groundwater has very low levels of PAHs, there is now a concern that needs more research.

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