Determination of Naphthalene Concentration in Gombe Urban Soils

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ABSTRACT

Petroleum hydrocarbon pollution of urban soils in advancing countries is on the rise as a result creating a public health concern. Urban soil pollution with hydrocarbons mostly originate from diverse anthropogenic sources including petroleum and petroleum products spills and uncontrolled disposal of spent oil in the environment. This study focused on the spectrophotometric analysis of naphthalene in thirty urban soils sampled from 10 urban sites with dissimilar anthropogenic pollution sources in Gombe metropolis. Spectrophotometric detection of naphthalene was optimized to enable the construction of a standard calibration curve using naphthalene standards and further applicability in determining naphthalene concentrations from prepared samples via automatic extrapolative determination. Naphthalene was detected optimally at 221.8 nm wavelength and further detection from soil samples produced significantly varied naphthalene concentrations from all the ten urban sites portraying 5.28 and 9.07 mg/kg as the lowest and highest naphthalene concentration loading from sites 4 and 6 respectively. However, naphthalene concentration levels in other sites were close with a range from 8.39 to 8.96 mg/kg and depicted significance from sites 4 and 6. Naphthalene concentrations in all the sites were high above the established allowable or intervention limits for urban soils. The naphthalene pollution is majorly attributed to human anthropogenic activities relating to the use of petroleum, petroleum products and derivatives. There is a need for regulatory policies and routine monitoring of urban sites with anthropogenic pollution sources that could overburden urban soils with petroleum hydrocarbons which are hazardous to humans and other receptors onsite.

Keywords: Petroleum hydrocarbon, Naphthalene, Pollution, Urban soils, Spectrophotometry.

INTRODUCTION

The pollution of urban soils with hydrocarbons from petroleum and petroleum products in advancing countries is now generating a public health concern. Urban soil pollution with hydrocarbons is majorly from diverse anthropogenic sources such as unregulated discharge and indiscriminate release of spent automobile oils (Adelowo et al., 2006). Others include petroleum spills from tanker accidents, indiscriminate oil waste disposal, storage tank leaks, discharge from gas stations and activities related to lubrication machine and automobile maintenance (Kadafa, 2012; Adelowo et al., 2006; Sojinu et al., 2010; Ite et al., 2013). However, airborne sources of combustion continue to be significant contributors to petroleum hydrocarbon contamination as urbanization intensifies (Doherty et al., 2015). Consequently, the soil and groundwater serve as essential pathways that are frequently subject to contamination from crude oil and refined petroleum products, such as petroleum motor spirit (PMS), diesel, jet fuel, paraffin, and derivatives, including motor oil and other lubrication oils (Ibrahim et al., 2022).



Petroleum hydrocarbons, ranging from the simplest aliphatic hydrocarbon to polycyclic aromatic hydrocarbons (PAHs), are the primary hydrocarbon pollutants found in crude oil and refined petroleum products, and the PAHs are pervasive and ubiquitous pollutants in many different environments (Anders *et al.*, 2005; Fuchs *et al.*, 2011).

Benzene, Toluene, Ethylbenzene and Xylene, other (BTEX) and PAHs such as typical Naphthalene are aromatic hydrocarbons from petroleum derivatives such as gasoline have a large spectrum of occurrence in contaminated soil and water environment (Hussein, 2019; Fuchs et al., 2011). Meckenstock et al., (2000) also related that PAHs are toxic substances commonly found in polluted locations, including old gas plant sites and mineral oil refineries.

Several studies cautioned about the rising concentration of hydrocarbon pollutants in urban environments, and this issue raises significant public health concerns due to their potential toxic effects, mutagenicity, and carcinogenicity (Estelmann et al., 2015) thus there are increasing apprehensions regarding their presence in the environment (USEPA, 1993). The main environmental concerns involve both single-ring aromatics (such as BTEX) and PAHs, which are hydrocarbons with multiple fused benzene rings, ranging from naphthalene (two rings) to coronene (seven rings) (Fuchs et al., 2011; Estelmann et al., 2015). The enduring polycyclic presence of aromatic hydrocarbons (PAHs) in the environment is influenced by several factors, including the chemical structure of the PAH, the

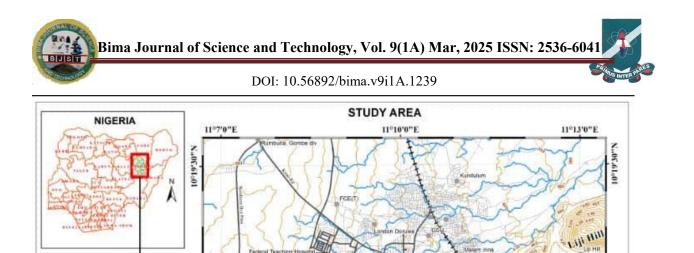
bioavailability, contaminant's and the concentration and distribution of the PAH (Bamforth and Singleton, 2005). Additionally, environmental aspects like soil composition, temperature, pН levels. availability of sufficient oxygen, water, and nutrients play a crucial role in determining how long polycyclic aromatic hydrocarbons (PAHs) remain in the environment (Sutherland et al., 1995).

Given the persistent nature of most hydrocarbons in the soil, low bioavailability for microbial natural attenuation and their potentially deleterious effect on human health; it is only indispensable to evaluate petroleum hydrocarbon contaminant loading in urban soils. This majorly justifies the study the spectrophotometric on determination of naphthalene concentrations in ten (10) different urban soils from petroleum hydrocarbon-contaminated urban within the Gombe sites metropolis. Furthermore, this research is crucial for gathering the earliest data on naphthalene levels in urban soils and understanding their contamination status as data on urban soil contamination are mostly scarce in advancing countries.

MATERIALS AND METHODS

Study area

For this research, urban soils with anthropogenic pollution were sampled from ten (10) different locations within the Gombe metropolis in Gombe State, Nigeria. Information regarding all the study sites is provided in Table 1 and the site map showing various sampling site locations is provided in Figure 1.



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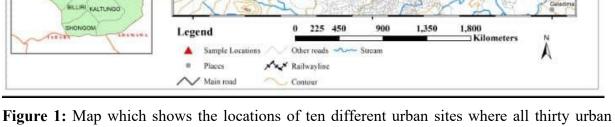


Figure 1: Map which shows the locations of ten different urban sites where all thirty urban soils were sampled from. The red triangles indicate the ten sample sites or locations where soil samples were collected.

Sample	Sites	Location	Latitude	Longitude	Land use
Sample 1	Site 1	Kumbia Kumbia	10.2803683	11.1684981	Auto workshop
Sample 2	Site 2	Kumbia Kumbia	10.2841713	11.1673457	Auto workshop
Sample 3	Site 3	Herwa Gana Road	10.2861072	11.1706774	Auto workshop
Sample 4	Site 4	Herwa Gana Road	10.2868581	11.1707649	Auto workshop
Sample 5	Site 5	Kumbia Kumbia	10.2841713	11.1673457	Motorcycle Servicing
Sample 6	Site 6	Herwa Gana Road	10.2868931	11.1707535	Motorcycle Servicing
Sample 7	Site 7	GT	10.2811681	11.1777365	Motorcycle Servicing
Sample 8	Site 8	Jekadafari	10.2876515	11.1615586	Motorcycle Servicing
Sample 9	Site 9	GT	10.2565767	11.1642047	Gas station
Sample 10	Site 10	By-pass road	10.256381	11.1616238	Gas station

Table 1: Details of the Ten (1	(10) different Samp	le Sites and Locations
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Key: GT = Gombe town.

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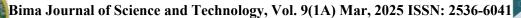
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Soil Sampling

A total of thirty (30) urban soils were sampled from the ten different sites within Gombe for the detection of naphthalene. Soil samples were collected in triplicate from each urban site for this study. A noncomposite (no mixing or homogenization of triplicate samples) sampling was adopted for this study where triplicates of shallow soils were sampled within 10 cm depth, and these triplicate soils were collected at 3 different positions which were 0.5 meters (50 cm) apart in a triangular pattern in the same site. The hand trowel was initially decontaminated with 70 % ethanol before being used for soil sampling from each site. Further decontamination of the sampling tool was strictly adhered to after sampling in one site and before use in another to prevent soil sample mixing and contamination. Soils were dispensed into sterile labelled sample bags and temporarily preserved in the field at 4 °C on ice before taken to the laboratory for analysis.

Preparation of Stock and Standard Naphthalene Solutions

The method described by Hussein (2019) was adopted in the preparation of a naphthalene stock solution. In preparing 7 mg/L naphthalene in water solution, the appropriate quantity of naphthalene was weighed and added to the required amount of distilled water (ddH₂O) contained in a sterile substrate bottle which was sealed and subjected to magnetic stirring for 5-6 hours. A scaled-down 200 mL quantity of naphthalene stock solution was prepared in a 500 mL flask to allow enough space for the stirring and vortexing in the shaker for dissolution. efficient For complete dissolution of naphthalene in water, the solution was further shaken at room temperature in the shaker at 200 rpm for 2 days. The 7 mg/L naphthalene stock was then subjected to double dilution with distilled water and vortexed to obtain lower standard concentrations such as 3.50, 1.75,

0.87, and 0.44 mg/L of naphthalene. These standards were immediately used for the construction of the standard calibration curve.

Construction of Standard Calibration Curve

This study utilized the spectrophotometric measurement of absorbance from the prepared naphthalene stock and standards for the construction of a standard curve and further applicability in determining naphthalene concentration from the prepared soil-water mixture. The spectrophotometric wavelength of 221.8 nm reported by Rohi et al., (2013) was adopted after careful optimization with other wavelengths (219.3, 275, 280, 290 and 300 nm) established in the literature to determine the optimum wavelength for spectrophotometric detection of naphthalene using the 7 mg/L stock solution of naphthalene.

For the calibration curve, the spectrometry was carried out on the naphthalene stock (7 mg/L) and standards (3.5, 1.75, 0.87, 0.44 mg/L) to determine the absorbance at these varied concentrations using a digital UV-VIS Spectrophotometer (Number: 21-1650-01-0111) at 221.8 nm optimized wavelength with 2.00 nm spectra bandwidth. Blanking was initially done with 4 mL distilled water on the Spectrophotometer to zero and eliminate any background spectra before the analysis. After blanking, the same quantity of the prepared naphthalene stock or standard solutions was added to the glass cuvette and the absorbance was determined in technical replicates using the digital UV-VIS Spectrophotometer. Average absorbance for the stock and standards were produced and used to automatically construct and produce a calibration curve by the digital UV-VIS Spectrophotometer displayed on the monitor.



Determination of Naphthalene in Urban Soils

Soil preparation and reconstitution

Slightly modified method described by Hussein (2019) was adopted for the soil preparation and reconstitution where urban soil samples devoid of dirt or non-soil particles were reconstituted in water by weighing 1 gram into 6 mL double-distilled water contained in a 30 mL glass sample bottle and sealed tightly. The soil-water mixture was thoroughly mixed on the vortexer for 30 minutes then further shaken at 200 rpm in the shaker for 10 hours at room temperature to ensure dissolution of hydrocarbons contained in the soil samples. The mixture was again thoroughly vortexed briefly and then allowed to settle on the bench for 2 hours. Afterwards, 4 mL of the supernatant solution was carefully pipetted into another sterile glass bijoux bottle and then closed with the lid while the soil was left undisturbed at the bottom. All the triplicate soils collected from the sampling sites were separately subjected to reconstitution to obtain triplicate solutions for the determination of naphthalene loading in the soil sample.

Spectrophotometric Quantification of Naphthalene Concentration

The 4 mL of hydrocarbon solution obtained from 2.5.1 was transferred into a glass cuvette and the spectrometry analysis of naphthalene in the samples was carried out using the digital UV-VIS Spectrophotometer (Number: 21-1650-01-0111) with 2.00 nm spectra bandwidth to determine the absorbance at 221.8 nm. Analyses were achieved in biological replicates with triplicates representing 3 sampling points from one sample site. The concentration of naphthalene in all the samples was resolved and determined via automatic extrapolation from the generated standard calibration curve on the Spectrophotometer. Triplicate samples were analyzed from each of the ten sites studied.

Statistical Analysis

One-way ANOVA was carried out to determine the statistical relevance of the naphthalene concentration between groups of sites studied at a 95% confidence level while Tukey HSD, a post-hoc test was carried out for multiple comparisons of naphthalene concentrations in the ten different urban sites within Gombe metropolis.

RESULTS

Naphthalene-in-water Calibration Curve

From the optimized spectrophotometric assay to determine the optimum wavelength for naphthalene detection, the 221.8 nm wavelength produced the highest absorbance relative to others implying that naphthalene absorbs ultraviolet light strongest at 221.8 nm wavelength which allows for its optimal detection using a UV spectrophotometer in this study. A straight line naphthalene calibration curve was produced by the digital spectrophotometer using the 7, 3.50, 1.75, 0.87, 0.44 mg/L of naphthalene solution, where a dose-dependent rise in absorbance recorded with an increase was in naphthalene concentration as shown in Figure 2. By inference, as the naphthalene concentration increases, the absorbance produced also increases portraying Conc Vs Abs direct proportionate increase.

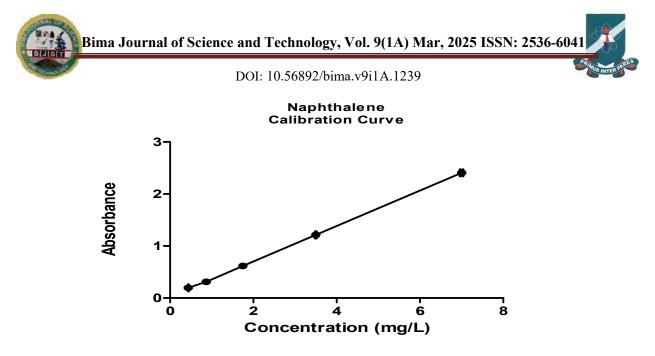


Figure 2: Standard calibration curve constructed using stock and standards with varied concentrations of naphthalene (7, 3.5, 1.75, 0.87, 0.44 mg/L) where absorbance was measured at the optimum wavelength of 221.8 nm using a UV-VIS Spectrophotometer. Values for this plot were the average of replicate measurements.

Naphthalene Concentrations Determined in Urban Soils

Based on the spectrophotometer's automatic extrapolation from the standard curve, triplicate samples from the ten (10) different urban soils produced closely related naphthalene concentration loading where samples 6A, 6B and 6C had the highest triplicate naphthalene concentrations of ~ 9.1 mg/L naphthalene with the corresponding highest absorbance. Conversely, samples 4A, 4B and 4C produced the lowest naphthalene concentration of ~ 5.0 , 5.2 and 5.6 mg/L respectively.

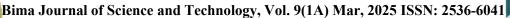
Mean Naphthalene Concentration in Sampling Sites

Table 2 below provides the average naphthalene concentrations resolved from all the ten (10) urban soils analyzed in this study.

Sample	Sites	Av. Absorbance	Av. Concentration (mg/kg)
Sample 1	Site 1	3.038	8.85
Sample 2	Site 2	2.883	8.39
Sample 3	Site 3	3.076	8.96
Sample 4	Site 4	1.824	5.28
Sample 5	Site 5	3.056	8.90
Sample 6	Site 6	3.115	9.07
Sample 7	Site 7	2.117	6.15
Sample 8	Site 8	3.052	8.89
Sample 9	Site 9	2.943	8.57
Sample 10	Site 10	3.029	8.82

Table 2: Mean Naphthalene Concentration Detected in Urban Soils from Ten Sites

Mean naphthalene concentration in all ten (10) different petroleum hydrocarbon-contaminated urban sites where soils were sampled. Naphthalene concentration detected in mg/L is equitable to mg/kg. Where Av = average.





ANOVA statistical analysis shows a significant difference in the mean naphthalene concentrations between groups of the 10 sites with p-value = 0.00 at 95% confidence level.

Soil samples from site 6 have the highest mean naphthalene concentrations of 9.07 mg/kg and depicted higher significant relevance (p<0.05) with the lowest naphthalene concentration attained in site 4 based on the post-hoc turkey HSD test. Though soils from site 7 had naphthalene concentration higher than site 4, its

concentration still significantly varies from other sites (1, 2, 3, 5, 8, 9, and 10) with close naphthalene concentrations which range from 8.39 to 8.96 mg/kg. Also, there was statistical relevance between site 6 with the highest naphthalene concentration and site 7 as per the post-hoc multiple comparison test.

Naphthalene Concentrations Based on Site Usage Type

Table 3 provides the mean naphthalene concentrations based on the three (3) diverse types of site usage leading to soil pollution via anthropogenic sources.

Site Usage Types	Sites	Average Concentration (mg/kg)	
Automobile workshop	1, 2, 3 and 4	7.8	
Motorcycle servicing outlet	5, 6, 7 and 8	8.3	
Gas stations	9 and 10	8.6	

Overall, the gas stations depicted the highest mean naphthalene concentration and were closely trailed by the motorcycle/tricycle servicing outlets, while the automobile repair workshops also known as mechanic workshops produced least the mean naphthalene contamination load as seen in Table 3.

DISCUSSION

Optimal Naphthalene Spectrophotometry Detection

Several studies have reported quantitative naphthalene detection via spectrophotometry using different wavelengths at which naphthalene can absorb UV light and this enables the quantification via absorbance spectrophotometer. produced by the However, the intensity of light absorption by naphthalene could vary at different wavelengths. In this study, 221.8 nm wavelength produced the highest absorbance for the detection of naphthalene stock solution in comparison to other literatureestablished wavelengths thus applied as the wavelength for optimal naphthalene detection. This agrees with Rohi *et al.*, (2012) who reported the exceptionally highest absorbance spectrum of naphthalene in methanol at 221.8 nm wavelength.

The naphthalene standard calibration curve in Figure 2 produced at 221.8 nm wavelength established a corresponding increase in absorbance as the naphthalene concentration increases which is equitably atypical of a standard curve for extrapolative quantification of unknown samples.

Naphthalene in Petroleum hydrocarboncontaminated Urban Soil

Urban soil hydrocarbon contamination is commonly from airborne combustion sources (Doherty et al., 2015), however, al., (2022)related Ibrahim et that contamination from refined petroleum derivatives could products and their significantly increase the hydrocarbon load in the environment implying anthropogenic



sources are among the major causes of urban soil pollution. Naphthalene was resolved from all the prepared soil-water mixtures as a result of absorbance produced signifying the presence of naphthalene in the soil samples, and this is contrary to the blank control (double distilled water) which produced a zero absorbance; though, a control soil was not analyzed for comparative study.

This study detected the presence of varied concentrations of naphthalene in the thirty different urban soils from urban sites with various anthropogenic activities namely gas stations, automobile repair workshops and motorcycle/tricycle servicing. It is only justifiable to detect naphthalene up to 9.07 mg/L in these sites owing to evident pollution sources chiefly of petroleum, spent and unspent petroleum products' origin. This is because petroleum hydrocarbons including the simplest aliphatic hydrocarbon and multiple fused-ring types such as PAHs are the prime hydrocarbon components of crude oil and refined petroleum products (Anders et al., 2005; Fuchs et al., 2011). Other literature among which are Butler and Mason, (1997) and Corsico et al., (1999) have widely reported higher hydrocarbon constituents in refined petrol and petroleum products. Chris, (2007) reported that an unused motor oil contains hydrocarbon having 18 to 34 carbon atoms per molecule and a complex mix of hydrocarbons amounting to 80 to 90 % of its volume. Irwin et al., (1997) reported phenol, naphthalene, benzo (a) anthracene, benzo (a) pyrene, and fluoranthene as the notable hydrocarbon of engine components spent oil. Consequently, the human activities in these sites leading to the indiscriminate discharge of petroleum, petroleum products and substantiates derivatives the elevated naphthalene concentrations detected in the urban soils from these sites.

The 10 different sites sampled are urban sites with typical urban settings and constituting both residential and commercial or business areas containing populations atypical of an urban expanse. According to the United States Environmental Protection Agency (USEPA, 2018), naphthalene screening levels in industrial and residential soils are 17 and 3.8 mg/kg respectively. Also, the intervention value for naphthalene in industrial and residential dry soils is 5.9 and 1.8 mg/kg respectively by the Environmental Agency of the State of Sao Paulo, Brazil (CETESB, 2017). As per these guidelines, all the ten urban sites sampled for this study portray higher naphthalene concentration limits for residential soils; particularly attributed to commercial dispensing of petroleum and petroleum derivatives and auto repairs that could lead to their release the environment. Based on into this inference, these sites could be tagged petroleum hydrocarbon-contaminated urban soils.

Consequently, the overburden of urban soil with continuous petroleum hydrocarbon contamination as а result of these aforementioned sources is of serious public health concern since naphthalene is among the sixteen high-priority hydrocarbon pollutants of concern recognized to possess mutagenic, toxic, and carcinogenic qualities (Cerniglia, 1992; IARC, 2002), as exposure to the high concentration of naphthalene can cause hemolytic anaemia via the destruction of red blood cells (USEPA, 2003). Exposure to naphthalene could be from receptor contact with contaminated soils, mostly from inhalation of contaminated ambient and indoor air and through the food chain (Stohs et al., 2002; Li et al., 2010). Unfortunately, the indiscriminate dumping of spent motor oil and diesel into drainages, water channels and soils has become a common practice in urban cities (Okonokhua et al., 2007). Adelowo et al., (2006) also stressed that ample gallons of used motor oil are frequently produced in automobile repair shops across the nation and disposed into the environment; all these cause the accumulation of various petroleum



hydrocarbons in the soil and water habitats. Furthermore, the high persistence in soil and low bioavailability of PAHs contributes to their potentially harmful effect on human health (Anders *et al.*, 2004).

CONCLUSION

In this study, spectrophotometric analyses of urban soils quantitatively provide significantly varied naphthalene concentration loading in all the urban soils from the study area. Findings exposed higher naphthalene concentration levels above intervention limits in all the urban soils sampled from the 10 different urban sites with contamination majorly attributed to human anthropogenic activities relating to the use of petroleum, petroleum products and derivatives. There is a need for urgent and effective regulatory policies and stringent by national monitoring environmental agencies regulatory regulate to the uncontrolled discharge of petroleum, petroleum products and their derivatives that is contributing to the elevated petroleum hydrocarbon pollution in urban soils. In addition, there is a need for adequate sensitization in these areas and related sites on proper handling and disposal of spent oils and education on the hazardous effects of petroleum hydrocarbons and the pollution implications of urban soils.

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