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ARTICLE

Spatial Distribution of Black Soot and Its Health Effects in Port Harcourt Metropolis, Nigeria

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ABSTRACT

This research presents a novel approach to assessing the health implications of black soot using a MiniVol air sampler. The MiniVol air sampler was used to collect PM from the ambient air at six monitoring sites in Port Harcourt, Nigeria. Sampling was conducted every day for seven days, for 24 hours. $PM_{2.5}$ concentrations at Uniport Junction, GRA Junction, Slaughter Roundabout, Abuloma Jetty, Rumuomasi Roundabout, and New Road Borokiri were 38.6 g/m^3, 28.3 g/m^3, 93.7 g/m^3, 72.9 g/m^3, 30.6 g/m^3, and 31.3 g/m^3, respectively. PM_{10} concentrations ranged from 71.2 g/m^3 to 60.6 g/m^3, with 103.3 g/m^3, 85.5 g/m^3, 40.1 g/m^3, and 35.2 g/m^3 being the highest. The level of $PM_{2.5}$ and PM_{10} pollution in the ambient air was high across the six sampling sites, with mean $PM_{2.5}$ and PM_{10} concentrations exceeding the WHO (2011) guideline. The flame atomic absorption spectrometry (FAAS) technique was used. The presence of heavy metals, such as mean metal concentrations of lead, cadmium, chromium, mercury, and nickel, ranged from 0.009 g/m^3-0.532 g/m^3, 0.002 g/m^3-0.544 g/m^3, 0.002 g/m^3-0.338 g/m^3, 0.001 g/m^3, and 0.001 g/m^3-0.432 g/m^3, across the six sampling sites. The GC-MS was used to determine the presence of PAHs in particulate matter. Correlation results revealed a strong positive correlation between $PM_{2.5}$ and PM_{10}. The findings also revealed a positive relationship between the metals as well as between the metals and PAHs, resulting in asthma, lung cancer, breathing difficulties, and miscarriages among pregnant women, which have affected the health implications of the people living in the environment.

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1. Introduction

As residents of Port Harcourt and its environs deal with the latest atmospheric threat, black soot, experts warn that long-term exposure to soot poses serious health risks, including cancer and other critical health problems that could lead to premature death. Soot produced as a byproduct of incomplete combustion of organic (carbon-containing) materials such as wood, fuel oil, plastics, and household waste contributes to air pollution, which is a major environmental health risk [1]. Carcinogens such as arsenic, cadmium, and chromium have been found in soot, a fine black or brown powder. In the last ten years, a large and well-documented literature on the effects and severity of air pollution on human health has emerged. The elderly and young infants are more vulnerable to illness as a result of air pollution. Air pollution has been linked to a variety of health effects, including eye, nose, and throat irritation, pneumonia, bronchitis, lung cancer, heart disease, brain, nerve, liver, and kidney disease [2]. According to Wikipedia, Port Harcourt is the capital of Rivers State, located within the southern region of Nigeria. Port Harcourt has a population of over 1.8 million people as of 2016, a 3 square mile coastline, and an elevation of 468 meters (Latitude 4.78N, Longitude 7.01E). Because of the presence of oil and gas, it is assumed that oil and gas-related businesses are the primary source of income for the majority of people, followed by farming and trading. This huge focus on oil and gas in the city has affected the city both positively and negatively. Air pollution, water pollution, and land pollution are among the negative effects it has on the environment and the people. From exhaust fumes to gas flaring, black soot, and oil spills on land and water bodies. This paper will be focusing on air pollution, chief among which is black soot.

A work on Satellite Determination of Particulate Load over Port Harcourt during Black Soot Incidents carried out by Ede and Edokpa [3] suggested that the black soot in Port Harcourt is a result of hydrocarbon combustion. 0.000035 mg/m^3 was the minimum and 0.18 mg/m^3 (0.035 g/m^3-180 g/m^3) was the maximum dispersed emission concentration found. He further inferred that the above-mentioned concentrations exceeded the national annual average limits, which is 40 g/m^3-60 g/m^3.

Black soot is a carbon constituent produced as a result of incomplete combustion of hydrocarbons. It is a climate forcer [4]. Generally, black soot is regarded as a very dangerous air pollutant. Black soot in Port Harcourt, Rivers State, was significantly noticed in the last quarter of the year 2016 and has carried on to date. Many residents suggest that the origin of the soot is a result of the burning of crude oil illegally with the use of various illegal refineries, the burning of tyres, gas flaring, and asphalt burning. Black soot has no doubt increased the amount of cardiovascular disease in the city.

The most visible air pollution within Port Harcourt, Rivers State and its environs is black soot, which is emitted daily with little or no strict rules and mitigating actions from the responsible bodies. Exposure to black soot in low or high concentrations frequently results in serious health issues and, in some cases, death. This underscores the dire need to understand the entirety of the problem (black soot) to enable the possibility of concrete, reliable solutions. Understanding the characteristics of black soot is a key step forward in getting to a concrete solution.

Study Area

The Port Harcourt is situated in the Niger Delta region of Nigeria and is the capital of Rivers state (Figure 1). Port Harcourt is located on latitude 4.91°N and longitude 7.09°E, 4.74°N and 6.89°E meters elevation above sea level with a population of 1,382, 592 according to Nigerian census [5]. It occupies an area of 1811.6 square kilometres and shares boundaries with the Gulf of Guinea along Bonny River. The city lies in the tropical monsoon climate with lengthy and heavy rainy season and very short dry season. The rainy season starts in March and ends in October while the dry season starts in November to February. December is the driest month of the year with an average rainfall of 20 mm while September is the month with the highest rainfall of about 367 mm. The average temperature is between 25-28 °C in the city with numerous hydrocarbon flow stations owned by the SPDC Total E& P and Agip Oil Company. In Port Harcourt and other Niger Delta states, gas flaring is a major environmental and public health issue. The human health consequences are diverse, encompassing a wide range of morbidities and fatalities [6]. The six monitoring sites include Uniport Junction, GRA, Slaughter round about, Rumuomasi round about, Abuloma Jetty and New Road Borokiri. The choice of the roundabout and junction is the area which experiences heavy vehicular traffic most often. The monitoring locations cover the traffic, residential and commercial areas in line with National Ambient Air Quality stipulations that monitoring must be undertaken where people may be exposed. Other factors considered in selecting the locations include accessibility, security, distance, cost and availability of electricity.

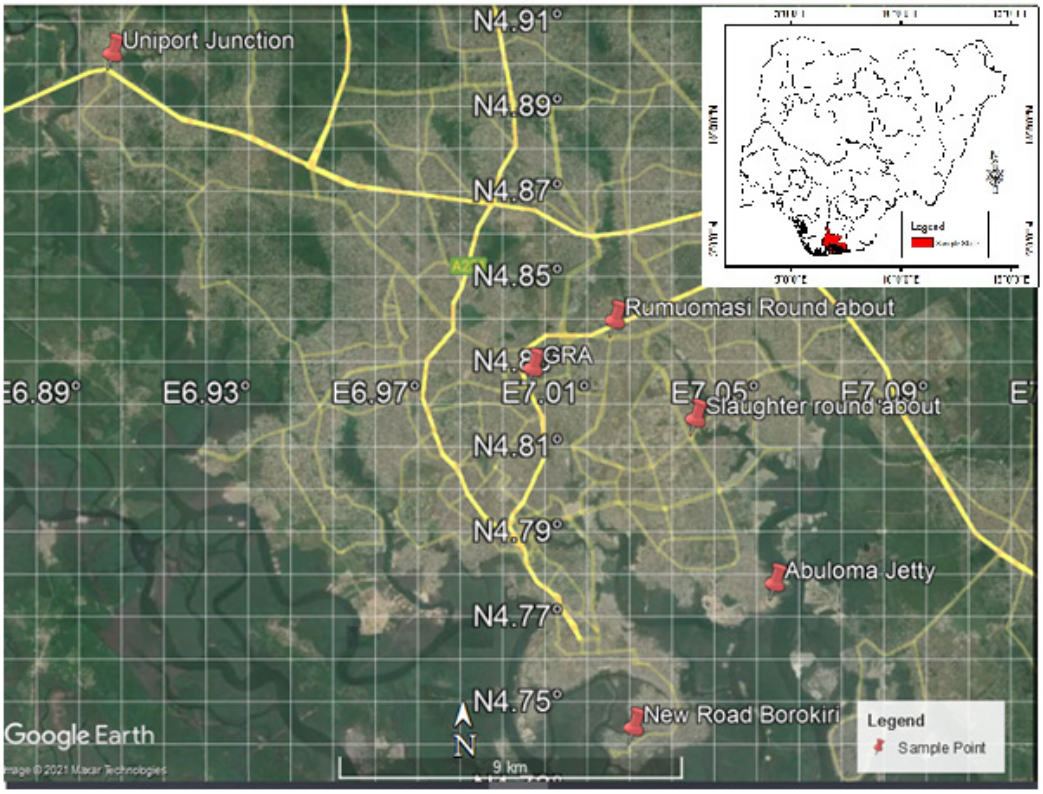

Figure 1. Map of the study area.

2. Literature Review

2.1 Sources of Air Pollution

Air pollution is the introduction of substances into the air that is not originally there or is above the standard concentration and it is harmful to the environment and living things within a short or long period of time. Pollution of air is hugely due to anthropogenic, geogenic and biogenic emissions [7]. Anthropogenic source of pollution is pollution caused by the activities of man, examples of such are gas flaring, black soot, chlorofluorocarbons. Geogenic source of pollution is air pollution that occurs naturally without any active influence by human beings but still has the potential to cause harm examples of such are volcanoes, the emission of sand by wind. Biogenic source of pollution is natural sources like plants and vegetation. These are temperature dependent mostly.

Weli [8] carried out research that included an in-depth quantitative analysis of the spatial and seasonal atmospheric levels of PM_{10} in Port Harcourt, as well as the environmental health implications of their presence at measured concentrations. Relative quantities of the pollutant were compared in various areas based on land use and time of year, including commercial, high-density residential, low-density residential, industrial, and rural. PM_{10} samples and analyses were collected and analyzed during the dry, transition, and wet seasons. The findings suggest that land use and seasons influence PM_{10} concentrations in the atmosphere. The seasonal trend in PM_{10} levels was dry > transition > wet for all land use types. During the dry season, the commercial and industrial areas had the highest values in terms of land use. The lowest PM_{10} value was found in low-density residential areas. The seasonal total atmospheric loading was 3436.1 g/m^3, 8573.12 g/m^3, and 16,148.87 g/m^3 for the wet, transition, and dry seasons, respectively. According to the study, there is also a statistically significant difference. There is a seasonal variation in PM_{10} concentrations across land use types. People who live and work in areas with high levels of PM are more likely to contract respiratory diseases. This includes densely populated areas.

Nwachukwu et al. [9] discovered that all of the criteria air pollutants were significantly higher in Rivers State than the WHO specification. They discovered that air pollution was linked to air-related morbidities and deaths in the state. Among the air-related morbidities studied, which included cerebrospinal meningitis (CSM), chronic bronchitis, measles, pertussis, pulmonary tuberculosis, pneumonia, and upper respiratory tract infection (URTI),

pneumonia was the most common for all of the years studied and was responsible for the most deaths in 2005.

2.2 Black Soot

Black soot produced by the incomplete combustion of hydrocarbon [10] is considered as an airborne environmental contaminant, which is very toxic to the environment and human beings. It is also considered to have a composition of particulate matter (PM), carbon mono oxide (CO), nitrogen oxides (NO_x) and sulphur dioxide (SO_2). It has a typical size ranging from 10 nm to 1 mm and the carbon content level is less than 60% of the particle [10]. We are all affected by these emissions, and the difference is our susceptibility which varies with health or age. Coarse particulates between 2.5 μm and 10 μm are said to be emissions of mechanical processes and dust. While finer particulates of 2.5 μm or less originate from a combustion source [11]. In most urban settlements, a mixture of both is observed but the ratio determines the dominant factor.

2.3 Black Soot in Port Harcourt

Due to the city's heavy reliance on oil exploration, this has not been mitigated to date; however, the ratio varies seasonally. During the dry season, it seemed to be more pronounced than during the rainy season. The major sources of black soot in Port Harcourt are mostly anthropogenic activities. Examples are gas flaring by the oil and gas industry, burning of crude by illegal refineries, burning of tyres, bombing of illegal refineries, and burning of asphalt. However, a paper by the National Environmental Standards and Regulations Enforcement Agency (NESREA) [12] on the "Impact of air pollution on the environment in Port Harcourt" inferred that the most likely reason for the prevalent soot is due to poorly maintained public transport diesel buses within the city, thermal power stations, and industrial enterprises. The black soot in Port Harcourt is more potent during the early hours of the day, which suggests that it is highly due to illegal refineries and the destruction of illegal refineries, which is done at that time of the day.

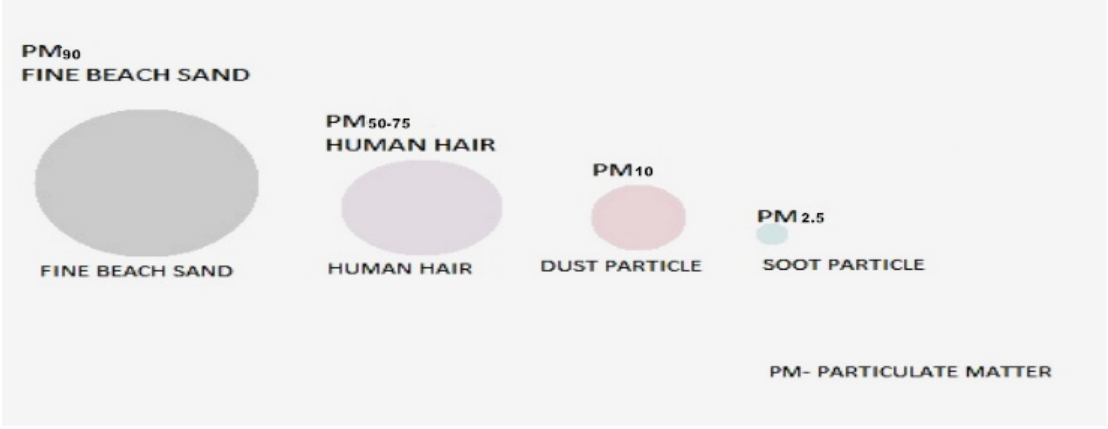

Figure 2. Sizes of particulate matter.

Figure 3. Depicting black soot in Port Harcourt.

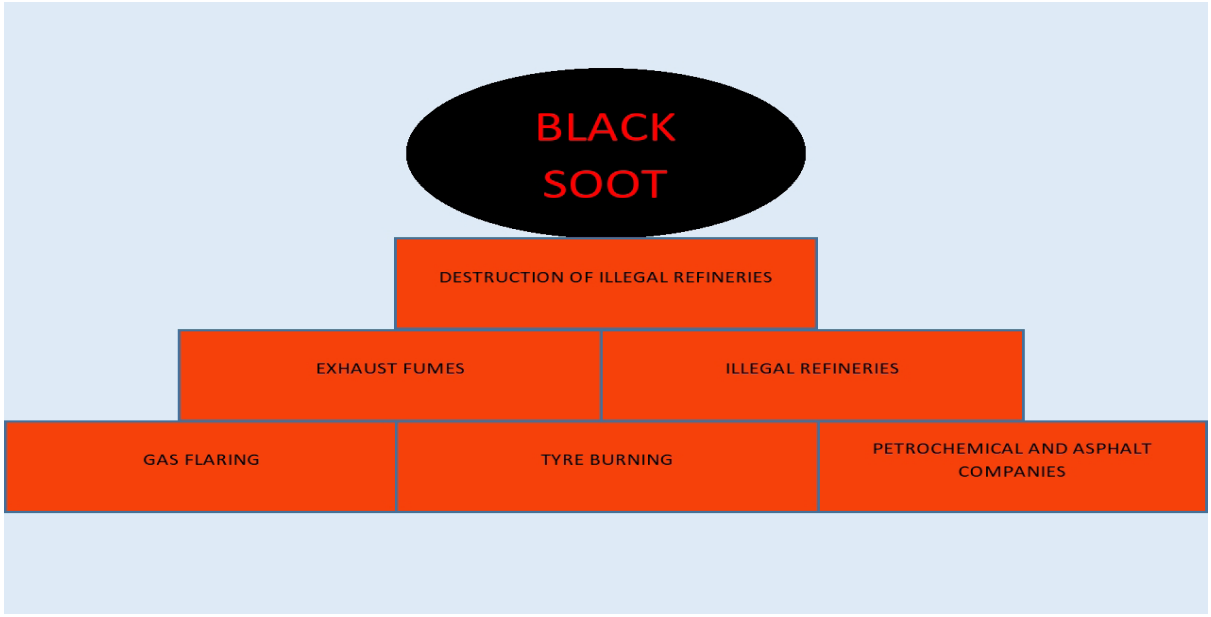

Figure 4. Sources of black soot.

2.4 Health Implications of Black Soot

Exposure to black soot can lead to a generation of cancerous cells in different body tissues by DNA methylation and histone modification, which provokes a lack of control over cell growth, changes in nuclear factor kappa B (this regulates cellular differentiation in the body) and trigger C-FOS activation (production of oncogene which overly expresses in many cancers).

Black soot can lead to an alteration in the expression of endothelia molecules or VCAM (vascular cell adhesion molecule). This can trigger various forms of cardiovascular malformation such as coronary heart disease, cardio myopathes and ischemic changes.

Black soot can also affect the respiratory system by affecting the eosinophyl and mast cell infiltration which leads to fibroblast activation, epithelial cell hyperplasia and deposition of extracellular matrix proteins which disintegrates into loss of lung functions or malformation of lung tissues.

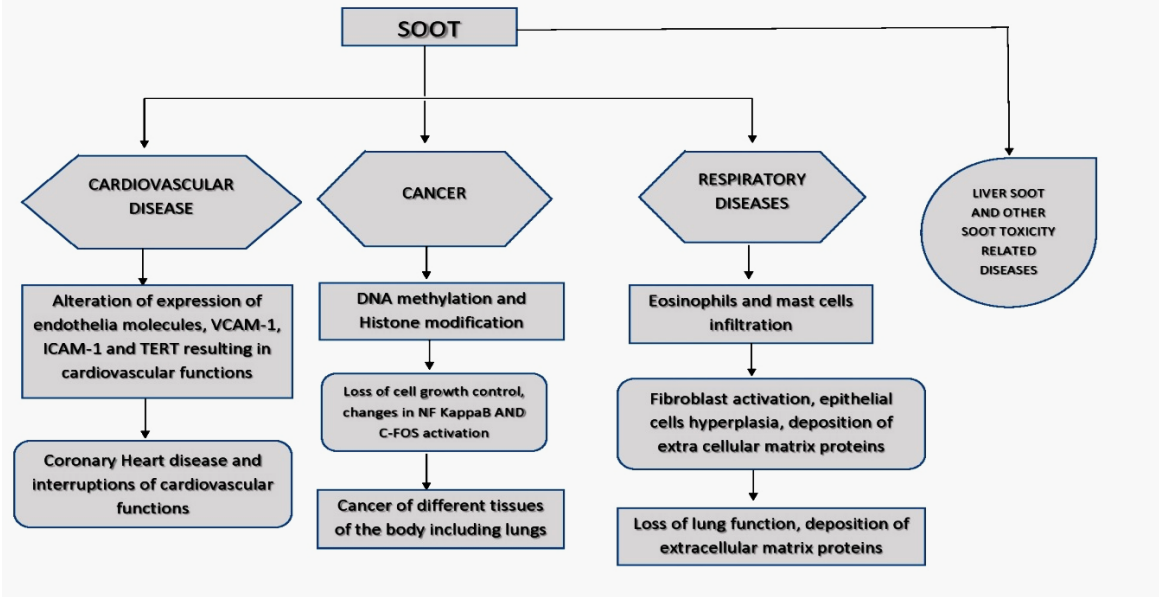

Figure 5. Implications of black soot by Niranjan et al. [10].

Table 1. Health effects of black soot components.

S/N	CHEMICALS FOUND IN THE "BLACK SOOT"	KNOWN HEALTH ADVERSE EFFECT
1.	THE PARTICULATE MATTER (PM)	Particulate Matter particles are >2.5 microns as such can and often do travel deep into the human body and sometimes are absorbed into the blood vessels. They are carcinogenic and often result in hypertension, lung liver and heart diseases. On the skin it is often an irritant, that causes allergic reactions to the eyes, nose, skin diseases.
	THE POLYAROMATIC HYDROCARBONS (PAH)	These are hydrocarbons found in black soot, they are persistent in nature, if introduced into the body system. they tend to remain in the system for a very long time without significant degrading which causes cancer in almost every part of the body.
2.	**GASES**	
	CARBON OXIDES	Heart and Respiratory diseases are common due to exposure to a certain limit of carbon oxide exposure. Dizziness and asphyxiation in extreme cases are also observed.
	SULPHUR OXIDES	Respiratory and heart diseases are generally observed including asthma.
	NITROGEN OXIDES	Hypertention and respiratory diseases often occur.
3.	**METALS**	
	NICKEL	The nickel itch is a common effect of nickel, respiratory, cardiovascular and stomach diseases are common also.
	LEAD	In acute cases shut down of nervous system, impairment of the brain also occurs.
	COBALT	Carcinogenic, causes ulcers and lung disease.
	COPPER	Kidney and liver disease, carcinogenic.
	CHROMIUM	Cardiovascular diseases are carcinogenic and often causes infertility.

Over 2 million deaths yearly are credited to air pollution [10], due to small particulate nature of black soot it travels deep into the human body, some consisting of PAH (poly aromatic Hydrocarbon) which is carcinogenic [10].

3. Material and Method

3.1 Measurement of TSP

Mini Vol Air Samplers were used to collect particulate matter (PM_{10} & $PM_{2.5}$) from the air at six different locations (East-West Road Uniport Junction, GRA Junction, Trans Amadi Slaughter roundabout, Rumuomasi Roundabout, Abuloma Jetty, and New Road Borokiri). To trap the particles, quartz filter papers with a diameter of 47 mm and high purity and efficiency were used. Prior to and after sampling, the Whatman quartz fiber filter papers on which the particles were trapped were stabilized in a desiccator for at least 24 hours to remove any moisture. The quartz filter papers were weighed before and after sampling, and the difference in weight (W2–W1) was used to calculate particulate matter concentrations in g/m^3 using the USEPA method for calculating PM10 (USEPA, 1999).

$$(\text{TSP})\ \mu g/m^3 = \frac{W_2 - W_1}{Q \times T} \times 10^6 \times 10^3$$

where:

W_1 = the initial weight of clean filter paper (g)

W_2 = the final weight of the exposed filter paper (g)

Q = average sampling rate (flow rate), m^3/min

T = Time (hours)

10^6 = g to g/m^3 conversion

10^3 = L to m^3 conversion

"The miniVol samplers' flow rates were set to 5.0 L/min." On each monitoring site, sampling was carried out over a twenty-four-hour period (Figure 6). During the sampling period, six (6) samples were collected from six monitoring locations for particulate matter characterization. Each sampling site received a sample identification in order to identify samples collected from each site. The sample identifications were created using the first letter of each sampling site's name, followed by the date of sampling (in subscript). For example, U17/09/18 identifies a sample collected on February 17th, 2020 at East West Road Uniport Junction.

Heavy metal analyses were performed at the Century Laboratory in Port Harcourt.

Figure 6. MiniVol air sampler.

3.2 TSP Extraction and Determination of Heavy Metals

Shimadzu Atomic absorption spectrophotometer was used to determine heavy metal concentrations in TSP (model AA-6650 Series Agilent Technologies). For the extraction process, the USEPA method IO-3.1 (USEPA, 1999) was used.

To remove heavy metals, the TSP-loaded filters were extracted in an acid mixture. This acid mixture was composed of hydrochloric acid and nitric acid in a 3:1 ratio. Each filter paper was carefully placed in a Teflon tube, and 10 mL of the acid mixture was added slowly to cover the samples. The Teflon tubes were sealed and placed in stainless steel bombs, which were then heated at 150 °C for 6 hours on a hot plate.

After allowing the digested samples to cool to room temperature, they were filtered and transferred into polypropylene graduated tubes. The Teflon tubes were rinsed three times with deionized water, filtered, and the contents were mixed with the digested sample in the polypropylene tubes. The resulting solution was diluted to 30 mL with deionized water. The flame atomic absorption spectrophotometer was then used to analyze heavy metals (FAAS). The same method as described for the exposed filter paper was used to prepare an unexposed filter paper as a blank. FAAS detection limits for cadmium and nickel were 0.002 gm^{-3} and 0.001 gm^{-3}, respectively. The detection limits for lead and mercury were 0.009 gm^{-3} and 0.001 gm^{-3}, respectively.

The following equation was used to convert metal concentration units from mg/L to g/m^3:

$$\text{Metal concentrations } (\mu g/m^3) = \frac{(C_1 - C_2) \times v}{W_t} \times 10^{-6}$$

where:
C_1 = metal concentration in the sample solution (mg/L)
C_2 = metal concentration in the blank filter solution (mg/L)
V = sample solution volume (mL)
W_t = particle weight on quartz filter paper (g)
10^{-6} = grams (g) to cubic meters (m^3) conversion

PAHs Analysis

The air filter particulate samples were extracted using USEPA 355 °C standard method. The filter paper was shredded and weighed into a 100 mL beaker made of borosilicate material and 5 mL of dichloromethane was added to the sample. The beaker and the content were placed in a sornicator to extract the hydrocarbons for 20 minutes. The extract was filtered into an extraction bottle, and the process was repeated to recover any adherent hydrocarbon content that was left during the first extraction. The total extract obtained was concentrated to 1 mL prior to GC/FID analysis I in accordance with USEPA 8015C standard method. The GC/FID was calibrated using 35 components TPH standards, manufactured by ACUU standard USA. The model of the Agilent GC/FID is 6890N series. The concentration of TPH was calculated as follows:

The air volume is calculated from the periodic flow reading taken during sampling using the following equation:

$$QXT = V$$

where:
Q denotes the average flow rate of sampling in m^3/minutes
T = sampling time in minutes
V = total sample volume in m^3 at ambient conditions

C (g/m^3 = Cs*Ve/V_1*Vs) gives the concentration of TPH compound in g/m^3 in the air sampled.
Where Cs concentration of TPH in g/mL is recorded by capital GC in the sample extract.

3.3 Data Analysis

Correlation, time series analysis and scatter plot will be used in the analysis of the data.

4. Results and Discussion

4.1 Results

4.1.1 PM_{10} Concentrations

Figure 7 compares the mean $PM_{2.5}$ and PM_{10} concentrations at the various sampling sites to WHO guideline values.

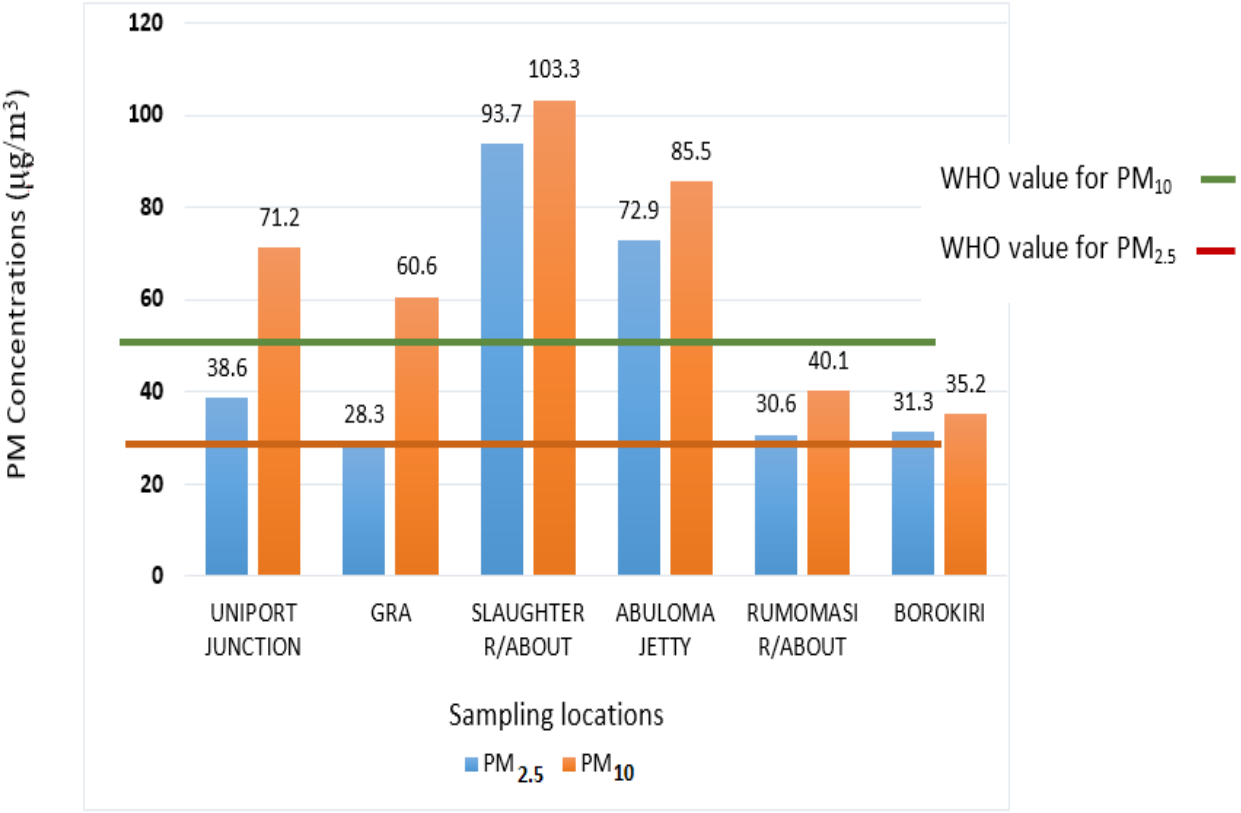

Figure 7. Mean $PM_{2.5}$ and PM_{10} concentrations at the sampling sites.

$PM_{2.5}$ and PM_{10} values recorded at all six sampling sites exceeded the 24-hour guideline values of 25 µg/m^3 and 50 µg/m^3 respectively from WHO. Slaughter roundabout recorded the highest mean PM_{10} concentrations (103.30 µg/m^3) followed by Abuloma jetty (85.50 µg/m^3), Uniport Junction (71.2 µg/m^3) , GRA(60.60 µg/m^3) , Rumomasi R/about (40.10 µg/m^3) and New road Borokiri (35.2 µg/m^3). For $PM_{2.5}$, Slaughter roundabout recorded the highest mean concentrations (93.70 µg/m^3) while New road Borokiri recorded the least mean concentration (31.3 µg/m^3).

$PM_{2.5}$ & PM_{10} concentrations recorded at Slaughter roundabout are the highest probably due to heavy vehicular traffic and mass burning in the slaughter while the least PM concentration is at GRA possibly due to low industrial activity. Meanwhile the overall mean $PM_{2.5}$ and PM_{10} concentration for the six sites respectively are 49.23 µg/m^3 and 65.98 µg/m^3.

Table 2. Daily $PM_{2.5}$ & PM_{10} concentrations at the sampling sites.

SAMPLING SITE	$PM_{2.5}$ MEAN (µg/m^3)	PM_{10} MEAN (µg/m^3)
UNIPORT JUNCTION	38.6	71.2
GRA	28.3	60.6
SLAUGHTER R/ABOUT	93.7	103.3
ABULOMA JETTY	72.9	85.5
RUMOMASI R/ABOUT	30.6	40.1
NEW ROAD BOROKIRI	31.3	35.2

4.1.2 Metal Concentrations at Different Sampling Locations

Metal concentrations measured at various sampling sites were compared to EPA cancer target risk (1 in one million) and European Union air quality standards.

As shown in Table 3, the highest concentration of lead is 0.532 g/m^3 at Abuloma jetty, which is slightly higher than the European Union AQS guideline value of 0.5 g/m^3 and also higher than the EPA cancer target risk of 0.03 g/m^3.

Table 3. The lead (Pb) concentrations in g/m^3 at the various sampling sites.

Sampling Site	Mean	Reference guideline/value
UNIPORT JUNCTION	<0.009	
GRA	<0.009	
SLAUGHTER R/ABOUT	0.490	0.5 µg/m^3 (EU AQS)
ABULOMA JETTY	0.532	0.03 µg/m^3 (EPA cancer TR)
RUMOMASI R/ABOUT	0.021	
BOROKIRI	0.017	

The mean Concentrations of Mercury for the six sampling locations were below 0.001 µg/m^3 which is below 0.014 µg/m^3 (US EPA National Ambient levels at urban sites) as shown in Table 4 below.

Table 4. Mercury (Hg) concentrations in µg/m^3 at the various sampling sites.

Sampling Site	Mean	Reference guideline/value
UNIPORT JUNCTION	0.001	
GRA	0.001	0.014 µg/m^3 (US EPA National ambient Air concentration for urban environment)
SLAUGHTER R/ABOUT	0.001	
ABULOMA JETTY	0.001	
RUMOMASI R/ABOUT	0.001	
BOROKIRI	0.001	

From Table 5 shown below, the highest mean Concentration of cadmium is 0.544 µg/m^3 at slaughter roundabout which is below 0.6 µg/m^3 (US EPA National Ambient levels at industrial sites) but above EPA cancer target risk (1 in one million) of 0.0014 µg/m^3.

Table 5. Cadmium (Cd) concentrations in µg/m^3 at the various sampling sites.

Sampling Site	Mean	Reference guideline/value
UNIPORT JUNCTION	0.002	
GRA	0.002	0.6 µg/m^3 (US EPA National ambient Air concentration for industrial environment) 0.0014 µg/m^3 (EPA (cancer TR)
SLAUGHTER R/ABOUT	0.544	
ABULOMA JETTY	0.41	
RUMOMASI R/ABOUT	0.011	
BOROKIRI	0.011	

From Table 6 below, the highest mean concentration of chromium is 0.338 µg/m^3 at slaughter roundabout which is below 0.4 µg/m^3 (US EPA National Ambient levels at industrial sites).

Table 6. Chromium (Cr) concentrations in µg/m^3 at the various sampling sites.

Sampling Site	Mean	Reference guideline/value
UNIPORT JUNCTION	0.012	
GRA	0.01	0.4 µg/m^3 (US EPA National ambient Air concentration for industrial environment)
SLAUGHTER R/ABOUT	0.338	
ABULOMA JETTY	0.274	
RUMOMASI R/ABOUT	0.002	
BOROKIRI	0.009	

From Table 7 below, the highest mean Concentration of Nickel is 0.407 µg/m^3 at Abuloma jetty which is above 0.17 µg/m^3 (US EPA National Ambient levels at industrial sites) and 0.01 µg/m^3 (EPA cancer target risk for 1 in one million).

Table 7. Nickel (Ni) concentrations in µg/m^3 at the various sampling sites.

Sampling Site	Mean	Reference guideline/value
UNIPORT JUNCTION	0.017	
GRA	0.001	0.17 µg/m^3 (US EPA National ambient Air concentration for industrial environment) 0.01 µg/m^3 (EPA cancer TR)
SLAUGHTER R/ABOUT	0.432	
ABULOMA JETTY	0.407	
RUMOMASI R/ABOUT	0.005	
BOROKIRI	0.016	

4.1.3 Heavy Metals in Particulate Matter Fraction

From Figure 8 below, it could be observed that the total PM concentration recorded across the six sampling sites constitutes 30% lead, 27% cadmium, 25% Nickel, 18% Chromium and 0% mercury. The most abundant metal in PM fraction is lead.

The pie chart shows the percentage composition of heavy metals in the PM fraction across the six sampling sites.

4.1.4 Correlation between Particulate Matter Concentration and Meteorological Parameters

From Figure 9 below, we can see a strong positive relationship between $PM_{2.5}$ and PM_{10} (r = 0.87) which can also be seen in Figure 9 straight line. We can see that $PM_{2.5}$ and PM_{10} have a weak but positive correlation with relative humidity and wind speed respectively. Meanwhile $PM_{2.5}$ and PM_{10} (r = –0.19, r = –0.20) have a weak and negative correlation with temperature respectively.

4.1.5 Correlation between Heavy Metals and Meteorological Parameters

Figure 10 below shows there is a strong positive correlation between heavy metals and PAHs. We can also see a weak and positive correlation between relative humidity, wind speed and heavy metals. While there exists a weak and negative relationship between heavy metals and temperature. Important to state is also the negative relationship that exists between wind speed, temperature and PAHs. But relative humidity is positively correlated with Poly Aromatic Hydrocarbons (PAHs).

4.1.6 Trend Analysis Concentration of $PM_{2.5}$ & PM_{10} Varies with Meteorological Parameters

Figure 11 shows that high particulate matter concentration occurs at a wind speed of 0.6 m/s to 0.62 m/s while the least PM concentration occurred at a wind speed range of 2.34 m/s to 2.86 m/s.

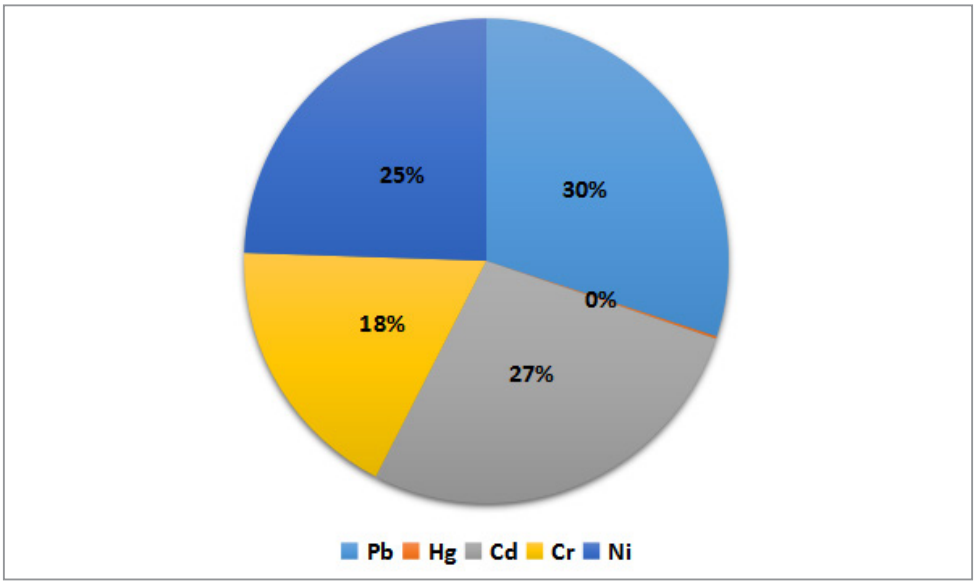

Figure 8. Percentage concentrations of heavy metals in PM fraction.

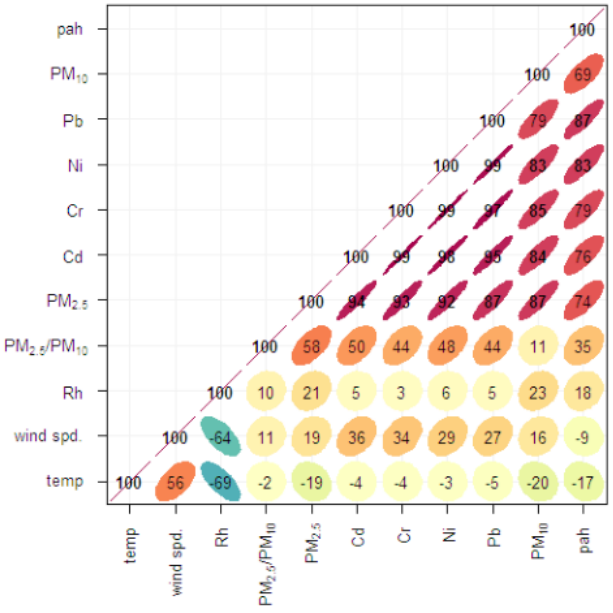

Figure 9. Correlation plot showing the relationship between pollutant and meteorological parameters.

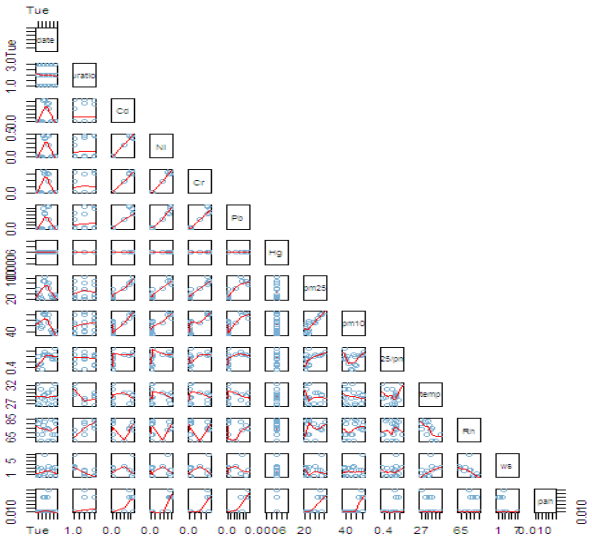

Figure 10. Pair plot showing correlation between heavy metals and meteorological parameters.

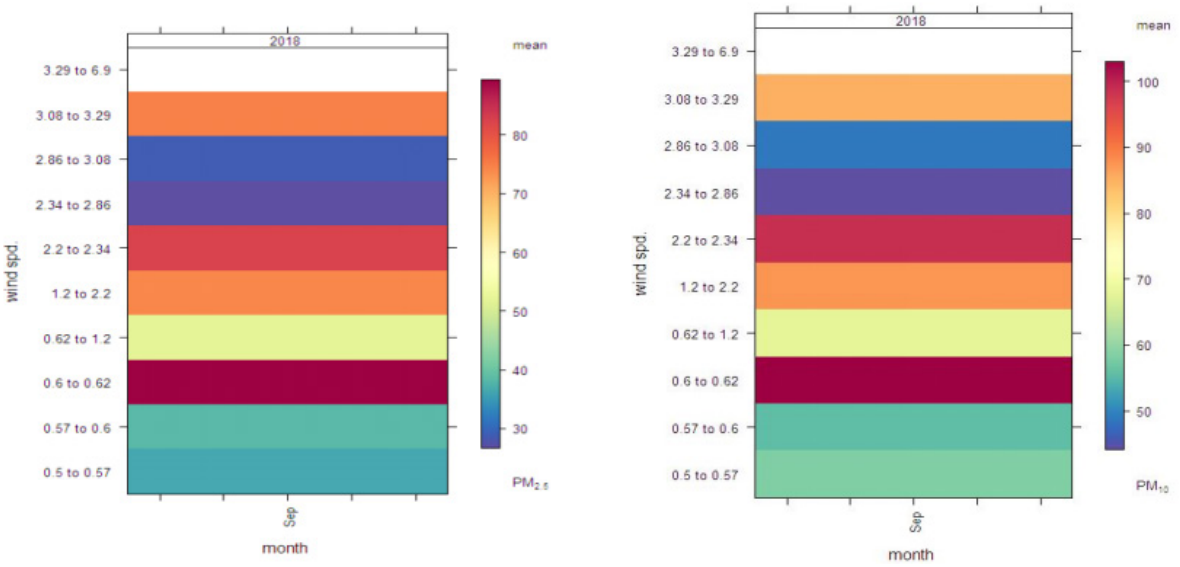

Figure 11. Trend plot showing variation in $PM_{2.5}$ & PM_{10} against wind speed.

Figure 12 shows that high particulate matter concentration occurs at a temperature range of 27.1 °C to 28.5 °C while the least PM concentration occurred at a temperature range of 30.6 °C to 31.5 °C.

Figure 13 shows that high particulate matter concentration occurs at a relative humidity range of 78.5% to 80.1% while the least PM concentration occurred at a relative humidity range of 61.5% to 68.1%.

4.1.7 Trend Analysis Concentration of $PM_{2.5}$ & PM_{10} Varies with Time

The diurnal (hourly) plot shows that $PM_{2.5}$ and PM_{10} concentrations are highest in the evening and lowest in the afternoon. Meanwhile, the day of the weak plot shows that the highest PM concentration was on Wednesday at the slaughter roundabout monitoring location. The calendar plot in Figures 14 and 15 equally confirmed that Wednesday 19th September experienced the highest particle pollution at Slaughter roundabout.

Figure 16 shows a ratio of 0.79 in the morning, 0.63 in the afternoon and a ratio of 1.1 in the evening depicting predominance of $PM_{2.5}$ fraction in all the areas in the day. But the mean $PM_{2.5}/PM_{10}$ ratio is 0.74.

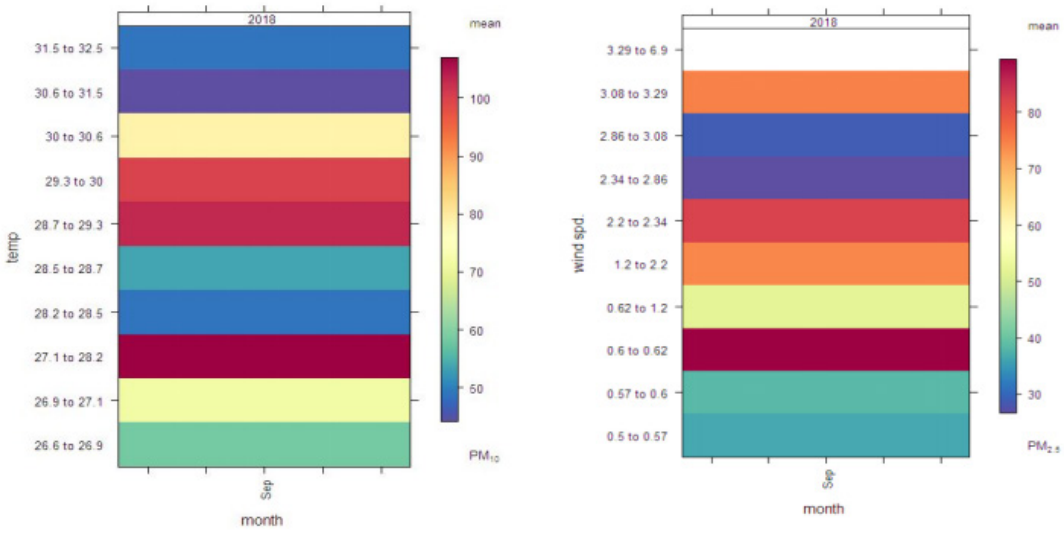

Figure 12. Trend plot showing variation in $PM_{2.5}$ & PM_{10} against temperature.

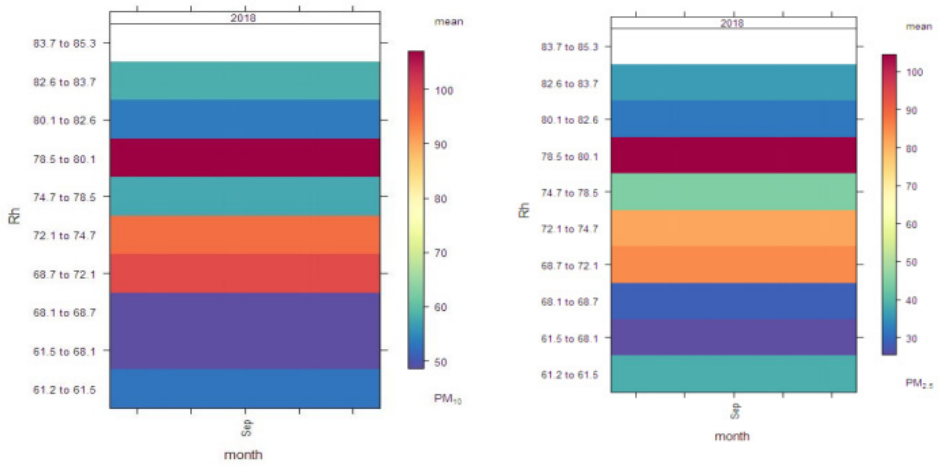

Figure 13. Trend plot showing variation in $PM_{2.5}$ & PM_{10} against relative humidity.

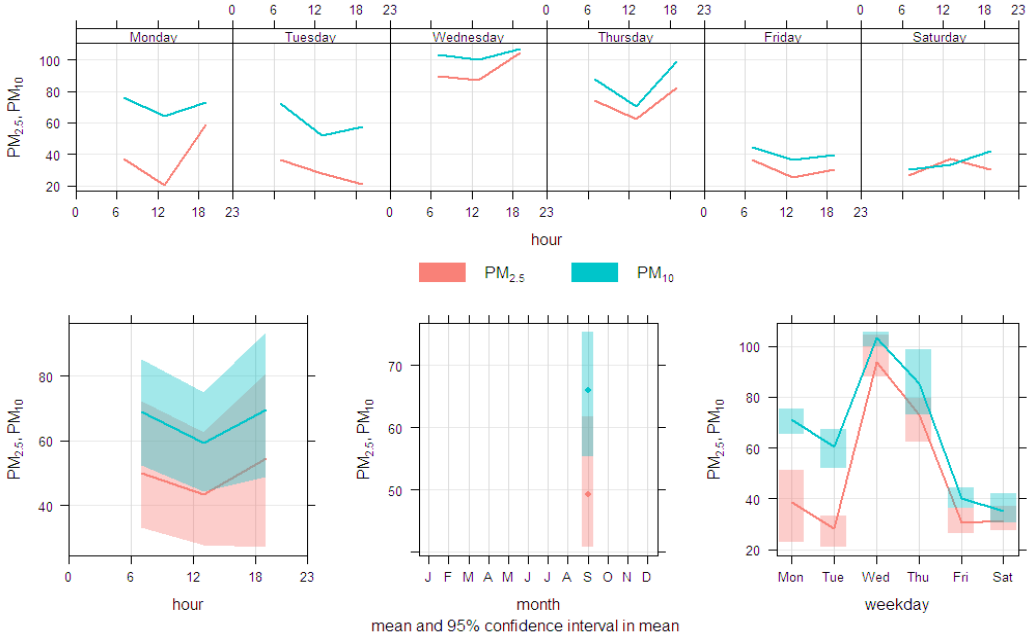

Figure 14. Time variation plot showing how $PM_{2.5}$ & PM_{10} varies with time at the monitoring sites.

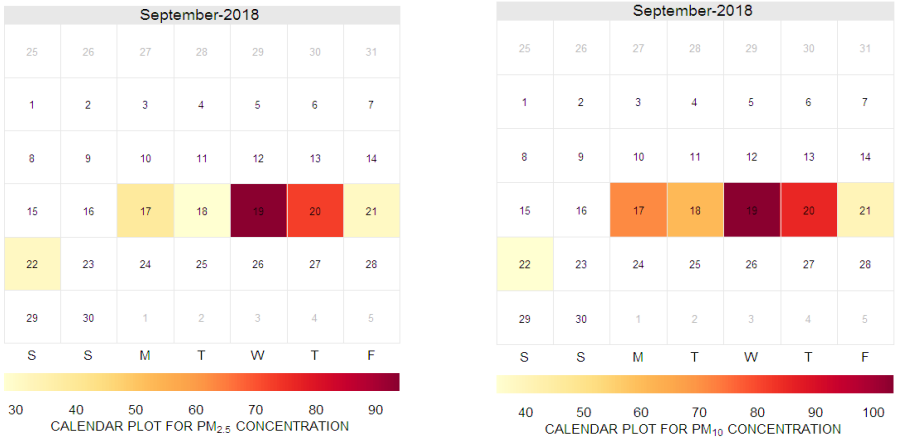

Figure 15. Calendar plot for $PM_{2.5}$ & PM_{10} concentration.

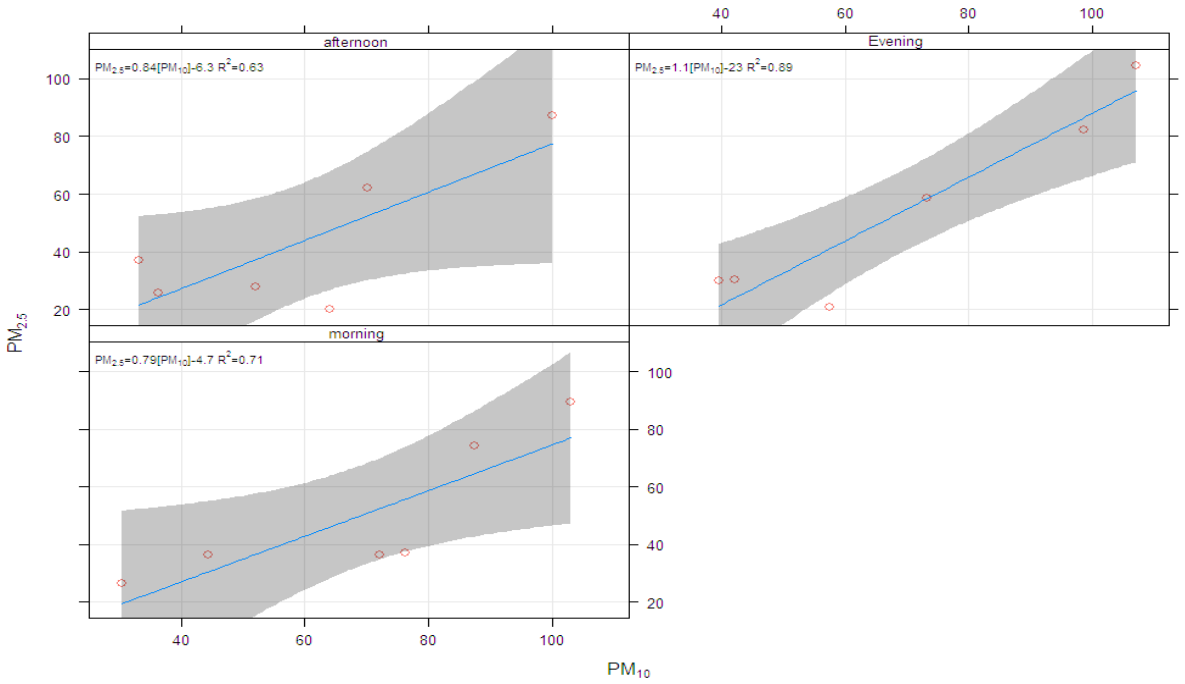

Figure 16. Scatter plot showing $PM_{2.5}/PM_{10}$ ratio.

4.2 Discussion

4.2.1 Particulate Matter

From Figure 7, it could be deduced that Slaughter roundabout had the highest mean $PM_{2.5}$ and PM_{10} concentrations of 103.3 µg/m^3 and 93.7 µg/m^3 respectively. GRA monitoring recorded the least $PM_{2.5}$ (28.3 µg/m^3). From Figure 7 it could be seen that $PM_{2.5}$ and PM_{10} concentrations for the six locations are above the WHO recommended value of 25 µg/m^3 and 50 µg/m^3 in 24 hours. It then means that these locations are non-attainment areas with particle pollution.

4.2.2 Heavy Metals Concentration in Particulate Mater

From Figure 8 above, it could be observed that the total PM concentration recorded across the six sampling sites constitutes 30% lead, 27% cadmium, 25% Nickel, 18% Chromium and 0% mercury. The most abundant metal in PM fraction is lead.

From Table 3, the highest concentration of lead is 0.532 g/m^3 at Abuloma jetty, which is slightly above the European Union AQS guideline value of 0.5 g/m^3 and also above the EPA cancer target risk of 0.03 g/m^3. All the sites have a value below the reference value except for Slaughter junction, which has the highest value. The high value of lead at the location can be attributed to the burning of oil and leaded waste. It is a serious public health concern because, at a high exposure level, most organs and systems, such as the kidneys and central nervous system, are injured.

According to Table 5, the highest mean concentrations of cadmium are 0.544 g/m^3 at the slaughter roundabout, which is less than 0.6 g/m^3 (US EPA National Ambient levels at industrial sites) but greater than the EPA cancer target risk (1 in one million) of 0.0014 g/m^3. According to the USEPA, it is carcinogenic to humans. Prolonged exposure to cadmium may cause renal dysfunction which may in turn lead to devastating bone disease in people with risk factors like poor nutrition. People who live in cadmium-polluted areas are more likely to develop diseases such as osteoporosis and have a higher risk of fractures. Vehicle exhaust emissions, including tyre abrasion; open burning of municipal waste containing Ni-Cd batteries; and plastics containing cadmium pigments are all potential sources of cadmium.

According to Table 4, the mean Mercury concentrations for the six sampling locations were less than 0.001 g/m^3, which is less than 0.014 g/m^3 (US EPA National Ambient levels at urban sites). Except for regional "hot spots", mercury levels in outdoor air are typically in the order of 0.005 g/m^3-0.010 g/m^3 and thus are marginal when compared to exposure from dental amalgam, according to WHO guidelines. At these air levels, exposure to mercury from outdoor air is not expected to have a direct impact on human health. However, to avoid potential health effects in the near future, mercury levels in the ambient air should be kept as low as possible.

According to Table 7, the highest mean concentration

of nickel is 0.407 g/m^3 at Abuloma jetty, which is higher than 0.17 g/m^3 (US EPA National Ambient levels at industrial sites) and 0.01 g/m^3 at other locations (EPA cancer target risk for 1 in one million). Nickel exposure has been linked to chronic bronchitis, reduced lung function, lung cancer, and nasal sinusitis. The EPA has determined that nickel refinery dust and nickel subsulfide are carcinogens to humans. The primary source of anthropogenic nickel emissions is oil combustion, which could explain the high concentration at Abuloma jetty.

According to Table 6, the highest mean concentration of chromium is 0.338 g/m^3 at the slaughter roundabout, which is less than 0.4 g/m^3 (US EPA National Ambient levels at industrial sites).

Chromium (III) is a trace element that is required by both humans and animals. Chromium(VI) compounds are toxic and carcinogenic, but the potencies of the various compounds vary greatly. Because the bronchial tree is the primary target organ for the carcinogenic effects of chromium (VI) compounds, and cancer is primarily caused by inhalation exposure, uptake in the respiratory organs is extremely important in terms of cancer hazard and subsequent risk of cancer in humans. According to the IARC, there is sufficient evidence of carcinogenicity in humans for chromium and certain chromium compounds.

4.2.3 Correlation between Particulate Matter Concentration and Meteorological Parameters

From Figure 9 we can see a strong positive relationship between $PM_{2.5}$ and PM_{10} (r = 0.87) which can also be seen in Figure 10 straight line. We can see that $PM_{2.5}$ and PM_{10} have a weak but positive correlation with relative humidity and wind speed respectively. Meanwhile $PM_{2.5}$ and PM_{10} (r = –0.19, r = –0.20) have a weak and negative correlation with temperature respectively. It therefore shows that wind speed and relative humidity slightly increases particulate matter concentration while increase in temperature slightly reduces PM concentration. However, increase in $PM_{2.5}$ gives rise to a corresponding increase in PM_{10} concentration.

4.2.4 Correlation between Heavy Metals and Meteorological Parameters

Figures 10 and 9 show there is a strong positive correlation between heavy metals and PAHs. We can also see a weak and positive correlation between relative humidity, wind speed and heavy metals. While there exists a weak and negative relationship between heavy metals and temperature. Important to state is also the negative relationship that exists between wind speed, temperature and PAHs. But relative humidity is positively correlated with Poly Aromatic Hydrocarbons (PAHs). It shows that PAHs increase as heavy metals increase in particulate matter showing a possibility of related origin. Also, relative humidity and wind speed slightly increase concentration of heavy metals in PM while temperature does not allow heavy metals to bond with PM. Relative humidity increases the concentration of PAHs in particulate matter.

4.2.5 Trend Analysis Showing How Concentration of $PM_{2.5}$ & PM_{10} Varies with Meteorological Parameters

Figure 11 shows that high particulate matter concentration occurs at a wind speed of 0.6 m/s to 0.62 m/s while the least PM concentration occurred at a wind speed range of 2.34 m/s to 2.86 m/s. This indicates that at low wind speed when the atmosphere is relatively stable, they tend to be more PM concentration due to lack of dispersion.

Figure 12 shows that high particulate matter concentration occurs at a temperature range of 27.1 ºC to 28.5 ºC while the least PM concentration occurred at a temperature range of 30.6 ºC to 31.5 ºC. It explains the fact that high temperature aids in air turbulence which consequently disperses the particulate matter.

Figure 13 shows that high particulate matter concentration occurs at a relative humidity range of 78.5% to 80.1% while the least PM concentration occurred at a relative humidity range of 61.5% to 68.1%. It clearly shows that high relative humidity does not support air dispersion instead it encourages suspension of PM in the air.

4.2.6 Trend Analysis Showing How Concentration of $PM_{2.5}$ & PM_{10} Varies with Time

The diurnal (hourly) plot shows that $PM_{2.5}$ and PM_{10} concentrations are highest in the evening and lowest in the afternoon. Meanwhile, the day of the weak plot shows that the highest PM concentration was on Wednesday at slaughter roundabout monitoring location. The calendar plot in Figure 15 equally confirmed that Wednesday 19th September experienced the highest particle pollution at Slaughter roundabout. The reason for high PM concentration in the evening and morning could be attributed to peak hours that entail high vehicular movement. There is a lot of human activities happening at slaughter roundabouts such as vehicular movement, mass burning and other commercial activities which gave rise to high PM concentrations.

4.2.7 PM Ration

According to WHO guidelines $PM_{2.5}/PM_{10}$ ratio within

the range of 0.5-0.8 shows predominance of $PM_{2.5}$ fraction while ratios below show dominance of PM_{10}. Figure 16 shows a ratio of 0.79 in the morning, 0.63 in the afternoon and a ratio of 1.1 in the evening depicting predominance of $PM_{2.5}$ fraction in all the areas in the day. But the mean $PM_{2.5}/PM_{10}$ ratio is 0.74 which is within the WHO range for developing countries. This high $PM_{2.5}/PM_{10}$ ratio is an indication that we have a predominance of $PM_{2.5}$ in the ambient air.

5. Conclusions

The result of the investigation shows the ambient air at the six monitoring sample stations was heavily polluted with $PM_{2.5}$ and PM_{10}. The PM concentrations exceeded the WHO (2010) guideline value, which could be the cause of the current PM episode in Port Harcourt, resulting in asthma, lung cancer, breathing difficulties, and miscarriages among pregnant women, which have affected the health implications of the people living in the environment. However, the constituents of PM contain heavy metals in extremely low concentrations that are unlikely to endanger human health due to their short half-life. Despite the fact that the PM concentrations recorded in this study were extremely high, the metal constituents have a low lifetime risk.

Recommendation

The need for more research to be conducted during both the wet and dry seasons to determine both seasonal and temporal variability, as well as long-term studies to determine the effects of PM on public health.

Conflict of Interest

There is no conflict of interest.

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