Source Identification and Pollution Factors of Elements in $PM_{2.5}$ Samples obtained in Akure, Ondo State, Nigeria

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Abstract

Air quality is a big concern all over the world. It affects both humans and animals in a variety of ways. Air must be quantified to monitor the impact, and the consistency of the air must be determined. Both stakeholders will use the knowledge collected to take effective action. To that end, we've taken measures in Nigeria to measure $PM_{2.5}$, elements, and meteorological parameters, as well as assess their enrichment, contamination, and emission levels. For a total of ten months, samples were collected at three locations in Ondo State, Nigeria: the Federal University of Technology, Akure (FUTA), Oba Ile, and Museum (January to October). The pollution factor (CF), enrichment factor (EF), and pollution load index (PLI), as well as Principal Component Analysis, were used to measure the PM and components (PCA). The average PM concentrations (101 g m^3 (FUTA); 120 g m^3 (Oba Ile); and 176 g m^3 (Museum) were found to be higher than the WHO (35 g m^3) and USEPA (15 g m^3) normal limits. The macro elements (K > Na > Ca > P > Al) were ordered in this order, while the trace elements were ordered in this order: Cu > Fe, > Zn > Ni > Cr > Mn > Pb. PCA listed elements from vehicular activities, biomass burning, dust, and soil as contributing elements. The findings are useful for identifying sources of $PM_{2.5}$, primary, and trace elements, enrichment, contamination assessment, and air pollution index, as well as contributing to regional monitoring programs.

Introduction

In recent decades, globally, one of the most pressing public health concerns has been air pollution (Suriano, 2020; Penza et al., 2018; Suriano, 2015). Atmospheric particulate matter has been linked to negative effects on human health, visibility, and atmosphere, as well as habitats and physical property degradation (United Nations Environmental Programme/World Health Organization (UNEP/WHO, 1994). The scale of atmospheric aerosols affects human health and the climate. As a result, studies of size-segregated particulate matter are required to gain a better understanding of the effects of aerosols. Coarse ($PM_{2.5}$) and fine (PM, fractions) size segregations are the most common. Different sources and atmospheric residence periods can exist for these fractions 2.5. As a result, it's critical to comprehend the chemical makeup of the substance. Our understanding of particulate matter's chemical and physical components assists in determining its effects on the atmosphere and people, as well as recognizing and quantifying its natural and anthropogenic origins. It also aids policymakers in developing well-informed policies to combat air pollution (Ezeh et al., 2015). Urban air pollution is typically caused by a complex mix of gaseous and particulate air pollutants such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), fine particulate matter ($PM_{2.5}$), and ground-level ozone (defined as aerodynamic diameter particulate matter ($PM_{2.5}$) (Abulude et al. 2021).

$PM_{2.5}$ exposure has a slew of negative health implications. In exposed populations, there have been increases in morbidity and mortality from infectious, cardiovascular, chronic pulmonary, and neurodegenerative diseases, as well as a decrease in life expectancy (Kim et al., 2015). $PM_{2.5}$ can be breathed into the deepest recesses of the lungs due to its vast surface area, small size, and the fact that it contains a significant amount of toxic properties. It settles on the alveoli and also makes its way into the bloodstream, posing a health risk to humans (Zhang et al., 2016). Ingestion and dermal touch are both ways for $PM_{2.5}$ to reach the human body. Trace elements in $PM_{2.5}$ have been found to play a key role in these negative effects, according to studies. Fe, Co, Ni, Cu, Zn, V, Cr, Mn, As, Pb, and Cd can increase reactive oxygen species production (ROS). ROS in excess can overpower the body's antioxidant defense mechanism, leading to oxidative stress, inflammation, and disease (Sameenoi et al., 2012; Charrier and Anastasio, 2015; Park et al., 2018). As a result, despite accounting for a small fraction of the overall mass of $PM_{2.5}$, trace elements pose a significant threat to human health.

Trace elements are efficient tracers (Querol et al., 2007) and are commonly used as input in receptor modeling studies to help in the interpretation of particular emission sources. The Principal Component Factor (PCA), is one of the versatile

modeling approaches which efficiently uses data and classifies potential source contributions. For the source apportionment of $PM_{2.5}$, this model has been used globally (Ndamitso, et al., 2016; Cesari et al., 2019). The characterization and source detection of trace elements in $PM_{2.5}$ are critical in air pollution prevention and control. These methods have attracted a lot of attention from researchers because they can increase air quality and minimize negative health effects.

To address the problem of air pollution, all stakeholders would need to have working knowledge or policies in place to reduce or eliminate the threat. The best tool – Source Apportionment (SA) must be used in this situation (Yu et al., 2013; Roy and Sigh, 2014; Ndamitso et al., 2015; Feng et al., 2007). The application of a multivariate technique to identify and assign sources to pollutants is known as SA. This method is now widely used throughout the world (Oluyemi and Asubiojo, 2001; Ndamitso et al., 2015). It's used to figure out and quantify how different sources contribute to pollution in the atmosphere. Different levels of information about the sources acting on a particular site and their emission profiles are needed for the technique to work (Kchih et al., 2015; Ndamitso et al., 2015). In Akure, Ondo State, there is very little published work on source apportionment and $PM_{2.5}$. This pattern prompted the study.

Road building, farming, industrial activity, and heavy traffic have all increased in Akure, Nigeria, in recent years. Wind or runoff waters undoubtedly carry metals, gas particles, and dust in these regions. Pollution occurs when these particles are deposited at high concentrations on road shoulders, soils, water, and other materials. Water, air, soil, and food samples are normally enriched concerning a series of metals in certain places according to Shaheen et al., (2016), Alpdogan et al., (2019), Bakyayita et al., (2019). These metals frequently have adverse effects on people and structures. To this effect, it is essential to characterize the distributions and concentrations of these metals and atmospheric deposits in the environment especially air and aquatic.

This study examines the elemental composition of particulate matter ($PM_{2.5}$) in Akure, Ondo State, Nigeria, as well as the source identification. The following are the specific objectives:

i. determining the mass levels of $PM_{2.5}$ in the samples;
ii. determining the mass levels of $PM_{2.5}$ in the samples.
iii. investigating the relationship between PM and weather variables.
iv. using the EDXRF technique, calculate the metal concentrations in PM10.
v. using PCA and an assessment of elements to identify air contaminants sources (Enrichment and Contamination factors, and Pollution load index).

Materials And Methods

The state's capital and largest city, Akure, is also the state's largest city. The city has a population of 421,100 people and is located at 5° 12' 0" East, 7° 15' 0" North, at a height of 353 meters (GeoNames Geographical Database, 2012). Africa/Lagos is the time zone for Akure. Akure is a fast-growing city that serves as a trading hub for cash crops such as cocoa, cola nuts, palm oil and kernels, bitter cola, and citrus fruits.

Within the area, three separate sampling locations (National Museum and Monuments, Oba-Ile, and the Federal University of Technology - FUTA) were chosen (Table 3.1 and Fig. 3.3). These sites serve a variety of industrial, residential, and educational settings. Monthly samplings lasted 8 hours (8 a.m. – 4 p.m.) for ten (10) months (January to October 2018). Thirty (30) samples (ten per sampling area) were collected at the end of the sampling period. GPS Map 76CSX was used to assess the sampling positions (longitude and latitude) (Garmin Ltd, Taiwan).

Table 1
The Sampling Locations

Location no	Location	Description of Sites	No. of samples
1	Oba Ile (SEDInst) (005 14 29.1 E), (07 16 04.4 N)	Residential, traffic, low dense forest area	10
2	The Federal University of Technology, FUTA (Science car park),(005 08 06.5 E), (07 18 07.6 N)	Educational setting low traffic area	10
3	National Museum, (005 11 40.2 E), (07 15 11.6 N)	Commercial, high traffic area	10

PM was collected using a Schlumberger Model M250 “Gent” stacked filter unit sampler (Maenhunt et al. 1993). The samples (10 each) were collected using Whatman Nuclepore filters that had been pre-weighed and pre-conditioned, with flow rates ranging from 16 to 18 L min. Until weighting, the filters were conditioned for 24 hours at °about 25°C and 50% constant humidity. The sampler was positioned at a height of around 1.7 meters so that air circulation around it was not obstructed (average nose level). To prevent filter clogging and keep the flow rate within the sampler's prescribed limits, the effective sampling time was varied. This ensured accurate size fractionation and efficient selection. The findings of the sampling have been published elsewhere (Ezeh et al., 2012). The exposed filters were held in a desiccator until they were analyzed using the XRF technique for elemental analysis.

To stabilize the weight, the filters were placed in a chamber at 20 degrees Celsius and 35 percent relative humidity (RH) for 48 hours. Using an analytical balance, the particulate mass was measured gravimetrically (by measuring the filters before and after exposure) (Model Sartorius Microbalance ME 5 Balance). These parameters were used to measure the mass concentration of PM:

At the Observatory Unit of the Federal University of Technology in Akure, Ondo State, Nigeria, wind direction and speed, rain, and relative humidity (RH) were measured. In the project, the ten-minute interval readings are provided.

The technique of Energy Dispersive X-ray Fluorescence (EDXRF) was used to accomplish this. At a voltage of 25 kV and a current of 50 A, an EDXRF model PX 2CR with an XR-100CR Si-pin Detector and a silver (Ag) anode was used. 300 mg of samples were exposed in the sample holder of the XRF device, which was bombarded by X-ray for 1200 counts or 20 minutes in an external chamber set up, for sample analysis. The sample's characteristic X-ray was detected using a solid-state Si-pin detector system, and spectrum acquisition was performed using an Amptek model multi-channel analyzer (model: AMPTEK – Oxford Eclipse II), while elemental analysis was performed using the International Atomic Energy Agency's thin aim mode (IAEA). Certified micrometer® thin films (Table 3.2) were irradiated for calibration purposes before the study (Ezeh et al., 2017).

Table 2
Calibration results of the equipment before analysis

Element	Certified Values (μg cm^{-2})	Experimental Values (μg cm^{-2})
Ca	47.4	46.5
Fe	46.3	46.1
Pb	52.8	51.3

Calculation

Principal component analysis (PCA) defined by James et al. (2015) was used to classify the sources of the pollutants (PM, Na, Mg, Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Se, Zn, and Pb) (2015). To classify possible sources of emissions in the study area, PCA with VARIMAX rotation was used. Jolliffe et al. (2016) and De La Cruz et al. (2016) identified methods for calculating the number of components (2019).

The enrichment factor (EF) of the element of interest is the ratio of the element's concentration to a reference value. As a reference element, an element with a high concentration in the atmosphere that does not exhibit such properties as antagonism or synergism with the examined element may be used (Gonzalez-Macias et al., 2006; Pandey et al., 2015). Fe was chosen as the study's reference factor because it is the most commonly used for normalization (Bhuiyan et al. 2010; Gowd et al. 2010). This factor was used to measure EF:

Where Ci denotes the concentration of trace elements in the sample, Cref denotes the concentration of the reference element in the sample, Bi denotes the background value of an element of interest, and Bref denotes the background value of the reference element in the study field. The results were categorized into seven classes based on the value of EF: If EF<1 no enrichment,<3 minor enrichment, 3–5 moderate enrichment, 5–10 moderate-to-severe enrichment, 10–25 severe enrichment, 26–50 very severe enrichment, >50 extremely severe enrichment.

Contamination factor (CF) as defined by Dantu (2009) and Bhuiyan et al., (2010) CFs of the elements of interest were used to calculate the overall contamination of soil by the elements (2010). These figures were calculated by dividing the concentration of the element of interest in the sample by the element's background concentration (Hakanson 1980).

Ci is the element i's concentration, and Bi is the element's geochemical background value. The pollution values are 0=none, 1=none to mild, 2=moderate, 3=moderate to heavy, 4=strongly contaminated, 5=strong to very strong, and 6=very strong in increasing order of contamination (Varol, 2011).

The pollution load index (PLI) was created after Tomlinson et al. (1980) used Eq. 8 to compare pollution levels at different sites or at the same site over time. The estimation of the concentration factor obtained by dividing the measured concentration of an element with the background concentration of the same element in shale is used to calculate the PLI (Turekian and Wedepohl 1961).

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Calculation of Air Quality Index

An index for any given pollutant is its concentration expressed as a percentage of the relevant standard, or:

Air Quality Index = ——————————

Where:

100 = The pollutant is currently at a concentration equal to an environmental standard level

Pollutant Standard Level = 50 µg/m3 24 hours of PM10 readings

80 µg/m3 hourly average PM10 reading (Abulude, 2016)

One-way analysis of variance (ANOVA) with Duncan Multiple Range test at 95 percent confidence or p 0.05 was used to analyze the results. The correlation coefficients were determined based on the results. Minitab 16 Statistical Software was used to compute basic descriptions and PCA. Microsoft Excel was used to calculate the enrichment factor, contamination factor, and wind rose.

Results And Discussion

The concentrations of $PM_{2.5}$ measured at Akure are summarized in Fig. 2 during the sampling periods, the mean concentrations of $PM_{2.5}$ ranged from 101 µg m^3 FUTA to 176 µg m^3 Museum. Compared with the results obtained elsewhere in some sub- Sahara mega-cities in Nigeria, the concentrations obtained in this study were lower than 150 to 606 µg m^3 (industrial) and 110 to 460 µg m^3 (high-density residential) reported by Ezeh et al. (2019) and Baoding (192 µg m^3)(Gao et al., 2018), while the mean concentration of PM obtained in this study were higher than the mean values recorded in China (95.53 µg m^3) and Taiwan (13-25.41 µg m^3) by Acciai et al. (2017) and Hwang et al. (2018) respectively. Also higher than that measured in Ulaanbaatar (Mongolia, 92.8 µg m^3) (Gunchin et al., 2019), Košetice (Czech, 13.6 µg m^3) (Pokorná et al., 2018), Terviso (Italy, 44 µg m^3) (Squizzato et al., 2017), and Athens (Greece, 14.2 µg m^3) (Grivas et al., 2018). In comparing the average PM results with the WHO and USEPA standard limits (Fig. 2). It is on note that results obtained in this study are more than three times higher than the limits. This may be dangerous for the vulnerable people living within the vicinities.

Considering the US EPA's index for reporting air quality (AirNow.gov, accessed, 2018) and the $PM_{2.5}$ concentration in the measurement, a daily $PM_{2.5}$ concentration 0–50 is defined as a Good, that in the range of 51–100 is Moderate, that in the range of 101–150 is Unhealthy for Sensitive Groups, 151–200 indicated Unhealthy, 201–300 denoted Very Unhealthily, and 301 and above is Hazardous. The average $PM_{2.5}$ concentrations obtained for FUTA and Oba Ile areas in this study are categorized as Unhealthy for Sensitive Groups and that of museums is categorized as Unhealthy (Table 3). This index implies that members of sensitive groups may experience health effects. The general public is less likely to be affected and also some members of the general public may experience health effects and members of sensitive groups may experience more serious health effects.

Table 3: Air Quality Index of the Selected Sampling Locations

	Air Quality Index					
Sample Locations	Good	Moderate	Unhealthy for sensitive groups	Unhealthy	Very Unhealthy	Hazardous 301 and above
	0 to 50	51 to 100	101 to 150	151 to 200	201 to 300	
FUTA	-	-	102.00±30.00	-	-	-
Museum	-	-	-	169.00±40.00	-	-
Oba Ile	-	-	120.10±30.00	-	-	-

Source: AirNow.gov (Accessed 2018).

Table 4: The Matrix of the PM and Meteorological Data on the Study Area

	FUTA	Museum	Oba-Ile	Rain	Temperature	Wind	Humidity
FUTA	1						
Museum	0.38	1					
Oba Ile	0.20	0.00	1				
Rain (mm)	0.30	**0.89**	**0.78**	1			
Temperature (°C)	**0.60**	**0.66**	**0.72**	0.45	1		
Wind (m/s)	0.35	**0.84**	**0.60**	**0.65**	0.171	1	
Humidity (%)	0.05	0.28	0.31	0.37	0.17	**0.60**	1

Although there was a mild positive association between $PM_{2.5}$ mass concentration and temperature (Table 4). It simply means that as the temperature rises or reduces, $PM_{2.5}$ levels rise or reduce. For the Museum, FUTA, and Oba-Ile sampling sites, wind speed (WS) has a significant association with $PM_{2.5}$ (r = 0.87, r = 0.61, and r = 0.35), with the Museum having the strongest connection. The Museum, FUTA, and Oba-Ile had r values of 0.59, 0.62, and 0.71 for ambient temperature and $PM_{2.5}$ values, respectively. With r values of 0.05 (FUTA), 0.28 (Museum), and 0.31 (FUTA), relative humidity (RH) had a weak relationship with $PM_{2.5}$ mass concentration (Oba-Ile). It was also discovered that the meteorological parameters had relationships based on the findings. Rain (r = 0.67) was found to be related to wind speed. Wind also had a positive (r = 0.50) relationship with humidity. All of these positive correlations suggest that local sources accounted for the majority of the $PM_{2.5}$ deposited.

Table 5: Summary of Weather Data in the Periods of Study (January – October 2018)

	Rain (mm)	Temperature (°C)	Wind Speed (m/s)	Humidity (%)
Mean	3.71	26.10	5.84	77.34
SE Mean	2.62	1.27	0.35	6.81
Std Dev.	1.27	4.01	1.12	11.54
Coef Var.	223.02	15.36	19.13	27.85
Minimum	0.00	19.75	4.00	21.25
Maximum	27.10	31.23	7.63	94.38
Skewness	3.08	-0.25	-0.22	-2.28
Kurtosis	9.63	-1.50	-0.44	5.93

The summaries of wind directions as percentages and directions as the wind rose are shown in Figs. 4. Every month, the wind directions are denoted by the letters 'N' to 'NNW.' Each percentage reflects the percentage of times each wind direction occurred during the study period. The wind blew from the east in January, while it blew in the following directions in the following months: ESE (February), SW (March), WSW (April), WSW (May), S (June), SSW (July), SW (August), SW (September), and SW (October) (SW). The findings suggest that the wind blew primarily from the SW and WSW directions during the sampling period. Table 1 provides a list of weather conditions. 3.71 mm, 26.10 °C, 5.84 m/s, and 77.34 % of the time, respectively, for rain, temperature, wind speed, and humidity. The variance ranged from 1.27 (rain) to 11.54 (humidity). The rain had positive values while others had negatives, according to the skewness results. Negative values were skewed to the left, while positive values were skewed to the right, according to the results. During the study period, the monthly mean wind speed ranged from 4 to 7.63 m/s, while the monthly mean temperature ranged from 19.75°C to 31.23°C, relative humidity ranged from 21 to 94.38 %, and rainfall ranged from zero during the dry

season to 3.5 mm during the wet season (Table 5). The relationships between various meteorological parameters and $PM_{2.5}$ mass concentrations measured during the investigation period were investigated.

Table 6: Elemental Concentrations compared with other countries

Element	*Typical Crustal Rock	Our Study (ng/m^3)		References						
		FUTA	Obafemi	Museum	[a]Saudi Arabia	[b]Nigeria	[c]Czech Republic	[d]China	[e]Taiwan	[f]China
Na	28300	20 (2)	17 (2)	27 (2)	ND – 700	22-2087	-	-	1708.06 -1772.9	-
Mg	20900	11 (3)	14 (2)	17 (3)	ND-2479	39-1518	12.4–299	-	42.80-46.32	-
Al	81300	6 (3)	7 (2)	11 (3)	ND-3572	300 – 21,511	10.2–392	-	23.22–39.19	-
P	1050	11 (5)	14 (5)	18 (4)	ND-61.3	89-1457	-	-		-
S	260	72 (3)	73 (2)	83 (4)	ND-2608.3	2-264	-		-	-
K	25900	82 (5)	88 (5)	76 (4)	ND-47.5	54-3250	-	489.51–20,311.00	-	390
Ca	36300	17 (2)	24 (2)	18 (2)	ND-783.5	159–796	50.1479	136.22–11,187.00	-	190
Ti	4400	14 (2)	26 (3)	35 (4)	-	22-2042			0.8–0.98	
V	135	15 (5)	27 (5)	28 (5)	-	1 33		0.00–58.63	1.35–1.73	26
Cr	100	12 (2)	28 (2)	24 (3)	-	1 25	4.2×10 – 1-10.4	0.29–103.51	0.55–0.87	4.5
Mn	50	13 (2)	17 (2)	25 (3)	ND-3.2	2-249		9.17–293.69	3.90–4.96	32
Fe	50000	45 (5)	52 (5)	47 (4)	ND-79.7	194-15903	50.1–456	247.71–7,685.00	66.08–69.6	410
Ni	75	15 (1)	22 (2)	28 (3)	ND-25.9	1 14		0.13–30.09	0.78–0.9	6
Cu	55	210 (8)	218 (8)	218 (8)	ND-0.4	1 25	2.2–15.6	3.88–191,63	3.92–5.17	12
Zn	70	27 (4)	31 (5)	35 (5)	ND-2.2	7-431	-	54.13–3,867.00	6.00-24.66	120
Se	0.05	ND	ND	ND	-	-	-	1.03–44.11	-	2.6
Pb	13	ND	ND	ND	-	1 69	-	25.06–598.02	-	
Total		570	658	690	-	-	-	-	--	

[a] Rushdi et al. 2013 (Saudi Arabia), [b] Ezeh et al., 2019 (Nigeria), [c] Jandacka and Durcanska, 2019 (Czech Republic), [d] Acciai et al., 2017 (China), [e] Hwang et al., 2018 (Taiwan), [f] Chang et al., 2018 (China), ND – Not Detected

For the Akure sites, the concentrations of major and trace elements in the PM were calculated, and the spatial and temporal variations in concentrations, as well as the enrichment factor of each element, were investigated. The amounts of Se and Pb were below the detection limits of the instrument (ND). The elements had similar differences, so it was believed that they originated from the same location (Furuta et al., 2005; Saliba et al., 2007; Rushdi et al., 2013). The element concentrations for this analysis are summarized in Table 6. The concentrations of elements varied throughout the region, with the highest overall concentrations in the Museum district (Fig. 4). The heavy human and vehicular traffic in the Museum area led to the high concentrations of major and trace elements found there. Main and trace elements were classified into two groups based on their temporal and spatial variation, with group 1 consisting of Na, Mg, Al, K, Ca, Ti, V, P, Cr, Mn, Ni, Zn, and Fe and group 2 consisting of S, K, and Cu. Cu was found in high concentrations in the Oba Ile and Museum regions, while S and K were found in high concentrations throughout the board. The mean concentration of V (15–28 ng m^3), Mn (13–25 ng m^3), Ni (15–28 ng m^3), and Pb (ND) were all within the limits set by the World Health Organization (WHO; 1000 ng m^3, 150 ng m^3, 25 ng m^3, and 500 ng m^3 for V, Mn, Ni, and Pb, respectively), the European Air Quality Directive (EU Directive 2007/107/EC; 20 ng m^3 and 500 ng m^3 for Ni and Pb, respectively), and the NAQQS of China (500 ng m^3 for Pb) (Liu et al., 2020).

The crustal composition (Taylor, 1964) and Fe as the normalizing factor were used to measure EFs for each element. Since Fe is a crustal variable with less anthropogenic impact, it is a good option for a normalizing agent. Elements with an EF close to unity have a strong natural component, while those with a high EF may be anthropogenic or due to other natural sources including marine aerosols. In Fig. 5, the enrichment factor for PM2.5 is shown, and most elements were highly enriched since their average EF values were less than 5. For example, the respective EF values were 0.67–1.02 (Na), 0.08–0.14 (Al), 3.05–3.39 (S), 1.6–3.52 (K), 1 (Fe), 1.33–2.69 (Cr), and 1.23–2.69 (V). Other elements had an EF of less than 7. For example, 0.00 (Se) and 0.00 (Pb) had low enrichment. Its nonanthropogenic origin is indicated by the low enrichment factor, especially of the sea spray elements (Na). The enrichment factor, or EF, is a tool for assessing the chemical structure of airborne particulate matter. It explains the relationship between the concentration of an element (X) in the air and the concentration of a crustal element (such as Al, Ti, or Fe) in the typical continental crust (Hoffmann et al. 1972; Wedepohl 1971; Zoller et al.1983).

The pollution load index (PLI), which had values ranging from 0.1 to 1.2, was also used to categorize ecological risk. The mean PLI value (0.1) in this analysis was much smaller than the threshold (1) and suggested that there were no baseline contaminants or loads similar to background levels (Tomlinson et al. 1980). Because of the low PLI values, no drastic rectification measures are needed in the surrounding areas; however, continued pollution releases can boost these values. The findings showed that ecological risk assessment approaches (PLI) can be used as decision-support mechanisms or instruments for determining the priority of air quality assessment studies.

In the sites, the concentrations of V, Cr, Mn, Fe, Ni, Cu, Zn, and Mn CF are 0.11–0.21, 0.12–0.28, 0.26–0.5, 1, 0.2–0.37, 3.82–3.96, and 0.39–0.5, respectively. Some of the other CF values include Na (0.001), Mg (0.001), Al (0- 8.61E-05), P (0.01–0.017), S (0.28–0.32), K (0.003–0.004), Ca (0.001), and Ti (0.001). (0.003–0.08). Of all the heavy metals, Cr had the lowest FUTA value (0.12), while Cu had the highest (0.22). (0.12). Cu had the highest value at Oba Ile and Museum for all heavy metals, while Cr had the lowest value at FUTA (0.12). (3.96). The following is a list of the average CF values for each metal: Cu > Zn > Mn > Ni > Cr is the order of the elements Cu, Zn, Mn, Ni, and Cr (Fig. 4). There are six stages of CF: 1–2 depletion to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 extremely high enrichment, and > 40 extremely high enrichment (Sutherland, 2000). The results suggest that the CF is somewhere between background and moderate enrichment.

For the PM sample parameters, PCA found five variables with eigenvalues (Table 7). PCA 1, 2, 3, 4, and 5 had 65.5, 65.3, 32.7, 23.2, and 11.5 percent average variation, respectively. Varimax factor (VF) 1 revealed significant loading for Mg, P, Ca, Cr, Fe, Ni, and Zn, indicating input from the burning of automotive fuels, wastes, and tobacco smoke in and around

the museum district, due to the high volume of vehicular traffic and waste generation generated by the market within the area. Without a doubt, there are a lot of smokers in the city, and a lot of people trade their hobbies. This aggravates the danger to the environment. Suffocation and worsening of asthma and chronic bronchitis, as well as respiratory inflammation, eye and mouth pain, and premature death, are all possible health effects. P, Fe, Cu, and K, as well as their sources, which were mostly parented rock material, dust, soil, and fertilizer, were all present in VF2. However, these metals are also used in liming processes, which can result in respiratory problems, metallic dust poisoning, pulmonary fibrosis, lung cancer, dizziness, headaches, bronchitis, stomachaches, diarrhea, vomiting, loss of appetite, kidney and liver damage, and death (Wei et al. 2010). Cu, Ti, and Na loadings were highest in VF3, suggesting biomass combustion, diesel and residual oils, tobacco smoke, and steel non-ferrous alloys manufacturing. In the tannery industry, manganese is used in the form of salts ($MnCO_3$ and $Mn(SO4)_2$) (Tariq et al. 2006). Ca sources from the PM were illustrated by VF4. Plants and animals, as well as the skeletons of animals, teeth, egg shells, coral, and many soils, are major sources of Ca in current PM. Calcium chloride is present in some water, especially seawater, at a concentration of 0.15 percent. Calcium does not occur in nature on its own. Calcium is mainly present in the form of limestone, gypsum, and other minerals. Significant loadings for S were found in VF5, indicating sources related to anthropogenic activities, specifically tire vulcanization. Many vulcanizers work along the streets in these neighborhoods, especially in the Oba Ile and Museum areas. Zinc is a vital trace element in living organisms, but it is insoluble and extremely rare in nature (Alloway 1990).

Table 7: Principal Component Analysis (PCA) of the Samples

	PCA 1	PCA 2	PCA 3	PCA 4	PCA 5
FUTA	**0.79**	0.45	0.43	0.06	0.23
Oba Ile	**0.68**	**0.64**	0.45	0.07	0.05
Museum	**0.67**	**0.52**	0.34	**0.77**	0.07
Na	0.32	0.44	**0.55**	0.05	0.05
Mg	**0.56**	0.45	0.34	0.05	0.04
Al	0.23	0.43	0.23	0.23	0.07
P	**0.65**	**0.51**	0.12	0.34	0.04
S	0.26	0.32	0.23	0.09	**0.62**
K	0.43	**0.55**	0.33	0.08	0.05
Ca	**0.97**	0.48	0.45	**0.5**	0.06
Ti	0.23	0.18	**0.51**	0.09	0.02
V	0.47	0.41	0.05	0.06	0.05
Cr	**0.79**	**0.62**	0.08	0.09	0.03
Mn	0.32	**0.55**	0.45	0.44	0.04
Fe	**0.64**	**0.64**	0.47	0.47	0.03
Ni	**0.55**	0.34	0.34	0.23	0.04
Cu	0.23	**0.56**	**0.6**	**0.5**	0.04
Zn	**0.88**	**0.65**	0.44	0.34	0.03
Se	0	0	0	0	0
Pb	0	0	0	0	0
Eigen Value	6.2	3.9	2.4	2	1.57
Total Variance (%)	65.6	56.3	32.7	23.2	11.5

Conclusion

The $PM_{2.5}$ levels found in this study were higher than those recorded by the WHO, the World Health Organization, and the US Environmental Protection Agency, and some countries in Asia, Europe, and the United States. The PM is dangerous for sensitive groups, according to the AQI of the places. PM2.5's effect on trace and heavy element enrichment, source apportionment, and pollution load index was also investigated. In contrast to previous research on PM performed elsewhere, measured concentrations of macronutrients and heavy metals were higher or lower. Cr, Ni, Cu, Mn, and Zn

were added to the PM. Pollution was minimal in the elements. Anthropogenic and non-anthropogenic origins of PM were identified through multivariate analysis. Metals in the air can be apportioned at the source, which can aid decision-makers in developing management strategies to minimize pollution. The climate should be continually and properly controlled in the locations under study.

Declarations

Declaration of Competing Interest

There are no known competing financial interests in this paper.

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Figures

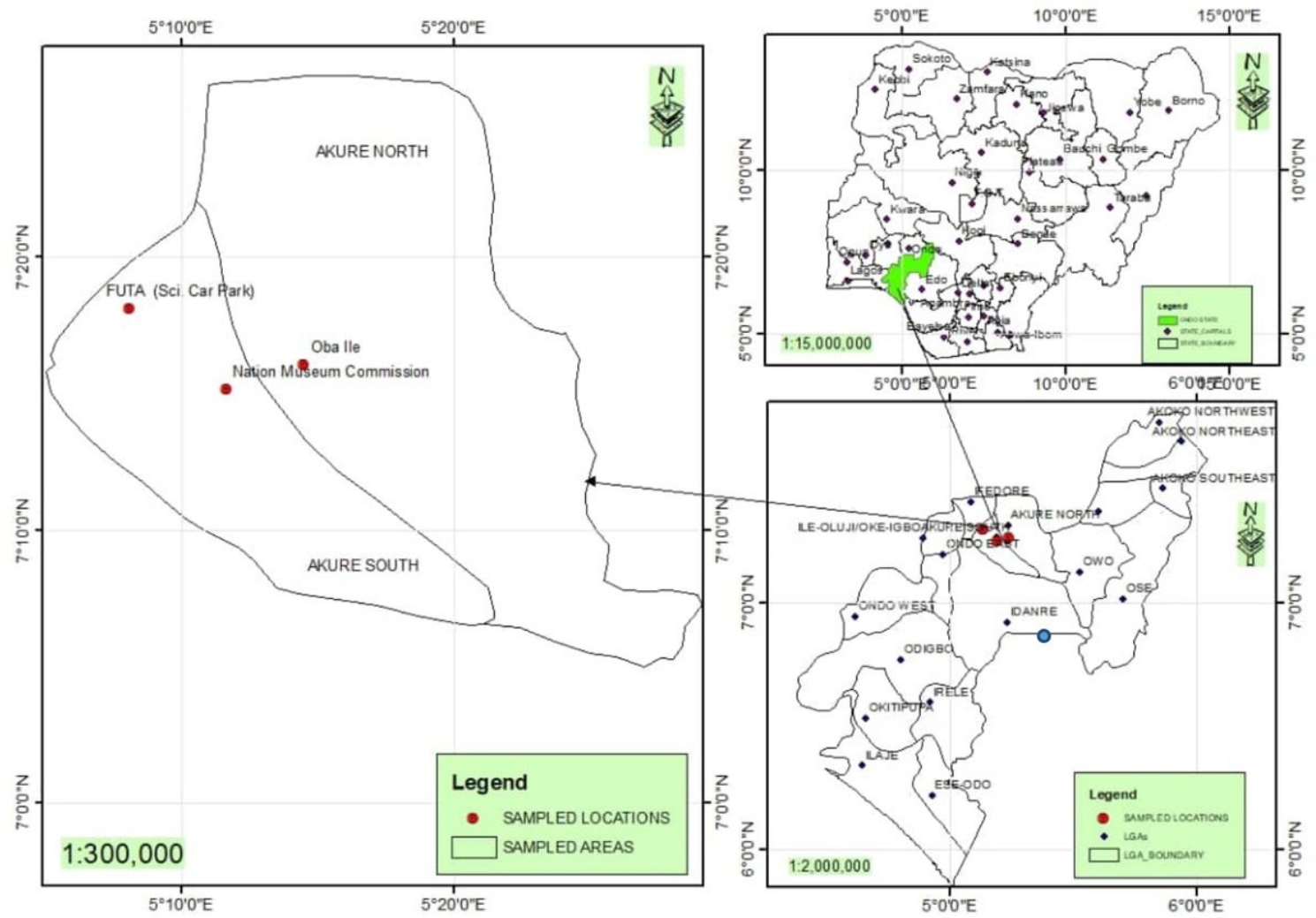


Figure 1

Akure study areas (Source: Field Work, 2018)

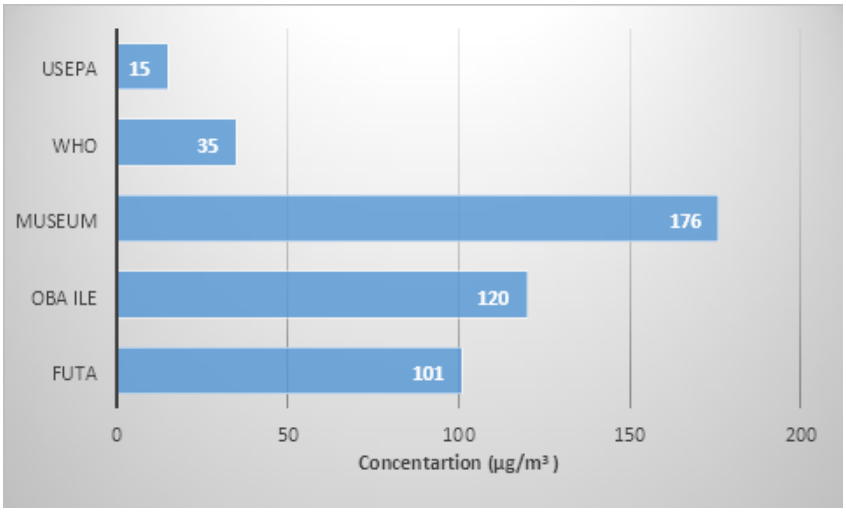


Figure 2

Particulate matter Concentration

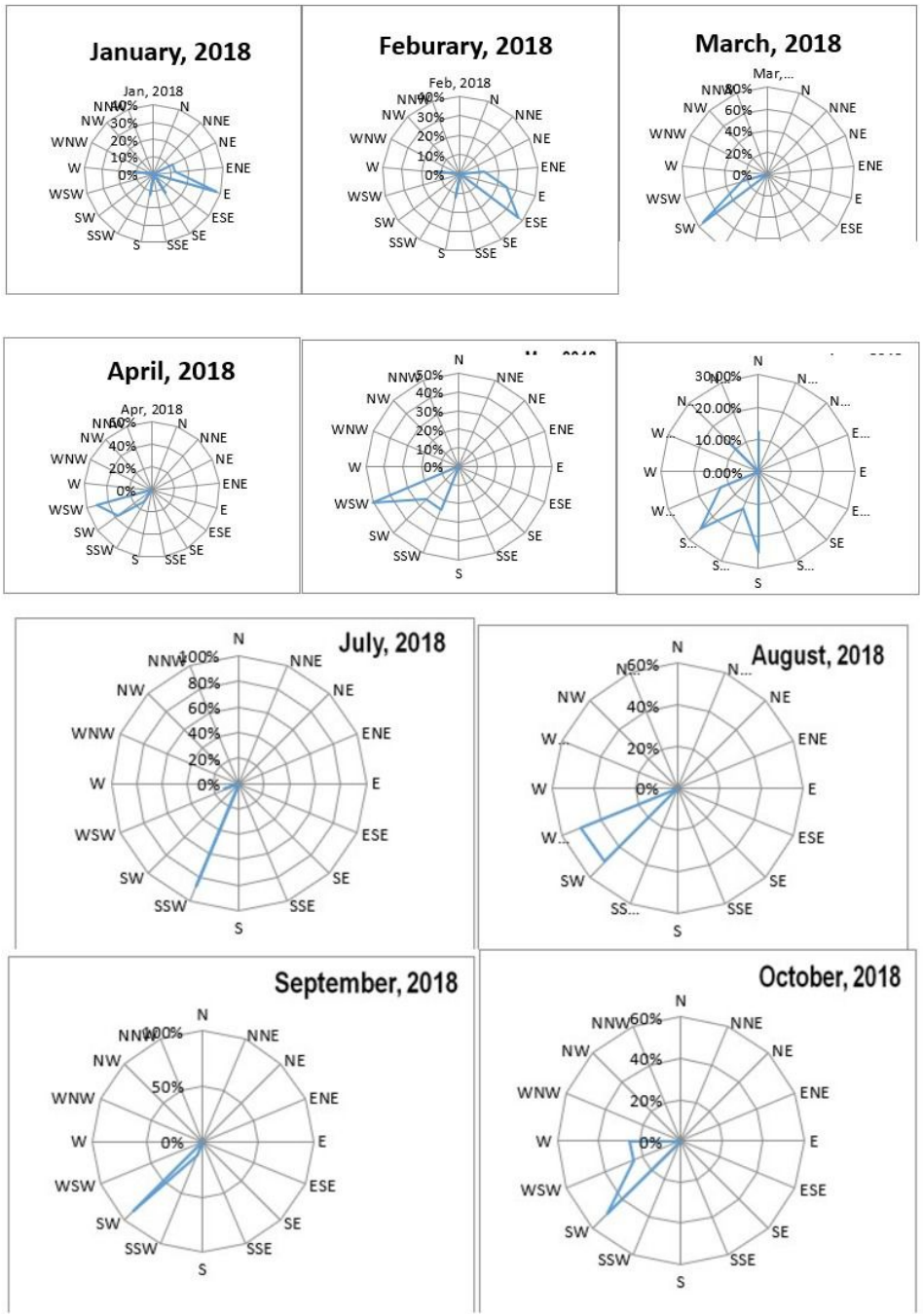


Figure 3

Wind Direction (July – October 2018)

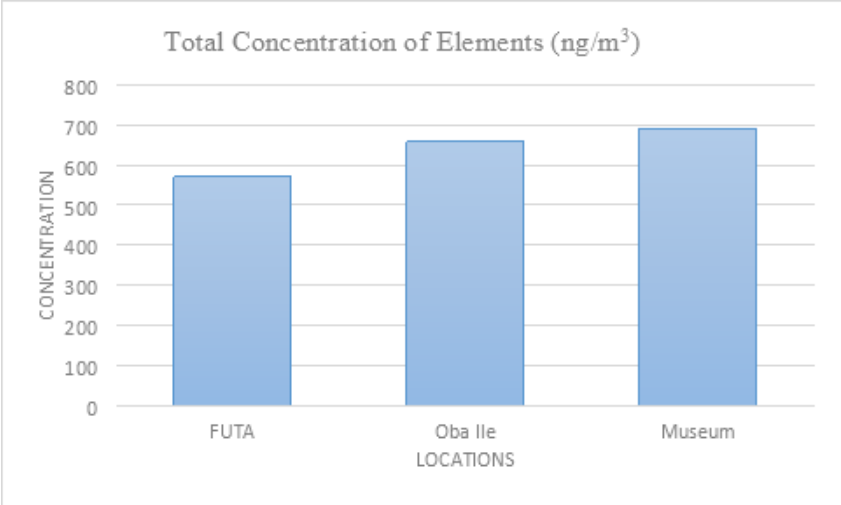
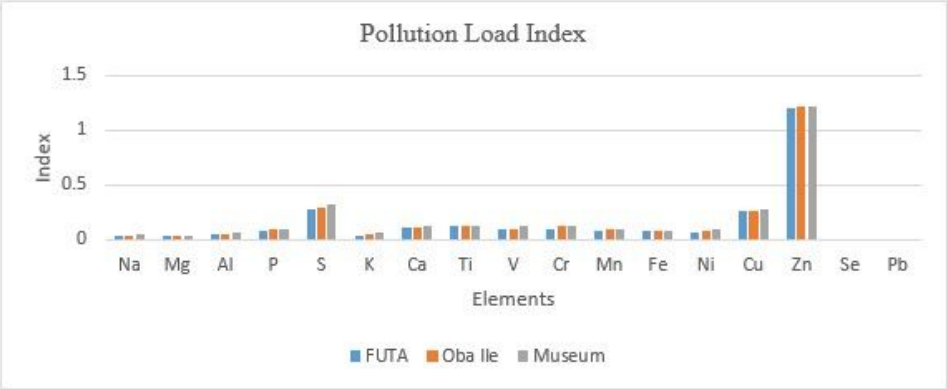


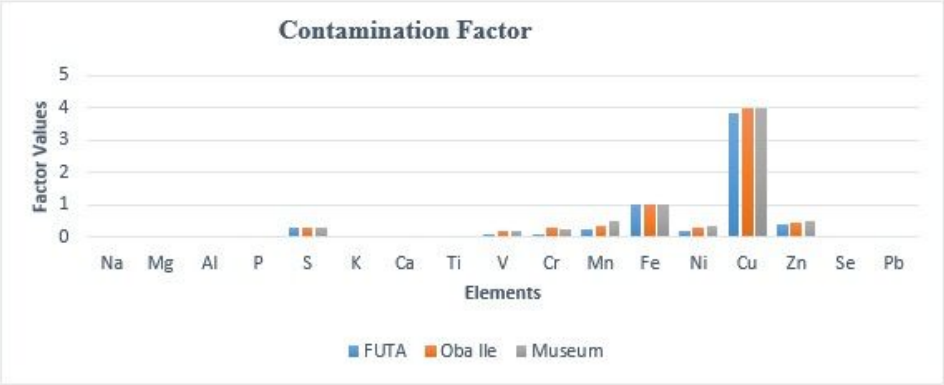
Figure 4

Total Concentration of Elements at the different Sites (January – October)

(a)



(b)



(c)

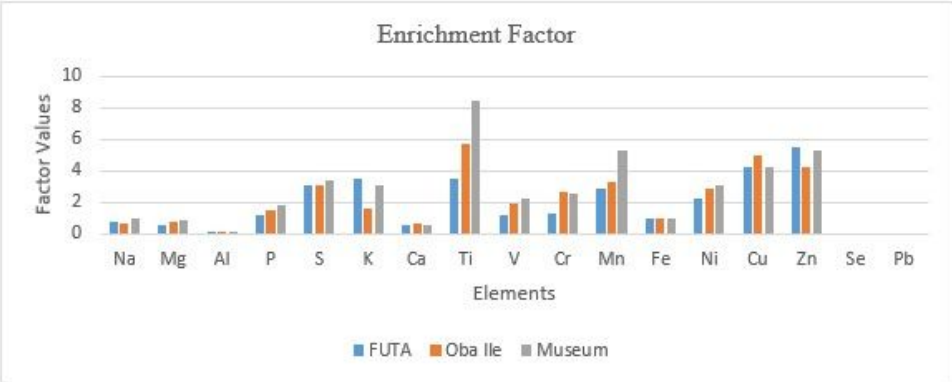


Figure 5

Plots showing the Pollution Load Index, Contamination Factor, and Enrichment Factor of element concentrations in PM2.5 at different sites.