

Characterization of Airborne Fine Particulate Matter (PM_{2.5}) and Its Air Quality Implications in Ogun State, Nigeria

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Abstract — Atmospheric aerosols pose a serious threat to environmental quality and health of the public. Several studies in Nigeria have documented the pollution levels from coarse particles but very few have elucidated the nature of the fine particles in the context of air quality index. Our investigation therefore focused on air quality index in relation to ambient fine particulate and composition of PM_{2.5} collected from an industrial area (IA) and a university community (UC) in Ogun State, Nigeria. The PM_{2.5} samples were collected using Environtech gravimetric sampler according to standard methods. The morphology and elemental composition of PM_{2.5} were assessed by scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX). The SEM images of fine particles indicated the following clustered groups: soot particles, alumino silicates, and mixture of alumino silicate with soot. Energy dispersive X-ray spectra showed nine most abundant elemental composition in all samples. Possible source emissions of elements identified by principal component analysis are industrial processes, vehicle emissions, crustal dust, fuel-oil and biomass burning. Air quality index (AQI), for particulate pollution was calculated for each location. Fine particle pollution indices scaled from 51 to 500, reflecting six out of the seven AQI categories in varying proportions. The absence of 0 to 50 gradation representing the good AQI category is conspicuously highlighted. Results indicate that most AQI values were above 100. Possible adverse health concerns mostly for the vulnerable populations are indicated considering the unhealthy air quality state of studied locations.

Keywords—PM_{2.5} pollution; elemental composition; SEM-EDX; air quality index

I. INTRODUCTION

Fine particulate matter (PM_{2.5}) refers to tiny subdivision of solid matter floating in a gas or liquid. It is characterised by small particle size, large surface area and high activity [1]. Given their minute size and effective ability to readily dissolve in fluids and produce a chemical reaction, exposure to PM_{2.5} has become a leading environmental risk factor associated with many cardiopulmonary and respiratory diseases as well as premature deaths [2]. Therefore, PM_{2.5} has aroused growing public health and environmental concerns, and has become a fundamental area of air pollution studies by many researchers [3, 4, 5]. They are associated with several chemical species, including trace metals and are emitted from natural

(windborne dust, sea spray, volcanic emission, road dust, dust outbreaks and biomass burning) sources, and anthropogenic (fossil fuel combustion and industrial emissions, coal and oil combustion, open solid waste burning, construction activities) sources [3, 6].

Depending on the location, variation in the morphology and chemical composition, some group of fine particles are sometimes observed. However, other specific groups namely carbon-rich fluffy soot aggregate from incomplete combustion of hydrocarbons, minerals with high content of metals from coal-fired power plants, and spherical fly ash made of metal-silicates from road dust, construction, coal combustion and secondary atmospheric reactions have been reported [3]. Understanding the chemical composition of fine particulates is not sufficient especially when considering the carcinogenotoxicity. Therefore, additional knowledge on their morphology can further authenticate their origin [7, 8]. Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) has been employed to access information on atmospheric fine particulate's chemical composition, morphological characteristics and origin [5, 9]. Despite the numerous observations of air pollution in different cities in Nigeria, there has been a lack of research on outdoor PM_{2.5} concentration in major institution sites and industrial areas in Ogun State. The Ewekoro industrial area and Covenant University community are two of such typical environment that have been investigated and reported in the present work. Therefore, the objectives of the present study are (a) to determine the PM_{2.5} air quality index of the study area (b) to investigate the morphology of atmospheric fine particulates using SEM- EDX, and (c) to identify the fine particle sources based on PM_{2.5} chemical composition.

II. METHODOLOGY

A. Sample Collection

Sampling of PM_{2.5} was carried out at Ewekoro community (31N 0523068 UTM 0763651) and Covenant University (31N 0517507 0737605) in Ogun State, Nigeria, between August and September 2014. For effective data management, the Ewekoro community and Covenant University sites were designated as IA and UC, respectively. PM_{2.5} samples were collected for 4 hours weekly at a height of 1.5 m from the ground level at each study location with Environtech

gravimetric sampler on glass filters (47 mm). The filters were equilibrated in a desiccator for 48 hours to eliminate the effect of humidity and also to obtain accurate PM_{2.5} measurements. Pre-weighed and conditioned filters were placed in the filter holder and screwed properly before operating the sampler. After sampling, the PM_{2.5} filter papers were removed with forceps, stored in a petri dish, conditioned, weighed, and stored in the refrigerator at 4°C to prevent thermal degradation and evaporation of volatile components prior to further analysis. Laboratory blank and field blank filters were collected to reduce the gravimetric bias.

B. Air quality index (AQI)

PM_{2.5} air quality index was calculated following a standard formula developed by the United State Environmental Protection Agency as shown below [10].

$$I_p = \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} (C_p - BP_{Lo}) + I_{Lo} \quad (1)$$

where:

- I_p = the index for pollutant p,
- C_p = the rounded concentration of pollutant p,
- BP_{Hi} = the breakpoint that is greater than or equal to C_p ,
- BP_{Lo} = the breakpoint that is less than or equal to C_p ,
- I_{Hi} = the AQI value corresponding to BP_{Hi} and
- I_{Lo} = the AQI value corresponding to BP_{Lo} .

Air quality index is a colour-coded tool for reporting the quality of air with respect to its effects on the human health [10, 11]. It is divided into six levels of health concern and their implications namely: good (0–50), implies that AQI is satisfactory; moderate (51–100*), AQI is acceptable; unhealthy for sensitive groups (101–150), implies that this AQI range may not affect the general public, but could affect persons with heart and lung disease, older adults and children; unhealthy (151–200), everyone may begin to experience some adverse health effects; very unhealthy (201–300), everyone may experience adverse health effects and hazardous (301–500), this triggers health warning of emergency conditions. Therefore to protect the public from fine particle pollution, EPA has set an AQI value of 100 as identified with the asterisk symbol [10, 12].

C. SEM-EDX analysis of PM_{2.5} particles)

The surface morphologies and elemental composition of airborne particles of PM_{2.5} samples were examined by field emission scanning electron microscopy (FESEM, Hitachi, SU-8020) coupled with energy-dispersive X-ray spectroscopy (EDX, Oxford X-Max^N Model). 0.5 cm of the dry and loaded glass fiber filter samples were cut and coated with a thin film of platinum (Pt) to make the samples electrically conductive for SEM-EDX analysis. Samples were placed in the corner of SEM-EDX chamber and three images of each sample were taken at a magnification of X1500, X5000, X20000. After

which, EDX spectra of individual particles were obtained for determination of individual elemental composition of particles after scanning an electron beam with an accelerating voltage of 20 kV, a beam current of 10 μA and a Si (Li) detector 15 mm away from the samples to be analyzed. Peaks were identified and the quantifying function of the computer programme was used to determine the peak intensities, which were converted to percentage weight [13].

D. Statistical analysis

The EDX data obtained from elemental analysis were analysed using the XLSTAT-Pro software (AddinSoft, Inc., NY, USA). Principal component analysis (PCA) was used to establish the interrelationship between investigated PM_{2.5}-bound elements and identify their sources. Varimax rotation was used as the rotation method for PCA analysis and the number of principal components was decided based on eigenvalues >1. The statistical methods were performed with a 95% confidence interval (significance $p < 0.05$).

III. RESULTS AND DISCUSSION

A. PM_{2.5} air quality index in IA and UC

Fig. 1, shows average of two months air quality index for UC and IA computed during the wet season (August and September). The “good” air quality category, which represents the index value 0-50, was significantly absent in both study areas. AQI for UC ranged from “moderate” to “very unhealthy” categories, while the IA fell within the range of “unhealthy for sensitive group” to “hazardous” categories. Comparatively speaking, the results indicate that UC site recorded no values within the hazardous gradation and showed relatively better AQI than IA site.

However, the present state of air is still of concern, particularly to those in the sensitive categories. Possible sources of pollutants in the University community (UC) includes, vehicular emission, construction activities, emission from power plant, transport of pollutants from neighboring environment, most especially the nearby Ota industrial estate with continuous active production involving scrap recycling, production of chemical, plastics, metals and steel etc.

Furthermore, particle pollution in IA (Ewekoro community) has been closely associated with diverse activities such as industrial emission, most especially the Lafarge Cement WAPCO Nigeria Plc, Portland Paints and Products Nigeria Plc, and Dulphin steel industry, limestone quarrying, vehicular emission, woodstoves, biomass burning, solid waste burning, power plants, unpaved roads etc. [14, 15].

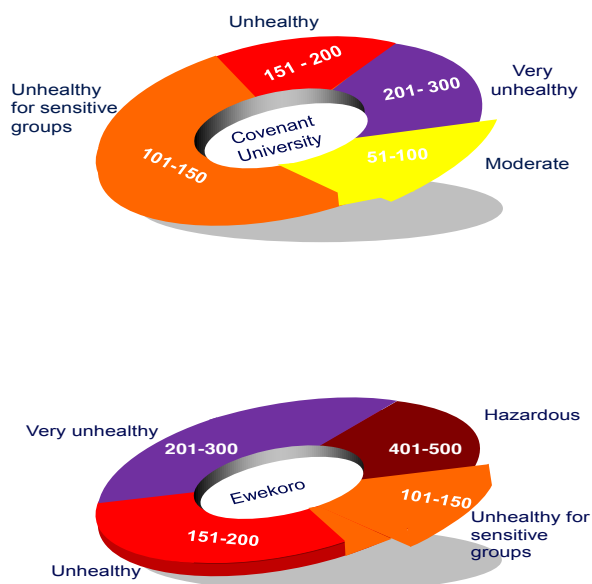


Fig. 1. PM_{2.5} AQI at the two measurement sites during wet season

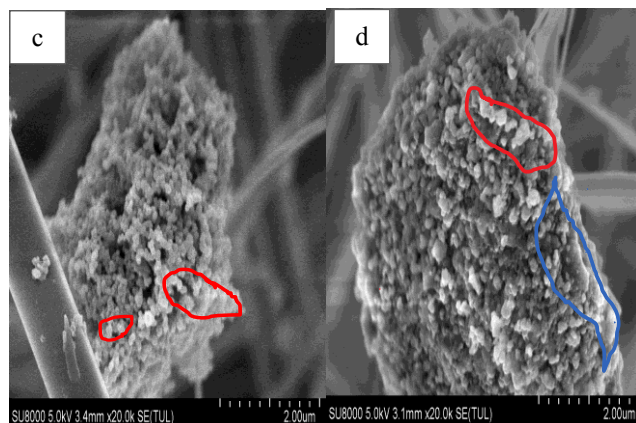
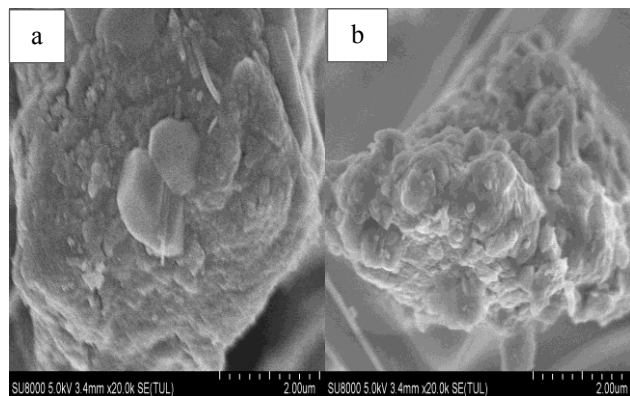


Fig. 2. SEM images of most abundant groups of PM_{2.5} particles identified: (a) aluminosilicate at IA; (b) aluminosilicate at UC; (c) soot particles at IA; (d) aluminosilicate- soot particles at UC

The observed categories of AQI for IA indicate that the air quality was unhealthy for both the sensitive groups and for everyone in this location [10].

B. Morphology and Elemental composition of PM_{2.5} particles

As shown in Fig. 2, the morphological characteristics of atmospheric fine particles (PM_{2.5}) detected at UC, and IA sites were classified into three most abundant groups such as soot aggregation, alumino silicate, and mixture of silica with soot.

1) *Aluminosilicates Particles*: These particles are formed basically from natural sources, and composed primarily of Si, Al, Ca or Si, Al, K classified as feldspar and Si, Al or Si, Al, Fe such as clay. Aluminosilicates also originate from road dust, agricultural activities, fuel and biomass burning [6, 9]. UC and IA aluminosilicate particles are shown on Fig. 2 (a) and (b) SEM images respectively. The distribution of the major elements and atomic percentages in the analysed particles for IA were O (47.6%), Si (17.7%) C (16.2%), Na (5.47%), Ba (3.51%), Zn (3.04%), Al (2.64%), K (1.85%), and Ca (0.95%). Also, for the UC particles the major elements and atomic percentages observed were O (49.7%), Si (18.3%), C (15.0%), Na (5.65%), Ba (3.52%), Zn (2.98%), Al (2.11%), K(1.83%) and Ca (0.90%) respectively.

2) *Soot particles*: Soot particles have unique morphology that distinguishes it from other groups of particles. It is present as agglomerates of many fine spherical primary particles in the form of chainlike soot particles, cluster soot particles, simple soot particles etc. They are major tracer of vehicular exhaust and are also emitted from diverse sources including heating systems, gasoline, diesel and fuel oil from incomplete combustion processes [5, 3].

As shown in Fig. 2c, cluster soot particles were identified at IA site and the distribution of major elements and atomic percentages in such aggregates include O (50.7%), Si (18.9%), C (12.9%), Na (5.69%), Ba (3.57%), Zn (2.43%), Al (2.43%), K(1.94%), Ca (1.14%) and Cl (0.23%) respectively, with high contents of O, Si, and C. Si is due to mixed sources such as crustal airborne particles and industrial combustion. Also, the high proportion of C confirms heavy carbonaceous emission already detected in the morphology. This findings indicates that anthropogenic combustion is the main source of soot in the investigated site [12,16].

3) *Alumino silicate- soot particles*: As shown in Fig. 2d, UC SEM image of PM_{2.5} particles revealed a mixture of aluminosilicate with absorbed smaller size soot particles. Their elemental composition and atomic percentages were

O (49.7%), C (15.6%), Si (17.8%), Na (5.2%), Ba (3.8%), Zn (2.50%), Al (2.31%), K (1.9%) and Ca (1.1%) respectively.

C. Source apportionment of $PM_{2.5}$ particles

The principal component analysis (PCA) of EDX elements (O, Si, C, Na, Ba, Zn, Al, K, Ca) was performed in order to study the correlation among the elements and for the source identification. Table 1 presents two rotated factor loadings with eigenvalues >1 , for UC and IA study areas. The PCA of the chemical data of the particles from UC site, shows two factors which accounted for 82.5%, of the overall variance. As shown in Fig. 3a, it is evident that the first factor, explains most of the variance (55.45%), and is characterized by high loadings of K, Si, Ca, Zn and Na and strong negative factor loadings for C and O while factor 2 explained 27.06% of the total variance with high loading of Ba and strong negative loading for Al.

The presence of Zn was suspected to come from wear and tear in brake line and tires associated with vehicular emission sources, corrosion of galvanized steel as well as metal processing due to the proximity of UC site to Ota industrial estate [9, 17], Ca is associated with, emission from buildings, road renovations/construction [18]. Also, K is a known marker of vegetation and biomass burning and it is associated with contributions from the neighbourhood and surrounding farm lands, while Na and Si has been identified as crustal elements from soil dust. Si is equally produced in large quantity in heavily industrialized areas during industrial combustion process and from generator sets usage in the neighborhood of the sites. Also, they are easily transported in airborne particles in the form of fly ash [19, 20, 21, 22]. In factor 2, Ba is associated with mineral origin (barite) from the soil, metallurgical production, open air solid waste burning and industrial activities [23, 24]

For the industrial site (IA), PCA revealed two (2) components that accounted for 95.51%, of the overall variance in Ewekoro.

Table 1: Factor loadings of trace metals after PCA varimax rotation at UC and IA

Trace Metals	UC		IA	
	PC1	PC2	PC1	PC2
O	-0.774	-0.391	0.429	-0.903
C	-0.973	0.193	-0.965	0.264
Si	0.976	-0.216	0.976	-0.218
Na	0.572	-0.276	0.925	0.204
Ba	-0.146	0.987	0.994	0.105
Zn	0.664	0.434	0.596	0.668
Al	-0.424	-0.804	0.660	0.751
K	0.988	0.156	1.000	0.031
Ca	0.713	-0.536	0.460	-0.795
Eigenvalue	4.990	2.434	5.941	2.655
Variability (%)	55.45	27.05	66.01	29.50
Cumulative %	55.45	82.50	66.01	95.51

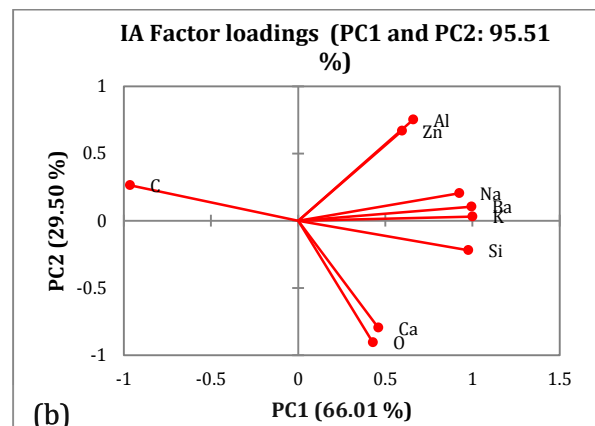
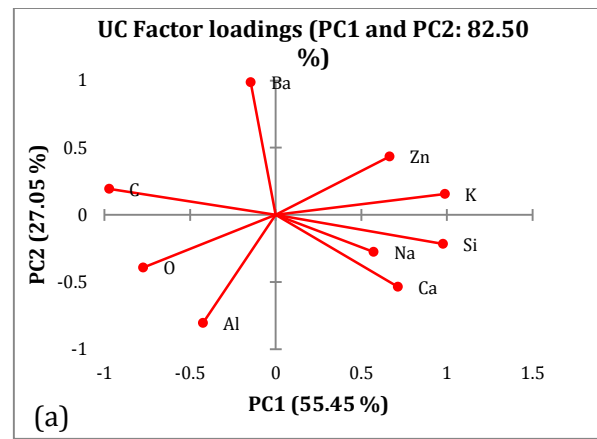


Fig. 3. Loading plots of the principal components obtained for elements at (a) UC and (b) IA

As shown in Fig. 3b, factor 1 (66.01%) had high loadings for K, Ba, Si, Na and strong negative loading for C while factor two (29.5) had high loadings for Al and Zn and strong negative factor loadings for O and Ca. The general description for sources of elements described above holds as well for IA elements. In addition to this Al are markers of emission from cement production, metal recycling, steel production, vehicle wear and tear and re suspended dust mineral dust, but their presence in the IA environment has been increased due to various anthropogenic activities such as, associated with construction [25, 26]. It was observed that in both UC and IA, different groups of elements were related to one or several sources. Hence, groups of elements associated with a specific type of origin were identified as tracers of the main emitted particles by the polluting sources.

IV. CONCLUSION

The SEM-EDX technique is a valuable tool for the characterisation of the morphology and chemical composition of fine particles. Our results presented in this paper showed three major clustered groups (soot particles, alumino silicates, and mixture of alumino silicate with soot), with greater percentage of aluminosilicate identified for the fine particles in both sites during the investigated period. Nine most abundant

elements present in all samples were indicated with Energy dispersive X-ray spectra and application of PCA to the elements highlighted industrial processes, vehicular emission, crustal dust, fuel-oil and biomass burning as sources of PM_{2.5}. However, the air quality index of fine particle pollution for the “good category” was not observed in both sites. From the findings UC, had no record of hazardous category, and recorded a better AQI when compared with IA. The AQI for IA indicates that the air quality was unhealthy for both the sensitive groups and for everyone in this location. There is need for adequate government regulation, industrial compliance and public awareness toward the control of PM_{2.5} pollution.

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