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Study of Surface Morphology, Elemental Composition and Sources of Airborne Fine Particulate Matter in Agbara Industrial Estate, Nigeria

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Abstract

Ambient atmospheric fine particle emission contribution to industrial pollution load is hard to quantify due to absence of air quality monitoring stations and difficulties in assessing suitable analytical instruments. Therefore, to keep abreast of air quality information, the use of physicochemical signatures to assess the sources of elements associated with fine particulate matter in Agabra Industrial Estate was explored with Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) and Principal Component Analysis (PCA). A greater proportion of Si and C were observed in the particles amongst other detected elements by EDX. Morphology results by SEM confirmed soot, alumino silicate and irregular shape mineral particles as the most common inhalable particles. Prominent among emission sources identified are industries, automobile exhaust, fugitive dust and solid waste combustion. The research suggests that adequate public awareness, industrial compliance, vehicle emission control, smooth operation of municipal solid waste incineration and government regulation will significantly reduce fine particulate pollution.

Key words: $PM_{2.5}$; Pollution; Elements; Industrial Area; SEM-EDX; PCA.

1. Introduction

Fine particulate matter otherwise known as $PM_{2.5}$ is a major environmental issue globally [1, 2]. It comprises of a complex mixture of dust, pollen, ash, soot, metals amongst numerous solid and liquid chemicals present in the atmosphere [3]. $PM_{2.5}$ triggers health effects upon inhalation and can be transported further by atmospheric circulation, due to its long residence time of days to several weeks in the atmospheres. They exhibit diverse shapes and chemical composition depending on their origin [4, 5]. Hence, a proper knowledge on these parameters would be helpful in identifying possible emission sources [6, 7].

Scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) is a non-destructive analytical method for high resolution surface imaging and quantitative identification of elements present in the sample [8]. This technique is capable of providing detailed information on chemical composition and particle morphology as well as improved understanding of the properties and sources of $PM_{2.5}$ (natural or anthropogenic) [9, 10]. Several applications of SEM-EDX to the investigation of the chemical and physical characterization of individual particles in environmental studies have been reported in the literature [8, 11, 12, 13]. The elemental composition of fine particulates is more useful with a view to establish their origin and their potential effects on human health. Till now, the studies on elemental composition of fine particulate matter using SEM-EDX analysis are limited in Nigeria [14].

Therefore, the objectives of the present study are (a) to investigate the morphology of atmospheric fine particulates matter using SEM (b) to identify the elemental composition of atmospheric fine particulates using EDX, and (c) to apportion the identified elements to their respective sources using PCA.

2. Materials and method

2.1 Study Area

Sampling of $PM_{2.5}$ was carried out at three sampling site in Agbara Industrial Estate (AIE) in Ogun State, Nigeria, from October to December 2014. For effective data management, the three sampling sites were designated as AA (31N 0509888 UTM 0719892), AB (31N 0508845 UTM 0719916) and AC (31N 0508802 UTM 0720895). AIE is a private estate located in Ado-Odo/Ota local government area which borders on metropolitan Lagos. It is a highly industrialized area sandwiched between Ogun state and Lagos state. It is a home to a number of manufacturing industries including Glaxo Smith Kline Nigeria Plc., Nestle Nigeria Plc., P&G Nigeria., Shell Petroleum Development Corporation (SPDC), Unilever Nigeria Plc. etc.) Also, two residential estates, Agbara Estate Phase II and Opic Estate are located in Agbara Industrial Estate. It also has a diversity of anthropogenic activities such as wood mill, mechanic workshop, solid waste combustion, heavy vehicular traffic, and high agricultural activity. The map of the study area is as presented in Figure 1.

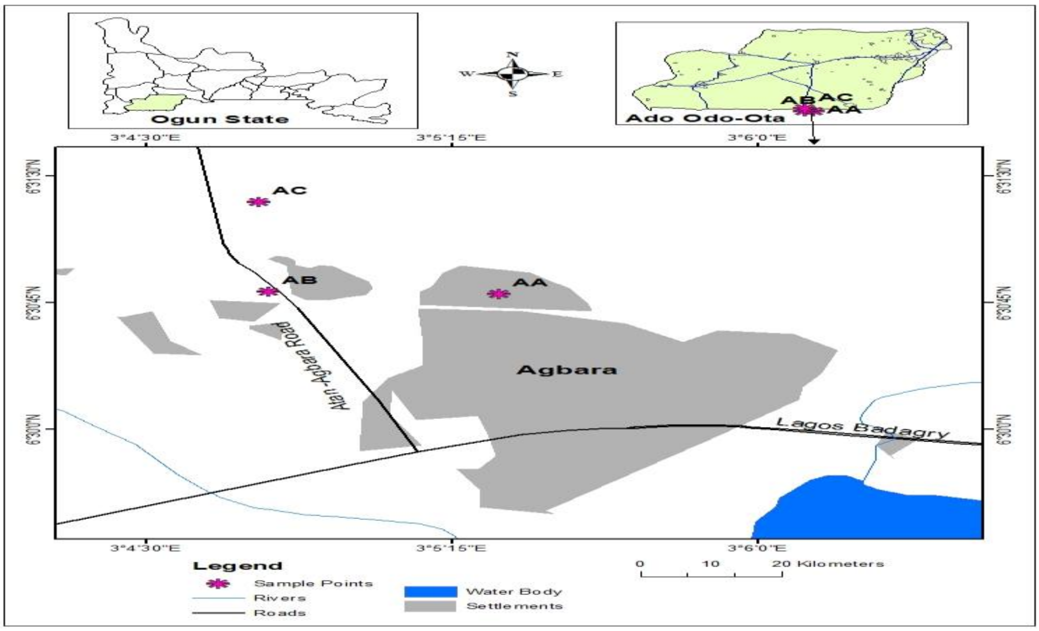


Figure 1: Sampling sites at Agabara Industrial Estate. Insert: map of Ogun State and Ado Odo-Ota showing the location of study areas.

2.2 $PM_{2.5}$ sample collection

$PM_{2.5}$ samples were collected twice in a week at each sampling sites for a period of 4 hours at a height of 1.5 m from the ground level with Environtech gravimetric sampler (SLE-FPS105) using $PM_{2.5}$ inlet on polytetrafluoroethylene (PTFE) Teflon 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^{o} C to prevent thermal degradation and evaporation of volatile components prior to further analysis. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination.

2.3 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 (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 two images of each sample were taken at a magnification of X5000 and X20000. After which, EDX spectra of individual particles were obtained for determination of individual elemental composition of $PM_{2.5}$ 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 [15].

2.4 Statistical analysis

The EDX data obtained from elemental composition of $PM_{2.5}$ were analysed using the XLSTAT-Pro software (AddinSoft, Inc., NY, USA). Principal component analysis (PCA) is an exploratory tool and operates by combining factor analysis with a multi-linear regression to establish the source of the pollutant. It is the most common model for source apportionment studies. PCA was used to establish the interrelationship between investigated $PM_{2.5}$–bound elements and to identify their sources. Varimax rotation was used as the rotation method for PCA analysis and the number of principal components was decided based on eigen values >1. The statistical methods were performed with a 95% confidence interval (significance $p<0.05$) [16, 17].

3. Results and discussion

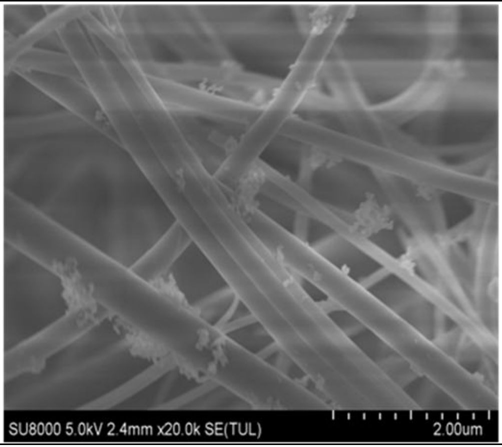
3.1 Fine particle morphology

The morphological characteristics of particles detected in $PM_{2.5}$ by SEM analysis are as presented in Figure 2. As shown by the SEM images the dominant single inhalable particles present in the sampling sites include the following:

(i) **Soot**: They are agglomeration of carbon particles due to incomplete combustion of fossil fuel and organic matter. Their origin is mostly from emissions of combustion sources, such as, burning fuel oil, power plant, vehicle exhaust and biomass burning. Therefore, they are known markers of anthropogenic emission in AIE most especially industrial and vehicular emission [9, 18].

(ii) **Aluminosilicates**: They are formed basically from natural sources, mainly from erosion of local geological formations. Most of silica particles (Si oxides) and aluminosilicates (containing Al, Si, K, Fe, and Ca) present in the fine fraction have irregular forms and are classified as dispersion of soil dust. Aluminosilicates with significant levels of Al, Si and K can also originate from crustal sources, agricultural activities, fuel and biomass burning [19, 20]. These particles contribute to the highest proportion of global aerosol mass in the atmosphere due to the ease at which they are dispersed into the air [21].

(iii) **Mineral particles**: These particles exist in two basic forms namely regular and irregular mineral particles and are derived from both natural and anthropogenic sources. The observed particles at AIE were irregular shape particles and their dominant natural sources are soil dust and suspension of dust from roads while anthropogenic sources include construction and vehicular emission [22, 15].



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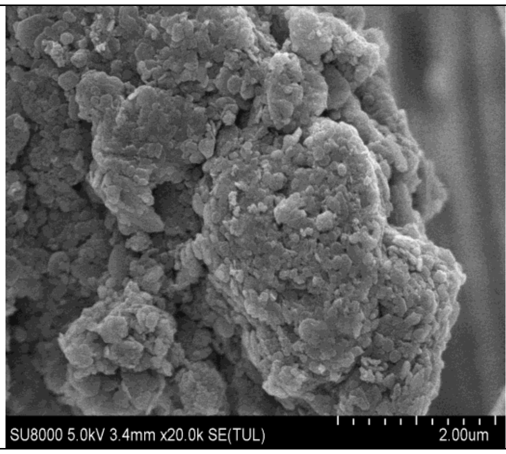

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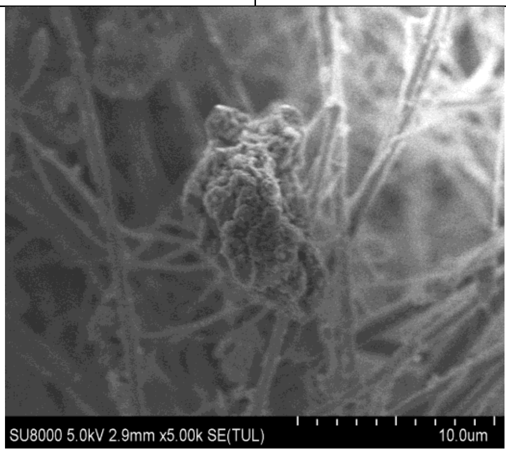

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Figure 2: Morphological types of $PM_{2.5}$ collected at AIE (a) cluster soot aggregation (b) alumino-silicates particles and (c) irregular mineral particle.

3.2 Elemental composition in $PM_{2.5}$

The EDX spectra revealed the relative abundance of nine elements – Si, C, Na, Ba, Zn, Al, K, Ca and Cl as shown in Figure 3. Elemental levels of Si and C were significantly higher than other elements. Silicon (Si) is one of the largest constituents of soil-derived mineral particles. Therefore its occurrence may be due to transportation of atmospheric airborne soil particles or from fly ash produced during industrial combustion. These particles usually contain Si and are abundant in heavily industrialized areas [23, 24].

Also, elevated level of carbon (C) was associated with high carbonaceous materials which might be expected due to combination of diverse anthropogenic activities at AIE such as high traffic congestion resulting in emission of spent and/or semi-burnt automobile fuels, power plant used in the industries, generator sets usage from the residential facilities and abrasion of vehicle tyres [13]. This compares with investigations reported in China [25] and India [15]. Higher levels of particulate carbon are of concern to human health since it acts as a good adsorption site for many semi volatile compounds [15, 26].

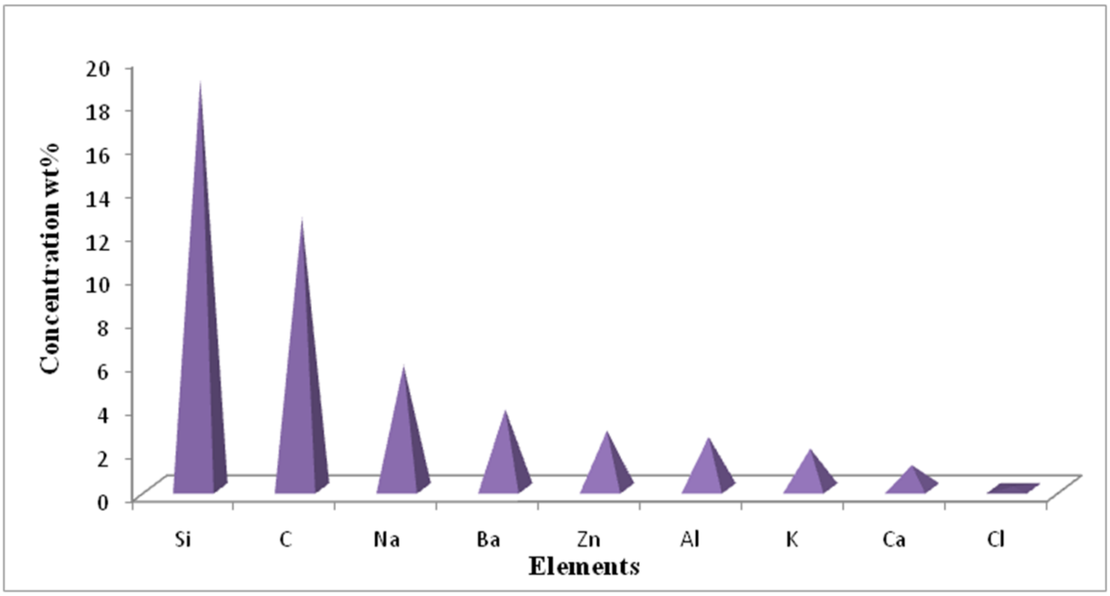

Figure 3: Elemental composition averaged in percentage weight at AIE

3.3 Source apportionment of $PM_{2.5}$ particles

The results of the principal component analysis (PCA) for nine (9) elements obtained from EDX (Si, Al, K, Ba, Zn, Na, Ca, C, Cl) in AIE are as presented in Table 1.

Table 1: Factor loadings of trace metals after PCA varimax rotation at AIE

Trace Metals	PC1	PC2
C	**-0.966**	0.166
Si	**0.994**	-0.041
Na	**0.929**	0.169
Ba	**0.969**	-0.122
Zn	**0.964**	-0.124
Al	**0.987**	0.026
K	**0.982**	-0.095
Ca	**0. 853**	0.041
Cl	-0.037	**0.958**
Eigen value	7.99	1.20
Variability (%)	79.9	12.0
Cumulative %	79.7	91.9

The PCA of the elemental composition of $PM_{2.5}$ particles from AIE shows two factors which accounted for 91.9%, of the overall variance. PC1, explains most of the variance (79.9%), and is characterized by high loadings of Si, Al, K, Ba, Zn, Na, Ca and strong negative factor loadings for C while PC2 explained 12.0% of the total variance with high loading of Cl. Na was identified as crustal element from soil dust. Si and Ba are associated with industrial combustion process, power plant, solid waste combustion and soil dust [13, 27]. The presence of Zn was attributed to vehicular emission due to abrasion of tyres [28], K are known markers of vegetation and biomass burning while Cl was associated with industrial emission, since it is not common in ambient natural mineral but mostly used in industrial processes [29]. Also, Ca and Al are markers of mineral dust due to buildings and road renovations/construction [30, 31, 18]. However elevated levels of Al in AIE can be influenced by the frequent open air solid waste burning coupled with multiple industrial activities [27].

4. Conclusion

Fine particulate matter morphology, elemental composition and sources in Agbara Industrial Estate have been identified. Si and C dominated the nine (9) most abundant elements present in all samples while soot, alumino silicate and irregular shape mineral particles were the most common inhalable particles. Prominent sources identified using PCA are industries, automobile exhaust, fugitive dust and refuse incineration. Therefore, adequate regulations should be enacted by relevant government agency (ies) to effectively cut down on fine particulate pollution.

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