MULTI-ELEMENTAL ANALYSIS AND SOURCE APPORTIONMENT OF URBAN AEROSOLS IN A LOW DENSITY RESIDENTIAL AREA: A CASE STUDY OF IKOYI LAGOS NIGERIA.

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ABSTRACT

Concentrations of size segregated aerosols ($PM_{2.5-10}$ and $PM_{2.5}$) were measured daily at a receptor site located in Ikoyi, Lagos, between August to September, 2007 in order to investigate the chemical compositions and sources. Size-segregated fractions were collected using a double staged 'Gent' stack filter unit sampler. Elemental characterization was carried out by Particle Induced X-ray Emission (PIXE) technique in an external ion beam analysis set-up. Data matrix of 35 by 23 species (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, and Pb) were obtained in each fraction and their elemental concentrations were assessed. Data obtained from the elemental analysis of both fractions were further subjected to Pearson correlation and Principal Component Analysis (PCA) for source apportionment and identification. Pearson inter-elemental correlations indicated that some elements could have common source origins or similar chemical properties. Source apportionment results by PCA resolved five sources (Soil dust, 31 %; Sea spray, 23 %; Heavy oil combustion, 14 %; Industrial, 13 %; Physical construction, 6 %) and six sources (Traffic, 20 %; Soil dust, 19 %; Non-ferrous smelting, 12 %; Heavy oil combustion, 10 %; Biomass burning, 9 %; Sea spray, 6 %) for $PM_{2.5-10}$ and $PM_{2.5}$ samples respectively. The study concluded that anthropogenic (traffic, industrial, and biomass burning) emission sources posed great hazard to Ikoyi receptors.

Keywords: Atmospheric, Compositions, Emissions, Ion Beam, Particulates, PIXE

INTRODUCTION

According to the United Nations Environmental Programme/World Health Organization, (UNEP/WHO, 1994), atmospheric particulate matter have been implicated to cause adverse effects on human health, visibility and climate, ecosystems and deterioration of physical properties The influence of atmospheric aerosols on human health and the environment depends on its sizes. Therefore, better understanding of the influence of aerosols requires studies of size segregated particulate matter. The most common size segregations are coarse ($PM_{2.5-10}$, aerodynamic diameter (d_{ae}), 2.5 μm < d_{ae} < 10 μm) and fine ($PM_{2.5}$, $d_{ae} \leq$ 2.5 μm) fractions. These fractions could have different origins and atmospheric residence times. It is therefore important to understand its chemical compositions. Our knowledge of the chemical and physical constituents of particulate matter helps in assessing their impacts on the environment and humans as well as to identify and quantify its natural and anthropogenic sources. It also assists policy makers in formulating well-guided policies for air pollution abatement strategies.

Accelerator-based ion beam analysis (IBA) techniques have been applied for the chemical characterizations of atmospheric aerosol particulate matter (PM) for many years (Cohen *et al.*, 2008). They are well suited for such studies as IBA techniques have several unique advantages. The techniques have multi-elemental analysis capabilities; low minimum detection limits (MDLs) for a very broad range of elements in the Periodic Table and can quantitatively detect picograms of material in micrograms of sample (Cohen *et al.,* 2004). With the use of IBA accelerator-based PIXE (Particle Induced X-ray Emission) technique, systematic investigations of atmospheric particulate matter have been performed at *LAboratorio BEni Culturali* (LABEC), in Florence, Italy, for several years (Calzolai *et al.,* 2010). External IBA set-up is a state-of-art analytical technique which is most suitable for aerosol and cultural heritage artifact sample elemental analysis (Lucarelli *et al.,* 2014).

The advantages of external PIXE set-up over the traditional in-vacuum set-up have been reported elsewhere (Calzolai *et al.*, 2010). Thus, with the application of external IBA set-up, an improved data set for source apportionment studies could be achieved as the result of source apportionment depends on the quality of the elemental compositions detected (Cohen *et al.*, 2004).

Literature on air pollution by source apportionment of size segregated suspended particulate matter are rare in most developing nations due to poor infrastructure (UNEP/WHO, 1994). However, there have been some studies to evaluate the contributions of different urban sources to ambient air pollution at different receptor sites in Lagos (Oluyemi and Asubiojo, 2001; Olise, 2003; Owoade, 2006). Conversely, most of these local references had an inherent problem of poor quality data sets owing to the analytical techniques employed for elemental concentrations. Again, underestimation and overestimation of sources were also synonymous in these studies probably because of non-availability of local elemental source 'signatures' or 'profiles' for anthropogenic emission sources (such as smelting, fossil fuel and biomass combustions) which could have been fed into the Chemical Mass Balance (CMB) receptor model, used for source apportionment. To address these challenges, Principal Component Analysis (PCA) which does not require input of local source profiles could be employed as it uses numerical approach to account for statistical variances by deriving the least number of major factors or sources (Chan and Mozurkewich, 2007). PCA model classifies elements according their concentration variances implying that the grouped elements are associated with each other and reduces the number of variables that explains the observed variations in the data set to a minimum.

This study utilizes the external-beam set-up for PIXE analysis available at Department of Physics and Astronomy, University of Firenze and *Instituto Nazionale di Fisica Nucleare* (INFN) laboratory in Firenze Italy was used to measure the elemental compositions of $PM_{2.5-10}$ and $PM_{2.5}$ samples collected in Ikoyi, Lagos Nigeria. The speciated data sets obtained from elemental characterization were further analyzed with Pearson correlation and Principal Component Analysis (PCA) statistical tools in order to obtain information regarding $PM_{2.5}$ and $PM_{2.5-10}$ source identification and apportionment.

Description of Sampling Site

Ikoyi (Lagos Island) is a well-planned typical low-density populated residential area within the Eti-Osa Local Government Area of Lagos Nigeria (Fig. 1). It is an island suburb that encompasses the eastern half of Lagos Island and lies at the edge of the Lagos Lagoon and few kilometers to the shores of Atlantic Ocean. The city of Ikoyi is also a traffic-prone area adjacent to the intersection of several main roads with high-traffic density. Commercial activities are increasingly getting much in Ikoyi due to its proximity to the popular “Balogun and Idumota” markets as well as to other Lagos Island hotspots (Victoria Island, Lekki and Ajah surburbs). However; no single industry exists in Ikoyi. Owing to its unique location, it is an ideal place for observing the impacts of atmospheric particulate matter due to transport processes. Although, Ikoyi is not a much stressed environment, the impacts of air pollution from the hinterlands could present significant health hazards for its inhabitants.

METHODOLOGY

Sampling

$PM_{2.5}$ and $PM_{2.5-10}$ were sampled at the identified site (Fig. 1) with a “Gent” stacked filter unit sampler, Schlumberger Model: M250 (Maenhunt *et al.* 1993). The samples (35 each) were collected on pre-weighed and pre-conditioned Whatman® Nuclepore filters with flow rate of between 16 and 18 L min^{-1}. The filters were conditioned at about 25°C and 50% constant humidity for 24 h before weighting. The sampler was placed so that air circulation around it was not hindered and at a height of about 1.7 m (average nose level). The effective sampling time was varied between 8 h to avoid filter clogging so that the flow rate would remain within the prescribed limits of the sampler. This ensured proper size fractionation and collection efficiency. Details of sampling have been reported elsewhere (Ezeh *et al.*, 2012). PM_{10} values were the sum of $PM_{2.5}$ and $PM_{2.5-10}$. The exposed filters were stored in a desiccator until elemental analysis using PIXE technique.

Elemental Analysis

For each $PM_{2.5}$ and $PM_{2.5\text{-}10}$ sample, elemental concentrations were analyzed using particle induced X–ray emission (PIXE) at external ion beam analysis (IBA) set-up of the 3 MV Tandetron accelerator at Department of Physics and Astronomy, University of Firenze and INFN laboratory in Firenze Italy (Calzolai *et al.,* 2006). Calibration of the PIXE system was performed by irradiating suitable certified thin target standards. X–ray spectra obtained from the PIXE measurements were analyzed with GUPIX software developed by Maxwell *et al.* (1995) to obtain net peak areas. Elemental concentrations were obtained via a sensitivity curve i.e. (counts μC^{-1} per $\mu g\ cm^{-2}$) from a set of thin standards of known areal density supplied by Micromatter® Inc. Detailed procedure for elemental analysis has been reported elsewhere (Ezeh *et al.,* 2014).

Pearson Correlation

The elemental concentrations of the analyzed samples $PM_{2.5}$ and $PM_{10\text{-}2.5}$ were also subjected to statistical analysis to determine the Pearson distance correlation (Székely *et al.*, 2007) matrix of the elements. This was calculated using the Statistical Package for Social Scientist (SPSS) software and the correlation was considered significant at 0.001 level (two tailed).

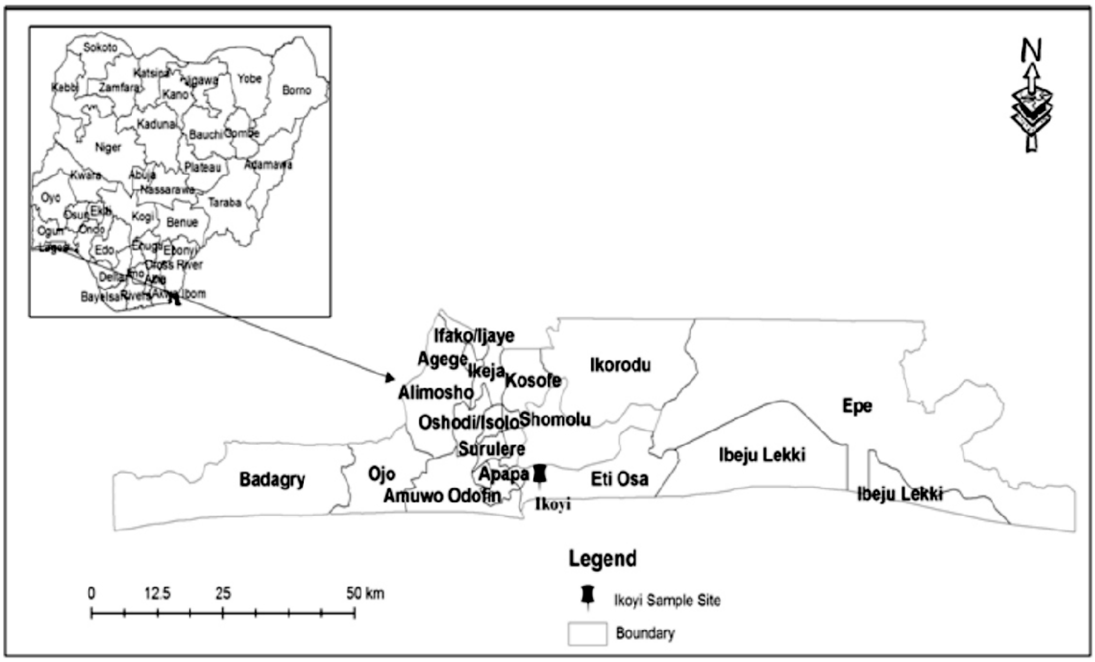

Fig. 1: Map of Lagos State Showing Study Site **(Cooperative Information Network (COPINE), Ile-Ife)**

Principal Component Analysis (PCA).

In order to identify the sources of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ at the study area, principal component analysis (PCA) of $PM_{2.5}$ and $PM_{2.5\text{-}10}$, with varimax rotation of the components, was achieved using Statistical Package for Social Scientist (SPSS) software. Varimax rotation was done to get a clearer pattern of the components without changing their relative positions. Detailed methodology for performing PCA can be found in Chan and Mozurkewich (2007).

RESULTS AND DISCUSSION

Mass concentrations of $PM_{2.5\text{-}10}$ and $PM_{2.5}$ fractions obtained in this study have been reported elsewhere (Ezeh *et al.*, 2012), hence only the elemental concentrations results were discussed herein. Table 1 displays the concentrations of Twenty-three (23) elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb) detected in both fractions. $PM_{2.5\text{-}10}$ contributed about 20 to 68 % of the overall mass loads while less than 5 % was accounted for by $PM_{2.5}$ fraction.

Table 1: Elemental Concentrations, Enrichment Factor (EF) and Pollution Indices (PIs) of PM$_{2.5-10}$ Aerosols

Element	Typical Crustal Rock (µg/g) (Taylor, 1964)	Mean Concentration (Error) ng/m^3		Enrichment Factor		Pollution Indices	
		PM$_{2.5-10}$	PM$_{2.5}$	PM$_{2.5-10}$	PM$_{2.5}$	PM$_{2.5-10}$	PM$_{2.5}$
Na	28300	627 (8)	19 (4)	0.80	3.75	0.02	0.03
Mg	20900	150 (4)	9 (3)	2.46	6.08	0.01	0.06
Al	81300	308 (4)	6 (2)	4.65	31.49	0.00	0.02
Si	277200	988 (7)	25 (2)	4.95	28.15	0.00	0.02
P	1050	18 (3)	12 (2)	1.06	0.21	0.02	0.71
S	260	381 (4)	86 (2)	0.01	0.01	1.47	0.22
Cl	130	902 (7)	25 (2)	0.00	0.01	6.94	0.03
K	25900	166 (4)	81 (2)	2.75	0.80	0.01	0.49
Ca	36300	1075 (9)	14 (2)	0.60	6.28	0.03	0.01
Ti	4400	38 (3)	11 (5)	1.00	1.00	0.02	0.14
V	135	9(5)	15 (6)	0.27	0.02	0.07	1.70
Cr	100	11(1)	11 (2)	0.16	0.04	0.11	0.53
Mn	950	9 (1)	9 (3)	1.85	0.12	0.01	2.26
Fe	50000	418 (4)	47 (3)	2.11	2.69	0.01	0.11
Ni	75	12 (4)	13 (1)	0.11	0.01	0.16	1.06
Cu	55	28 (3)	365 (9)	0.03	0.00	0.52	12.81
Zn	70	38 (1)	26 (5)	0.03	0.01	0.55	0.68
Se	0.05	nd	nd	0.00	0.00	6.75	0.24
Br	2.5	25 (5)	9 (1)	0.00	0.00	10.00	0.36
Rb	90	2 (1)	nd	1.04	1.91	0.02	0.08
Sr	375	15 (2)	2 (1)	0.44	0.58	0.04	0.11
Zr	165	8 (1)	nd	0.36	0.19	0.05	0.27
Pb	13	16 (4)	23 (7)	0.01	0.00	1.27	1.39

This implies that bulk constituents of the PM$_{2.5}$ fraction were not analyzed and could probably be elemental carbon or organic compounds as evidenced by the black colour of the exposed filters. Measurement errors were typically of the order of ± 1 to ± 15 % for most species in both fractions.

For PM$_{2.5-10}$ size fraction (Table 1), Ca (average: 1075 ng m^{-3}), was the most abundant element.The mean concentration obtained in this study is simillar to the average value (640 ng m^{-3}) reported for Mushin (Ezeh *et al.*, 2014), but lower than the value (6000 ng m^{-3}) for Abuja (Abiye *et al.,* 2013). This could be due to the geographical locations of these sites. Whereas Ikoyi and Mushin are situated in Lagos, Abuja is located in the Northern part of Nigeria (≈ 800 Km away from Lagos). As Ca is a typical marker of soil dust, it is quite reasonable to observe higher concentrations in Abuja which is closer to Sahara region of Africa. Other elements with high values in this fraction are Na (627 ng m^{-3}), Al (308 ng m^{-3}), Si (988 ng m^{-3}), S (381 ng m^{-3}), Cl (902 ng m^{-3}), and Fe (418 ng m^{-3}). The high values recorded for the entrained dust marker elements (Ca, Al, Si, and Fe) could be attributed to their ubiquitous nature in the earth crust as well as the fact that particulates due to dust could be likely significant in urban areas such as Lagos where some road networks and walkways are unpaved and poorly maintained (Tunde, 2009). Conversely, the origin of Al and Fe could also be linked to other sources such as ferrous and non-ferrous smelting industries which are hitherto located in Lagos mainland. Abiye *et al.* (2013) in their study of Abuja PM$_{2.5-10}$ aerosols reported Si concentration in the range of 573 to 6683 ng m^{-3} and 475 to 6204 ng m^{-3} in low and high density residential areas respectively. Na and Cl are typical marine sea-salt elements. However, Lagos is endowed with aquatic habitats and their high values can also indicate terrestrial sources (Wetlands and Freshwater). Conversely, the concentration of Na and Cl obtained at Mushin (Ezeh *et al.*, 2014) which is in the mainland of Lagos were higher than values registered for Ikoyi (an Island).The observed result can be explained using the assumption that wind-field follows the land-sea breeze flow pattern shown in Figure 2. Under this scenario, warm air rises over the ocean, gets transported inland retaining as much of its marine finger-print as possible. At a certain distance inland, air experiences subsidence and travels as ground level back to the ocean. As the air parcel moves from the zone of subsidence to the ocean, it continues to be modified by the influence of the land processes, during which it may gradually loose its finger-prints. Thus, Ikeja appears to be the closest to the point of subsidence and experiences the impacts of marine activities more than the sites closer to the ocean. Although Na and Cl are not classified as toxic metals, persistent exposure could cause itching and discomfort to humans (Cohen *et al.*, 2008). Average Pb concentration (16 ng m^{-3}) observed in the $PM_{2.5-10}$ size fraction is lower than the World Health Organization (2003) Europe guideline value of 50 ng m^{-3}. Reduction in the concentration of Pb could be as a result of ban in the importation of leaded gasoline in Nigeria as well as the increasing use of catalyst-equipped automobiles. However, Pb concentration in this study could be due to local sources.

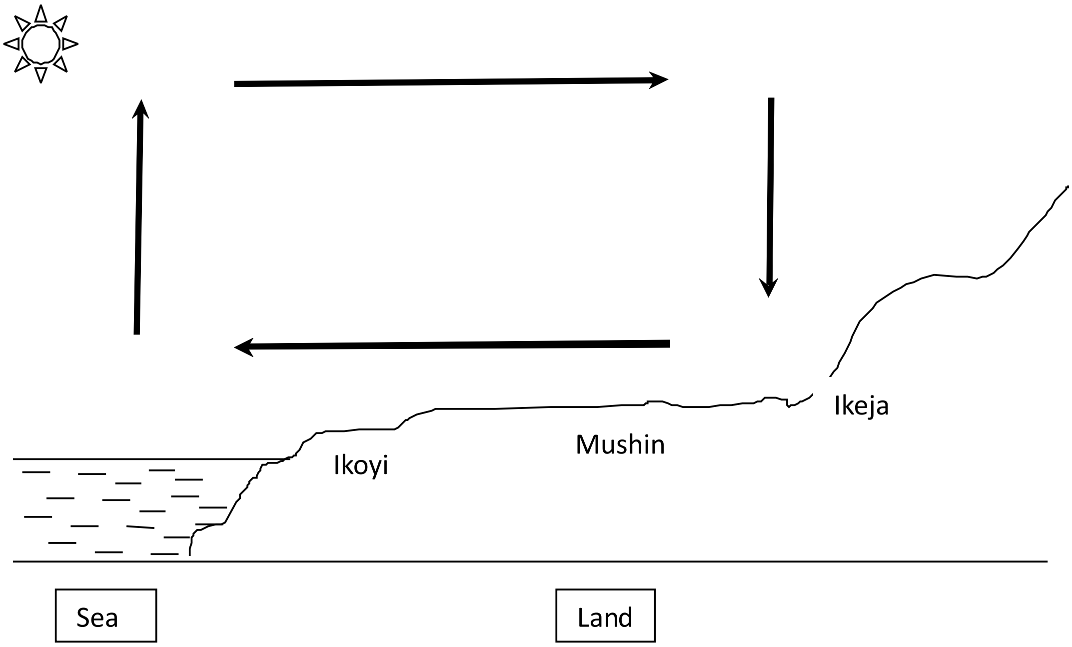

Fig. 2: Possible Configuration of the Land-Sea Breeze System over the Study Area

On the other hand, the mean concentrations of V (9 ng m^{-3}) and Ni (12 ng m^{-3}), the two markers for heavy or gasoline oil combustion emissions were higher than values of 2 ng m^{-3} and 1.4 ng m^{-3} for Lagos (Oluyemi and Asubiojo, 2001).

For fine ($PM_{2.5}$) fraction (Table 1), Cu (365 ng m^{-3}) was the most pronounced element. This could likely be due to tyre wear, refuse incineration, and other anthropogenic sources such as smelting activities (Oluyemi *et al.,* 1994). Abiye *et al.* (2013) and Ezeh *et al.* (2014) reported average Cu concentrations of 623 ng m^{-3} and 2 ng m^{3} for Abuja and Mushin Lagos cities respectively. High concentration of Cu was observed in this study than in Mushin probably due to local sources or atmospheric transports as we expected higher concentrations of trace elements at Mushin owing to its urban class (high density/industrial). Other elements with significant average concentrations include; K (86 ng m^{-3}), S (86 ng m^{-3}), Fe (47 ng m^{-3}) and Zn (86 ng m^{-3}). Abiye *et al.* (2013) and Ezeh *et al.* (2014) reported average sulphur concentration of 643 ng m^{-3} and 136 ng m^{-3} for Abuja and Mushin cities respectively. Sulphur origin in the fine fraction could be mainly anthropogenic (energy production, biomass burning, refuse incinerations or emissions from ships using heavy oil). Airborne sulphur rarely occurs as a pure element but it is usually produced as SO_2 gas which readily converts to sulphate SO_4^{2-} ions under normal atmospheric conditions. The ions can exist in the atmosphere as sulphuric acid producing acid rain or be partially neutralized to ammonium bisulphate or fully neutralized to ammonium sulphate (Lee *et al.*, 2001).

High contribution of K and S observed in the coarse fraction than in the fine fraction showed that the influence of soil dust source could be higher than that of anthropogenic sources. This is evidenced by the wide disparity in their mean ratios (0.94 and 0.44) of K/S in fine and coarse fractions respectively. Inter-elemental ratio is often used to study the variations in emission sources as source markers tend to display close or similar ratio. Average concentrations observed for Ni (12 ng m^{-3}) was also low compared to the 20 ng m^{-3} European guideline standard. Ni is also classified as a non-toxic metal; however exposure to it could cause skin rashes and irritations. Some Ni compounds such as $Ni(CO)_4$ have been reported to be very toxic upon continuous inhalation. Average concentrations of the markers for metallic industrial emissions, namely Pb (23 ng m^{-3}) and Zn (26 ng m^{-3}), were comparable with values observed in the coarse fraction. World Health Organization (2003) set 50 ng m^{-3} as Pb guideline value for Europe. Though, Zn is potentially non-toxic, on the other-hand Pb is a toxic and carcinogenic metal. Other elements detected such as Cu, Cr, Se and Cs are known to be toxic; exposure even at low concentrations could pose adverse health effects on humans and animals (World Health Organization, 2006).

Due to the designation of Lagos as a coastal city, we estimated the contributions of the sea salt (ss) and non-sea salt (n-ss) components of Na, S, K and Ca respectively as they can be directly emitted from the sea as sea spray or implicated in other sources such soil dust and biomass burning. The n-ss component of Na concentrations in the coarse and fine particulate fractions were estimated using the crustal Na/Al ratio of 0.348 (Mason, 1966) as shown in equations 1:

$$n - ssNa = [Al] \times \left[\frac{Na}{Al}\right]_{CRUSTAL} \quad (1)$$

Where, $n - ssNa$ is the concentration of non-sea salt component of Na, $[Al]$ is the concentration of Al in the study and

$\left[\frac{Na}{Al}\right]_{CRUSTAL}$ is the ratio of the concentrations of Na with Al in crustal material.

Sulphur was one of the major elemental components measured by PIXE in both particulate matter size fractions. In the fine fraction, its origin could be mainly anthropogenic (as aforementioned), as it can be directly emitted from fossil-fuel combustion processes and also produced from SO_2 oxidation in the atmosphere. While sulphur concentration in the coarse fraction could mainly be due to sea spray as evidenced from particle size distribution studies (Lee *et al.*, 2001). The n-ssS concentrations in the coarse and fine particulate fractions were estimated using sea water S/Na ratio of 0.084 (Cohen *et al.*, 2004) as shown in equations 2 and 3 respectively:

$$ssS = [Na]_{ssNa} \times \left[\frac{S}{Na}\right]_{SEAWATER} \quad (2)$$

$$n - ssS = [S]_{TOTAL} - ssS \quad (3)$$

Where, ssS is the sea salt concentration of S,
$n - ssS$ is the non-sea salt concentration of S,
$[S]_{TOTAL}$ is the total concentration of S in the study,
$[Na]_{ssNa}$ is the concentration of sea salt component of Na in the study and
$\left[\frac{S}{Na}\right]_{SEAWATER}$ is the ratio of the concentrations of S with Na in sea water.

The sea-salt components of K and Ca were estimated using the generally accepted seawater K/Na (0.036) and Ca/Na (0.038) ratios (Weast and Astle, 1982) as showed in equations 4 and 5 respectively:

$$ssK = [Na]_{ssNa} \times \left[\frac{K}{Na}\right]_{SEAWATER} \quad (4)$$

$$ssCa = [Na]_{ssNa} \times \left[\frac{Ca}{Na}\right]_{SEAWATWER} \quad (5)$$

Where, ssK and $ssCa$ are the sea salt components of K with Ca in the study respectively, $\left[\frac{K}{Na}\right]_{SEAWATER}$ is the ratio of the concentrations of K with Na in sea water and $\left[\frac{Ca}{Na}\right]_{SEAWATER}$ is the ratio of the concentrations of Ca with Na in sea water.

As shown in Table 2, Na is mainly of marine origin (ssNa is about 63 and 85 % of total Na in the fine and coarse fractions respectively). Conversely, only a small fraction of S is due to sea salt; the n-ss components of S accounted for ≈ 100 % (fine) and 89 % (fine) of total S. This could be an indication that the S origin was mostly anthropogenic in nature or due to other natural sources such as biogenic emissions. Similarly, low percentages of S for the fine fraction have been reported elsewhere (Cohen *et al.*, 2004) while it is quite unusual for the coarse fraction. The n-ss component of K and Ca accounted for about 89 % of their total concentration in both fractions.

Table 2: Sea salt (ss) and Non-sea salt (n-ss) Na, S, K and Ca Components

Elements	$PM_{10-2.5}$ (ng m^{-3})	$PM_{2.5}$ (ng m^{-3})
	Mean (Standard Deviation)	Mean (Standard Deviation)
ssNa	520(8)	2 (1)
n-ssNa	107(6)	4(2)
ssS	44 (2)	≈ 0
n-ssS	337(6)	81 (4)
ssK	19 (2)	≈ 0
n-ssK	148(7)	81 (8)
ssCa	20(2)	1
n-ssCa	1055 (12)	13 (3)

It was observed that the mean K/Na (< 5) and Ca/Na (< 2) ratios obtained in the fine and coarse fractions respectively were in accordance with values reported elsewhere (Weast and Astle, 1982; Ezeh *et al.,* 2014).

To have the first indication on the extent of the contribution of anthropogenic emissions to atmospheric elemental levels, enrichment factors (EF) were calculated for each element using the crustal composition (Taylor, 1964) and Ti as the normalizing element. The use of Ti as a normalizing agent is quite appropriate because it is a crustal element with less anthropogenic influence. Elements with EF next to unity have a strong natural component while elements with high EF could have anthropogenic origin, or are due to other natural sources such as marine aerosols. Enrichment factor calculated for $PM_{2.5}$ and $PM_{2.5-10}$ particulates are presented in Table 1. For $PM_{2.5-10}$ fraction, most elements were not highly enriched as their average EF values were below 5. For instance, 0.80 (Na), 4.65 (Al), 0.01 (S), 2.75 (K), 2.11 (Fe), 0.01 (Zn) and 0.01 (Pb) were registered as the respective EF values. For $PM_{2.5}$ fraction (Table 1), with the exception of Al and Si with EF of 31.49 and 28.15, EF recorded for other elements were < 7. For instance, 0.04 (Cr), 0.12 (Mn), 0.01 (Ni), 0.02 (V), 0.00 (Cu) and 0.00 (Br) were poorly enriched. Conversely, Ezeh *et al.* (2014), in their study of Mushin aerosols observed S, Cl and K as highly enriched elements. Low enrichment factor especially of the sea spray elements (Na and Cl) depicts that its non-anthropogenic origin.

Pollution indices (PIs) of the elements were also investigated to assess the environmental quality of elemental concentrations obtained in both fractions. PIs of each element was calculated using (Mason, 1966) values for the elemental compositions of crustal rock and were classified as either low (PI < 1), moderate (1< PI ≤ 3) or high (PI > 3) for both size fraction (dos Anjos *et al.,* 2000). Calculated PIs for $PM_{2.5-10}$ fraction are displayed in Table 1 and varies greatly across the different elements. For instance, PIs of the sea spray markers (Na and Cl) were found in different pollution classes. While Na displayed low pollution class in all the cities, Cl was in the highly pollution class. PIs of Al and Si displayed simillar values; both together with K, Ca and Fe are classified in the low pollution range. However, Br was classified in the highly pollution class. Equally, Pb was in the moderately pollution class. Source of Pb pollution in Lagos could be due to local sources (waste incineration, smelting, industrial activities or atmospheric transport since leaded gasoline have been abolished in 2003 and little or few industries are located in the city. For $PM_{2.5}$ (Table 4), S average concentrations were all within the low pollution class unlike in the $PM_{2.5-10}$ whose PIs were in the moderate pollution class. Conversely, V, Ni and Pb were within the moderate PIs range. As earlier mentioned S, Ni and V are markers for emissions associated to petroleum oil combustion. Interestingly, only Cu in this fraction was in the highly polluted class (PI > 12). Cu concentration in the fine fraction could be due to tyre wears, waste incinerations and industrial emissions. In general, the PIs of other elements in this fraction were found in the low pollution class.

Pearson Elemental Correlation

The Pearson elemental correlation matrices for $PM_{2.5-10}$ and $PM_{2.5}$ particulates are presented in Tables 3 and 4 respectively. The elements displayed both negative and positive correlations. For instance, in the coarse ($PM_{10-2.5}$) fraction, Na has strong positive correlations with Mg ($r^2 = 0.84$) and Cl ($r^2 = 0.88$). Si has strong positive correlations with Al ($r^2 = 1.00$), Ca ($r^2 = 0.85$), Ti ($r^2 = 0.99$), Fe ($r^2 = 0.99$), Sr ($r^2 = 0.74$) and Zr ($r^2 = 0.64$) due to their association with crustal sources. Despite its ubiquitous nature as well as its associations with many elements, Fe only showed negative correlation ($r^2 = -0.10$) with Cl. Similarly, Cu ($r^2 = -0.09$) and Zn ($r^2 = -0.19$) registered negative correlations with Na. Similarly, in the $PM_{2.5}$ fraction, negative and positive correlations were also displayed by the elements. Unlike in the $PM_{10-2.5}$ fraction with many strong elemental correlations, it was observed that fewer elements were strongly correlated in the $PM_{2.5}$ fraction. For instance, unlike in the coarse fraction, Na displayed weak correlation ($r^2 = 0.41$) with Cl and could be an indication of different source origin. Sulphur has strong correlation values ($r^2 = 0.80$, 0.70, 0.64, 0.67 and 0.55) with K, V, Ni, Zn and Cu respectively. The marker elements (Zn and Pb) for industrial emissions also displayed strong positive correlation ($r^2 = 0.92$). Thus, strong correlations found between the elements could indicate a common source or chemical similarity, whilst weak correlations could imply different source origin or non-chemical similarity (Adebiyi *et al.,* 2006).

Principal Component Analysis (PCA)

The numbers in Table 5 are loadings of each species to the components, except for % Var., which is the percentage of the variance that is explained by the different components. Factor loading higher than 0.5 were retained and shown. For $PM_{2.5-10}$, five factors with eigenvalues greater than 1 were resolved (Table 5). The cumulative explained variance was 88%.

In factor 1, elements with high scores are Al, Si, P, K, Ca, Ti, Fe and Ca and could be associated to a soil dust (Hueglin *et al.*, 2005). The factor explained about 31% of the variance of the $PM_{2.5-10}$ elemental concentrations. As previously mentioned, high percentage of explained variance attributed to soil dust could be due to entrained and re-suspended dust from poorly maintained road networks and unpaved. As expected, the second component in the coarse particulate fraction clearly implied a sea spray (Yli-Tuomi *et al.*, 2003; Kothai *et al.*, 2008) source with high loadings of 0.92, 0.82, 0.86 and 0.77 for Na, Mg, Cl and Br respectively. About 23% of the total variance explained in the factor is expected as the study site is an Island and located few kilometers away from the shores of the Atlantic Ocean. High loadings of S (0.81), V (0.85) and Ni (0.75) in the third component implied emissions from the heavy oil combustions (Hueglin *et al.*, 2005). Chromium (0.64) and Se (0.83) high loadings in the second factor could be an artifact from industrial, biomass or waste incineration emissions. The third factor accounted for about 14% of the explained variations. The fourth components displayed high loadings of Cr (0.63), Cu (0.52), Zn (0.88), Zr (0.74) and Pb (0.81). This component could be identified as emissions emanating from industrial activities such as smelting works (Kelly *et al.,* 1995). However, Zn could also indicate vehicular emissions as it is an indicator for two- stroke vehicles since it is used in formulation of automobile lubricating oils (Chueinta *et al.*, 2000).

Table 3: Elemental Correlations of the $PM_{2.5\text{-}10}$ Fraction

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Rb	Sr	Zr	Pb
Na	1.00																						
Mg	0.84	1.00																					
Al	0.09	0.57	1.00																				
Si	0.07	0.55	1.00	1.00																			
P	-0.05	0.33	0.84	0.85	1.00																		
S	0.38	0.71	0.68	0.66	0.47	1.00																	
Cl	0.88	0.68	-0.06	-0.06	-0.16	0.21	1.00																
K	0.36	0.73	0.84	0.84	0.73	0.75	0.19	1.00															
Ca	0.06	0.48	0.85	0.84	0.65	0.78	0.00	0.66	1.00														
Ti	0.00	0.50	0.99	0.99	0.84	0.63	-0.10	0.80	0.83	1.00													
V	0.19	0.50	0.54	0.54	0.28	0.74	0.14	0.47	0.68	0.54	1.00												
Cr	0.08	0.46	0.67	0.66	0.46	0.59	0.02	0.53	0.71	0.66	0.55	1.00											
Mn	0.12	0.53	0.88	0.87	0.82	0.76	-0.09	0.80	0.81	0.86	0.52	0.55	1.00										
Fe	0.00	0.49	0.98	0.99	0.83	0.63	-0.10	0.79	0.83	0.99	0.58	0.65	0.86	1.00									
Ni	0.25	0.54	0.55	0.55	0.35	0.72	0.19	0.45	0.66	0.56	0.94	0.54	0.55	0.60	1.00								
Cu	-0.09	0.27	0.74	0.74	0.70	0.43	-0.15	0.56	0.60	0.73	0.42	0.45	0.69	0.75	0.37	1.00							
Zn	-0.19	0.19	0.55	0.53	0.36	0.37	-0.36	0.32	0.41	0.54	0.48	0.31	0.46	0.57	0.46	0.49	1.00						
Se	0.02	0.20	0.32	0.32	0.02	0.47	0.05	0.09	0.61	0.29	0.61	0.55	0.25	0.31	0.53	0.21	0.17	1.00					
Br	0.31	0.50	0.47	-0.50	0.46	0.45	0.43	0.48	0.47	0.47	0.41	0.22	0.40	0.50	0.46	0.39	0.20	0.29	1.00				
Rb	0.05	0.48	0.89	-0.90	0.81	0.58	-0.02	0.76	0.73	0.90	0.56	0.47	0.82	0.92	0.62	0.63	0.53	0.18	0.54	1.00			
Sr	0.15	0.54	0.75	0.74	0.50	0.82	0.08	0.66	0.95	0.74	0.73	0.73	0.73	0.73	0.67	0.49	0.35	0.59	0.39	0.62	1.00		
Zr	-0.32	-0.06	0.40	0.64	0.34	-0.06	-0.34	0.22	0.09	0.43	0.00	-0.13	0.37	0.46	0.04	0.51	0.61	-0.32	0.16	0.45	-0.02	1.00	
Pb	-0.10	0.31	0.65	0.40	0.53	0.50	-0.27	0.50	0.50	0.63	0.43	0.35	0.63	0.65	0.38	0.60	0.90	0.11	0.25	0.58	0.45	0.59	1.00

Note: $n = \alpha = 0.001$, $r \geq 0.519$ at 95 % (Confidence Interval Level, strongly correlated are shown in bold type)

Table 4: Elemental Correlations of the $PM_{2.5}$ Fraction

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Rb	Sr	Zr	Pb
Na	1.00																						
Mg	0.35	1.00																					
Al	0.20	0.50	1.00																				
Si	0.26	0.52	0.79	1.00																			
P	-0.06	0.07	0.51	0.62	1.00																		
S	0.40	0.18	0.21	0.43	-0.01	1.00																	
Cl	0.51	0.26	0.15	0.54	0.40	0.07	1.00																
K	0.34	-0.01	-0.01	0.31	-0.07	0.80	0.00	1.00															
Ca	-0.04	0.18	0.47	0.72	0.51	0.35	0.49	0.40	1.00														
Ti	0.04	0.28	0.57	0.83	0.68	0.08	0.58	0.19	0.76	1.00													
V	-0.02	0.07	-0.08	0.17	0.09	0.70	0.13	0.44	0.43	0.06	1.00												
Cr	-0.14	0.49	0.65	0.56	0.21	0.10	0.11	0.00	0.30	0.32	-0.19	1.00											
Mn	0.15	-0.46	-0.10	0.07	-0.09	0.54	0.08	0.44	0.17	0.14	0.17	-0.34	1.00										
Fe	0.09	0.28	0.64	0.86	0.67	0.37	0.58	0.37	0.89	0.39	0.25	0.39	0.21	1.00									
Ni	0.15	-0.14	0.02	0.33	0.39	0.64	0.42	0.42	0.53	0.90	0.73	-0.26	0.48	0.44	1.00								
Cu	0.22	0.07	0.28	0.53	0.09	0.55	0.34	0.51	0.47	0.49	0.08	0.17	0.59	0.62	0.31	1.00							
Zn	0.23	-0.14	-0.08	0.15	-0.09	0.67	0.06	0.57	0.36	0.10	0.39	-0.23	0.75	0.26	0.52	0.53	1.00						
Se	0.03	0.40	0.26	0.16	0.05	0.08	0.17	-0.03	0.16	0.08	0.12	0.44	-0.30	0.10	0.08	0.22	-0.09	1.00					
Br	0.31	-0.09	0.14	0.29	0.12	0.58	0.05	0.62	0.18	0.06	0.11	0.12	0.36	0.22	0.37	0.43	0.36	0.10	1.00				
Rb	0.34	0.17	0.15	0.18	-0.05	0.35	-0.05	0.44	0.08	0.13	0.09	0.00	0.46	0.17	0.12	0.12	0.55	-0.71	0.13	1.00			
Sr	-0.28	0.04	-0.05	0.21	0.02	0.36	0.58	0.10	0.45	0.11	0.44	0.10	-0.02	0.21	0.46	0.12	0.10	0.33	-0.03	-0.28	1.00		
Zr	-0.07	-0.08	0.12	0.22	0.22	0.31	0.22	0.51	0.40	0.38	0.05	0.26	-0.05	0.41	0.00	0.37	0.32	0.32	0.00	0.63	0.58	1.00	
Pb	0.38	-0.09	0.09	0.32	0.14	0.42	0.18	0.39	0.18	0.25	0.11	-0.20	0.57	0.26	0.33	0.46	0.92	-0.76	0.44	0.62	-0.24	-0.25	1.00

Note: $n = \alpha = 0.001$, $r \geq 0.519$ at 95 % (Confidence Interval Level, strongly correlated are shown in bold type)

Table 5: Loadings obtained by Principal Component Analysis, Normalized by Varimax Rotation

Elements	$PM_{2.5-10}$ (Coarse)					$PM_{2.5}$ (Fine)					
	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
Na		0.92									0.82
Mg		0.82						0.72			0.50
Al	0.87						0.88	0.75			
Si	0.89				0.52		0.96				
P	0.86									0.77	
S			0.81			0.69			0.52		
Cl		0.86									0.97
K	0.74									0.77	
Ca	0.77				0.57		0.72				
Ti	0.89						0.91				
V			0.85						0.89		
Cr			0.64	0.63				0.82			
Mn	0.72					0.77					
Fe	0.86						0.83			0.58	
Ni			0.75						0.87		
Cu				0.52		0.59				0.54	
Zn				0.88		0.80		0.52			
Se			0.83							0.82	
Br		0.77				0.59					
Rb	0.78					0.67					
Sr					0.81				0.60		
Zr				0.74						0.74	
Pb				0.81		0.76		0.50			
% age Var. Explained	31.45	22.99	13.73	12.94	6.35	20.01	19.35	12.05	10.61	9.09	5.86

It accounted for about 13% variations in the $PM_{2.5-10}$ elemental concentrations. The fifth factor resolved for the coarse fraction registered high scores of Si (0.52), Ca (0.57) and Sr (0.81). Thus, could be considered as emissions from physical construction activities (Hueglin *et al.*, 2005), a scenario which may be attributed to the construction activities at the Old Federal Secretariat, Ikoyi, separated by a distance of about 1 km away from the receptor site used for this study.

For $PM_{2.5}$ (Table 5), six components were extracted from the PCA with a cumulative explained variance of 77%. The first factor with high loadings of S (0.69), Mn (0.77), Cu (0.59), Zn (0.80), Br (0.59), Rb (0.67) and Pb (0.76) was strongly influenced by traffic related sources (vehicular exhausts, tire and brake abrasion). Considering the fact that no industry is located in Ikoyi, heavy traffic flow suggests that traffic related sources and waste incineration could be the dominant emission sources for the first factor. However, the first component explained about 20% $PM_{2.5}$ total variance. The elements with high scores of over 0.5 were found in factor 2, including the soil dust elements; Al, Si, Ca, Ti and Fe. As expected, the explained variance (19%) was lower than 31% recorded for $PM_{2.5-10}$ because soil dust is more pronounced in the coarse fraction. The third component with high scores of Mg, Al, Cr, Zn and Pb suggests emission from non-ferrous smelting works (Hueglin *et al.*, 2005). It accounted for 12% explained $PM_{2.5}$ variance. The fourth factor is clearly emission from heavy oil combustion as it displayed high loadings of S (0.52), V (0.89) and Ni (0.87). About 10% of $PM_{2.5}$ explained variance was attributed to fourth factor. Factor five displayed high scores of P (0.77), K (0.77), Fe (0.58), Cu (0.54) and Se (0.82), thus could be associated with biomass burning emissions. Although, Ikoyi (our study site) is a sedentary well planned area where most inhabitants do not use biomass as alternative source of energy. However, there is no doubt the influence of biomass emissions from the hinter land with higher population density could impact Ikoyi through atmospheric transport of particles. PCA revealed that the fifth factor accounted for about 9% explained $PM_{2.5}$ variance. The influence of the sea spray emissions was pronounced in the sixth component as it showed high scores of Na (0.82), Mg (0.50) and Cl (0.97). Conversely, the percentage explained variance (6%) is about 600% lower than explained variance of sea spray component in the coarse fraction probably due to differences in particle size morphology.

CONCLUSION

Twenty three (23) elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr and Pb) were detected in both $PM_{2.5-10}$ and $PM_{2.5}$ fractions of suspended particulate matter collected at a receptor site located in Ikoyi, Lagos. As typical of sub-Saharan African aerosol, elemental concentrations of the crustal markers (Al, Si, Ca, Ti, Fe and Zr) were more pronounced in $PM_{2.5-10}$ fraction while anthropogenic elements recorded higher concentrations in $PM_{2.5}$ fraction. Enrichment factor calculation revealed that some elements were highly enriched thus, indicating anthropogenic origin while pollution indices displayed different pollution classes for the elements. Due to the coastal nature of Ikoyi Lagos, an estimate of the sea salt components of Na revealed 85% and 63% $PM_{2.5-10}$ and $PM_{2.5}$ particulates. While n-ss components of S, K and Ca were greater than 85% in both fractions. Pearson elemental correlation matrices of $PM_{2.5-10}$ and $PM_{2.5}$ showed that most source markers correlated strongly while some elements were weakly correlated. PCA apportioned five and six sources for $PM_{2.5-10}$ and $PM_{2.5}$ fractions with cumulative explained variances of 88% and 77% respectively. For $PM_{2.5-10}$ fraction, contributions from soil dust and sea spray were more pronounced. However, PCA result of $PM_{2.5}$ fraction revealed that its sources were mainly anthropogenic; industrial or traffic related emission sources and heavy oil combustions.

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