

Trace Metals and Source Identification of Air-Borne Particulate Matter Pollution in A Nigerian Megacity

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Abstract

Background: The megacity status of Lagos has led to increased pressure on the urban environment especially on air quality. Twelfth decade of serving as Nigeria former capital and currently the economic nerve centre of the country, there is yet no holistic information on source apportionment of atmospheric aerosols in the city. Hence, the study was conducted to provide an understanding of the chemical compositions and source identifications of PM_{2.5} (aerodynamic diameter, $d_{ae} \leq 2.5 \mu\text{m}$) and PM_{2.5-10} ($2.5 \mu\text{m} < d_{ae} < 10 \mu\text{m}$) particulate matter over Lagos, Nigeria.

Methods: Sampling of PM_{2.5} (fine) and PM_{2.5-10} (coarse) were collected on nuclepore polycarbonate filters using a low volume GENT sampler (Schlumberger Model: M250) equipped with double staged stacked filter units. A total of 192 samples were collected (96 of each fraction). Elemental analyses of both fractions were carried out using Particle Induced X-ray Emission (PIXE) while Proton Induced Gamma-ray Emission (PIGE) was also employed to complement for X-ray self-absorption effect among low Z elements by PIXE technique.

Results: Data on twenty-four elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, Cs and Pb) detected in both particulate sizes were displayed, discussed. Receptor modelling of the data for source apportionment and identification were achieved for both fractions via positive matrix factorization (PMF). Five source categories with stable profiles were identified in both fractions.

Conclusions: The study concluded that anthropogenic emissions from gasoline oil combustions, industrial, and biomass burning emissions were more predominant and could pose great hazard to Lagos receptors during the sampling period.

Keywords: Source apportionment; PIXE; Positive matrix factorization; Emissions

Introduction

Lagos (6.45° N and 3.39° E) is the former capital of Nigeria. It is also the industrial and commercial nerve center accounting for over 40% of the industries in Nigeria. Lagos is also a coastal city with relatively small land mass (3577 km²) and population density of about 2400 persons per km² [1]. The city is also the hub of the nation's aviation activities as it handles about 74% international departures and 37% domestic connections [2]. It is therefore obvious that most inhabitants of Lagos could face serious environmental pollution challenges especially on air pollution; owing to the fact that her high population density and associated anthropogenic activities could impact much pressure on the relatively small land mass. As typical of a sub Saharan tropical city, Lagos climate is seasonally damp and very humid. Its climate is influenced by monsoons originating from South Atlantic Ocean and brought by maritime tropical air mass, a warm moist sea to land seasonal wind. Lagos temperature is almost constant throughout the year and averaged to 26°C. The annual rainfall received in Lagos is very high, usually above 4000 mm of rainfall [2] and with two distinct seasons; Harmattan (October, November, December, January and February) while the rest of the months are in Rain Season.

A number of urban areas across Nigeria are known to experience elevated levels of atmospheric particulate matter (APM) pollution [3]. Scientific studies of APM concentrations are needed to understand and regulate the factors that contribute to air quality deterioration. Source-receptor relationships for particulate matter could be identified and quantified using a number of techniques such as receptor modeling based on measurements done at receptor site. Few works on receptor model based source apportionment of APM have been reported in Nigeria; [4] applied chemical mass balance (CMB) receptor model on the elemental

composition data obtained from Lagos and identified four (entrained dust, marine, regional sulphate and vehicular emissions) sources of APM. Recently [5] identified soil, automobile, marine, residual oil combustion and biomass burning emissions as the major sources of PM_{2.5-10} in Lagos hot-spots with CMB model. However, these earlier studies had inherent problems of underestimation or overestimation of sources. In addition, few sources were resolved probably due to usage of imported source profiles in the CMB based modeling [6]. Unfortunately, methodologies for source profiles measurements are often cumbersome, time-consuming, and expensive hence, information on local source profiles is largely lacking in Nigeria.

A different but highly effective tool for receptor modelling exists in using positive matrix factorization (PMF) model to apportion sources without the prior knowledge of local emissions source profiles. PMF offers a viable alternative given the absence of a local source profile library for air pollutants especially in most developing countries such as Nigeria. PMF have been applied successfully in the studies of aerosol sources of many cities; Toronto, Canada [7]; Atlanta, USA [8] Pittsburg, USA [9]; Beijing, China [10]; Bangladesh [11] and Costa Rica [12]. An

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Received March 17, 2017; Accepted April 21, 2017; Published May 03, 2017

Citation: Ezeh GC, Obioh IB, Asubiojo OI (2017) Trace Metals and Source Identification of Air-Borne Particulate Matter Pollution in A Nigerian Megacity. J Environ Anal Toxicol 7: 463. doi: [10.4172/2161-0525.1000463](https://doi.org/10.4172/2161-0525.1000463)

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excellent review of PMF modeling was presented in [6]. PMF have not been applied in the studies of aerosols in Nigeria until recently [13], applied it in their study of occupational exposures of aerosols in a smelting plant. Inadvertently, PMF is yet to be applied for study at receptor sites in Nigeria, hence a key motivation for the work.

Therefore, the focus of this study is to identify natural and anthropogenic sources of $PM_{2.5}$ and $PM_{2.5-10}$ chemical compositions as well as to apportion their contributions by applying PMF receptor model. The data generated from this work will be a key tool in understanding particulate matter sources as well in providing vital information for policy makers in designing effective control strategies.

Materials and Methods

Description of sampling sites

Three sampling sites (Figure 1) located at Lagos Nigeria were used for this study due to their reflection of variations in urban infrastructures such as usual high traffic, residential areas and industrial features. These are Ikeja ($6^{\circ} 36' 16.76''$ N and $3^{\circ} 20' 12.99''$ E), Ikoyi ($6^{\circ} 29' 21.17''$ N and $3^{\circ} 23' 2.45''$ E) and Mushin ($6^{\circ} 31' 57.65''$ N and $3^{\circ} 20' 58.52''$ E). Ikeja represents a typical industrial and medium residential area, Mushin is a typical high density residential area while Ikoyi is a well-planned and secluded area exclusively reserved for the opulent class and it represents the low density populated area.

Samplings

A total of one hundred and ninety-two samples of $PM_{2.5}$ and $PM_{2.5-10}$ were collected simultaneously in the study sites from July to September 2007 to capture rain season variations effectively. Sampling was

achieved using “Gent” stacked filter sampler [14] capable of segregating both size fractions. The samples were collected by gravimetric analysis on pre-weighed and pre-conditioned $8 \mu\text{m}$ (coarse) and $0.4 \mu\text{m}$ (fine) pore sized Whatman polynuclepore filters (supplied by Essque Nigeria Limited, Lagos, Nigeria). Detailed methodology for $PM_{2.5}$ and $PM_{2.5-10}$ sampling using Gent stacked filter sampler have been reported [15]. Mass-balance analyses of the exposed filters were achieved in triplicate measurements using a digital micro-weighing balance (Sartorius, Göttingen, Germany) which was calibrated using the automated *isoCAL* function in-order to ensure accuracy. PM_{10} values were the sum of $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations. The exposed filters were stored in the desiccator before taken to the laboratory for elemental analysis.

Elemental characterization

Elemental concentration for each sample was energy-analyzed by Particle Induced X-ray Emission (PIXE) at external ion beam analysis (IBA) set-up of 3 MV Tandemron Nuclear Accelerator available at *Istituto Nazionale di Fisica Nucleare* (INFN) Firenze, Italy. Calibration of the PIXE system was performed by irradiating suitable Micrometer thin target standards. X-ray spectra obtained from the PIXE measurements were analyzed with GUPIXWIN software developed in Guelph University [16] in order to obtain their net peak areas. The elemental concentrations of the aerosol samples were done using the net peak areas obtained from GUPIXWIN and sensitivity curve, i.e. (counts per μC) per ($\mu\text{g cm}^{-2}$), obtained by the analysis of certified thin elemental standards [17]

Enrichment factor (EF) and pollution indices (PIs)

To have a first indication on the extent of the contributions of

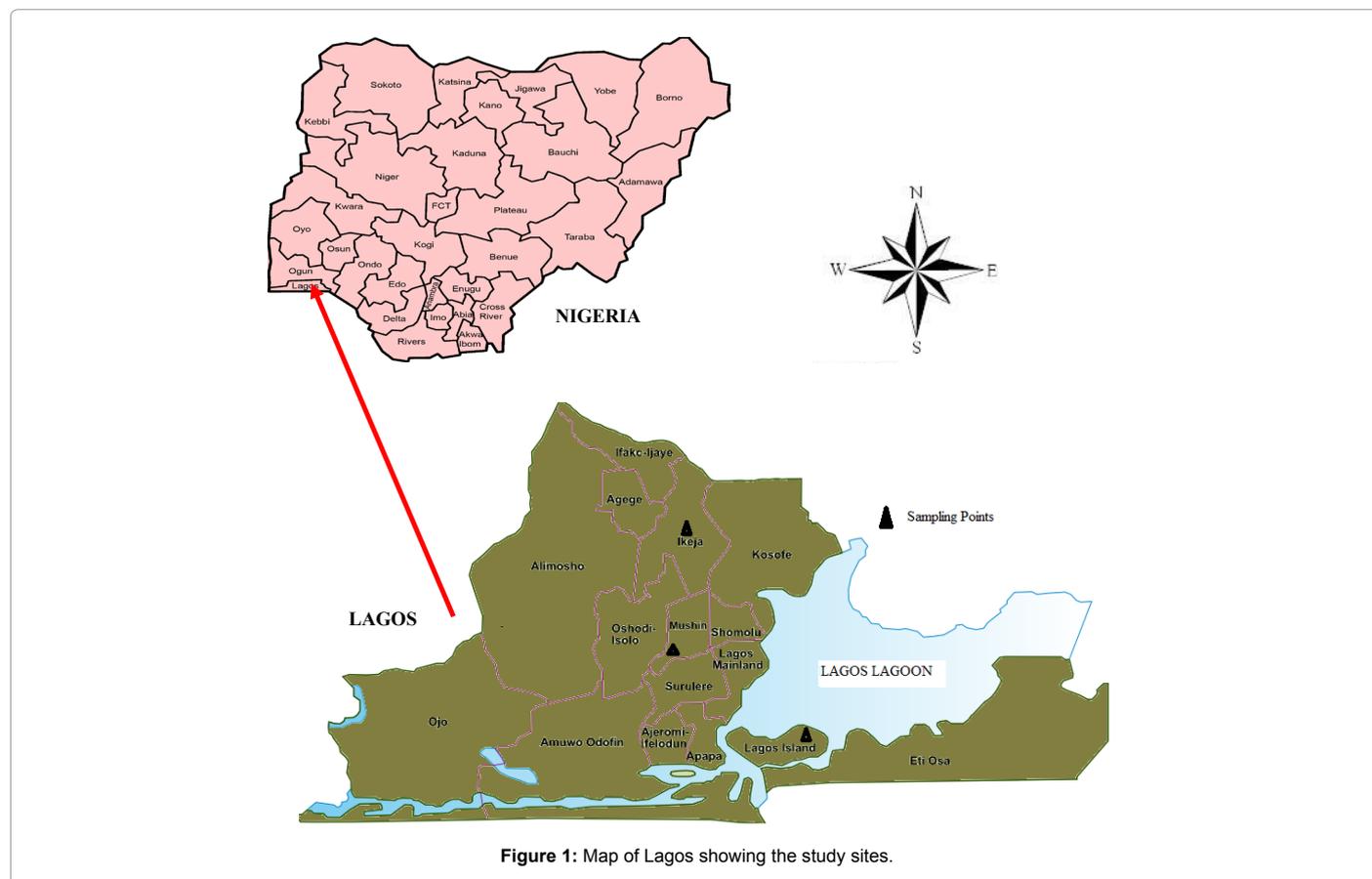


Figure 1: Map of Lagos showing the study sites.

anthropogenic emissions to atmospheric elemental levels, enrichment factors (EF) were calculated for each element using the crustal composition reported elsewhere [18] and Ti as the normalizing element.

The use of Ti as a normalizing agent is quite appropriate since, it is a crustal element with little or no 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. Pollution indices are also commonly used to assess the environment quality and it is defined as the ratio of element concentration in the study to the background content of the abundance of chemical elements in the continental crust. The PIs of the elements were calculated and classified as either low ($PI < 1$), moderately ($1 < PI \leq 3$) or high ($PI > 3$) for both size fraction [19]

Elemental correlation

The elemental concentrations of the analyzed samples of $PM_{2.5}$ and $PM_{2.5-10}$ were subjected to statistical analysis to determine the Pearson distance correlation [20] matrices of the elements. This was calculated using Statistical Package for Social Scientist (SPSS) software and correlation was considered significant at the 0.05 level (two tailed). In order to determine which of the correlations are significant in the statistical sense, the critical multiple correlations coefficient (r) was obtained from the table of significant values. The critical value r with $n=96$, at 98% confidence interval, r^2 of 1.99 was considered significant.

Source apportionment by Positive Matrix Factorization (PMF)

The algorithm for PMF model used in the study has been described in detail [21] and implemented in the PMF2 program [22]; therefore, we present a brief description of the model hereafter. PMF receptor model is based on the overlying principle that a relationship between sources and receptors exist when mass conservation is assumed. A conventional factor analysis model can be written as;

$$Y = XC + E \quad (1)$$

Where, Y is a $n \times m$ matrix, with n measurements and m number of elements, x is $n \times p$ source contribution matrix with p sources, C is $p \times m$ source profile matrix and E is $n \times m$ matrix of residuals.

In this case, when chemical speciation of ambient PM is available, a mass balance equation of the following form can be written as:

$$y_{ij} = \sum_{m=1}^p x_{im} c_{mj} + e_{ij} \quad (2)$$

Where, y_{ij} is the j^{th} species concentration measured in i^{th} sample, x_{im} is the contribution of the m^{th} factor to the receptor on the i^{th} day, c_{mj} is the fraction of the m^{th} factor that is species j , e_{ij} is the residual for the j^{th} species on the i^{th} day and p is the total number of independent sources.

PMF provides a solution that minimizes an object function, $Q(E)$, based upon uncertainties for each observation [24]. This function is defined as;

$$Q(E) = \sum_{m=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \quad (3)$$

Where e_{ij} is the un-modelled portion and σ_{ij} is the standard deviation of the j^{th} element measured in the i^{th} sample.

PMF applies non-negative constraint to source profiles and its contributions. It does not allow chemical species with lots of uncertainty to influence the estimation of the contributions and profiles. The uncertainty estimation provides a useful tool to decrease the weight of missing and below detection limits data in the solution; this is a particularly interesting feature when fine fractions with very low elemental concentrations are analyzed. In this work, the widely adopted procedure for data treatment suggested by [23] was used for the treatment of concentrations and the associated uncertainties data which serves input for the PMF model. For improved resolution of sources, the PMF receptor model requires a large matrix of chemical species, source apportionment was performed by combining all the data from the three sites and a data matrix of 96 (samples) \times 23 (variables) and 96 (samples) \times 19 (variables) were used for $PM_{2.5}$ and $PM_{2.5-10}$ respectively. About 3% extra modelling uncertainty was applied to all $PM_{2.5}$ species in order to accommodate errors which were not considered during measurements. This is evidenced in the high missing and below detection limit values observed for most species in the $PM_{2.5}$ fraction. Prior to PMF modelling, the species were classified into three groups; strong ($S/N \geq 1$), weak ($0.5 < S/N < 1$), and bad ($S/N < 0.5$). While there was no down-weighting of good species, species with weak signal-to-noise ratio triples the provided uncertainty while categorizations of "bad" were excluded. Therefore, five elements (Ti, Se, Rb, Zr, and Cs) were excluded from modelling of $PM_{2.5}$ while only Cs was excluded in the $PM_{2.5-10}$ data. The concentration scatter plots as well as the trend plots among the species were also examined for expected relationships which might indicate their possible sources. To ensure that the appropriate number of factors was chosen, the scaled residuals, ratio of the observed concentrations and the PMF-modeled concentrations were also examined. Detailed methodology on PMF modelling have been reported [23].

Results and Discussions

Mass concentrations

Manual gravimetric methods have been widely used as the reference method for particulate matter measurements, hence it was employed in the determination of mass concentrations of $PM_{2.5}$ and PM_{10} (aerodynamic diameter, $d_{ac} \geq 10$) as presented in Figure 2. The lowest and highest mean mass concentrations of $PM_{2.5}$ stood at $4 \mu\text{g m}^{-3}$ and $16 \mu\text{g m}^{-3}$ respectively while PM_{10} recorded $32 \mu\text{g m}^{-3}$ (lowest) to $75 \mu\text{g m}^{-3}$ (highest). Interestingly, $PM_{2.5}$ average values were lower than the 24 h $PM_{2.5}$ Air Quality Guideline (AQG) value of $25 \mu\text{g m}^{-3}$ [24]. This could be due to time of sampling, amidst Rain season, when most suspended PM has been precipitated. However, for PM_{10} fraction, the 24 h World Health Organization PM_{10} AQG ($50 \mu\text{g m}^{-3}$) was slightly violated during the sampling period. This is not unexpected as PM_{10} are usually made of re-entrained dust compared to $PM_{2.5}$ which emanates mostly due to anthropogenic contributions. Entrained dust is expected to contribute more to particulate loadings in an environment such as Lagos with many unpaved roads and walkways. PM mass concentrations in this study were similar to those reported for urban sites in Ethiopia [25], Morocco [26] and Kenya [27].

Trace elements

Table 1 displayed average concentrations, enrichment factor (EF) and pollution indices (PI) of twenty-four elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, Cs and Pb) detected in both particulate sizes.

For $PM_{2.5}$, average concentrations of S (100 ng m^{-3}), Ca (48 ng m^{-3}), Si (42 ng m^{-3}), Cl (36 ng m^{-3}), K (33 ng m^{-3}) and Na (30 ng m^{-3})

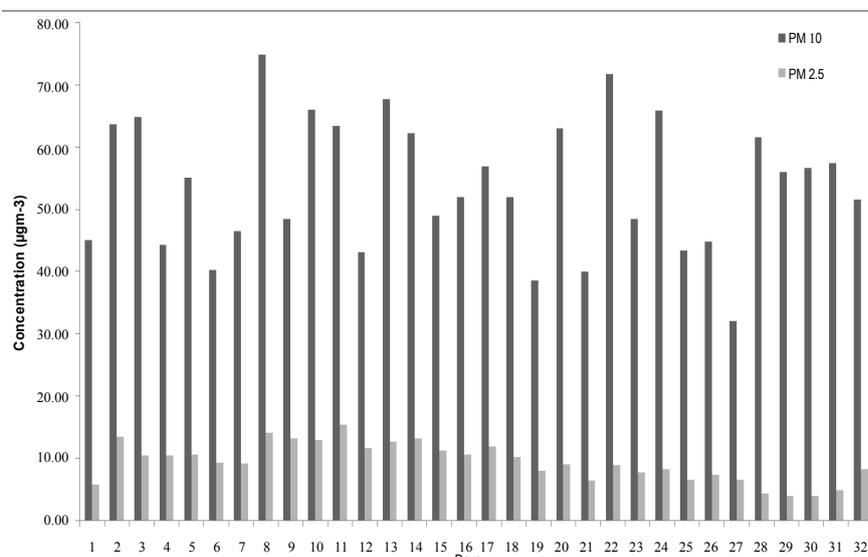


Figure 2: Average PM_{2.5-10} and PM_{2.5} mass concentrations.

Elements	Crustal rock (Mason, 1966)	Concentration (ngm ⁻³)		Enrichment Factor (EF)		Pollution Indices (PIs)	
		PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}	PM _{2.5}
Na	23600	819 ± 11	30 ± 5	2.54	4.11	0.03	0.00
Mg	23300	235 ± 7	11 ± 4	0.74	1.55	0.01	0.00
Al	82300	616 ± 6	15 ± 3	0.55	0.58	0.01	0.00
Si	28150	1525 ± 9	42 ± 3	3.97	4.72	0.05	0.00
P	n.d	20 ± 4	8 ± 3	n.d	nd	n.d	n.d
S	260	485 ± 5	100 ± 3	136.78	1225.73	1.87	0.38
Cl	130	1095 ± 8	36 ± 2	617.02	891.90	8.42	0.28
K	20900	281 ± 6	33 ± 2	0.99	5.07	0.01	0.00
Ca	41500	1789 ± 44	48 ± 10	3.16	3.73	0.04	0.00
Ti	5700	78 ± 5	2 ± 3	1.00	1.00	0.01	0.00
V	135	4 ± 2	1 ± 1	1.87	22.56	0.03	0.01
Cr	100	3 ± 1	2 ± 1	1.82	54.48	0.02	0.02
Mn	950	12 ± 1	1 ± 1	0.93	3.20	0.01	0.00
Fe	56300	640 ± 7	14 ± 1	0.83	0.80	0.01	0.00
Ni	75	2 ± 0	1 ± 0	1.70	41.92	0.02	0.01
Cu	55	5 ± 0	1 ± 0	6.74	45.88	0.09	0.01
Zn	70	42 ± 1	11 ± 0	43.95	502.46	0.60	0.16
Se	0.05	1 ± 0	n.d	792.16	n.d	10.81	2.35
Br	2.5	7 ± 1	1 ± 0	198.00	1681.49	2.70	0.53
Rb	90	3 ± 1	n.d	2.01	n.d	0.03	0.00
Sr	375	7 ± 1	n.d	1.44	n.d	0.02	0.00
Zr	165	3 ± 1	n.d	1.31	n.d	0.02	0.00
Cs	n.d	1 ± 0	2 ± 3	n.d	n.d	n.d	n.d
Pb	12.5	7 ± 3	1 ± 1	43.19	241.81	0.59	0.08

"n d" means "not detected"

Table 1: Average elemental concentrations, enrichment factors and pollution indices of PM_{2.5-10} and PM_{2.5} aerosols.

were most pronounced. Sulphur origin in fine particulate could be mainly anthropogenic (energy production, biomass burning, refuse incinerations, emissions from ships using heavy oil). Airborne sulphur rarely occurs as a pure element; it is usually produced as SO₂ gas which readily converts to sulphate SO₄²⁻ ions under normal atmospheric conditions. The SO₄²⁻ 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 [28]. Ca and

Si influence in fine fraction could be due to soil dust which is typical of sub-Saharan African aerosol. Interestingly, Ca/Si ratios (1.1) in fine and coarse fractions were the same, indicating similar sources origin. Chlorine (Cl), potassium (K), bromine (Br) and lead (Pb) were found to be major fine fraction components from pyrogenic emissions [29].

Sulphur and Chlorine have also been identified in emissions from savannah grass fires. However, average EF result revealed that S, Cl, Br and Pb were highly enriched (EF>100) in both fractions. PIs results of

coarse fraction grouped S, Cl, and Br in highly polluted class. Although, average concentrations (1 ng m^{-3}) recorded for Se in coarse particulate is 1 ng m^{-3} and it is highly enriched. This is evidenced by its high PI (10.81) in coarse fraction. Selenium is found impurely in metal sulphide ores, where it partially replaces sulphur. Hence, its introduction in atmosphere could be from emissions associated to smelting activities, glass factories or from electronic waste due to its usage as semi-conductors. Interestingly, Ni and Pb average concentrations in fine fraction were lower than European guidelines [30].

For $\text{PM}_{2.5-10}$ fraction, average concentrations of Al (616 ng m^{-3}), Si (1525 ng m^{-3}), Ca (1789 ng m^{-3}), Fe (640 ng m^{-3}), Na (819 ng m^{-3}) and Cl (1095 ng m^{-3}) were dominant. High concentrations of Na and Cl were ascribed to sea spray and emissions related to crustal materials. Sea spray emissions are produced when sea becomes supersaturated with hydrocarbon causing a flux from aqueous to gas phase, releasing halogenated organic and inorganic compounds. Imminently, high concentration values recorded for crustal elements (Al, Si, Ca and Fe) could be due to entrained/re-suspended soil dust source. The influence of soil dust is expected in Lagos because most roads and walk-ways are not paved and poorly managed. Though, high concentrations of Ca and Fe have been linked to anthropogenic activities such as physical construction, quarry, cement factories and metallurgical industrial emissions. PIs revealed low pollution class for crustal elements (Al, Si, Ca and Fe) as their EF values were <5 . Due to designation of Lagos as a coastal city, we estimated contributions of sea salt (ss) and non-sea salt (n-ss) components of Na, S, K and Ca in coarse fraction. The n-ss component of Na was estimated using crustal Na/Al ratio of 0.348 [18]. While, n-ss of S, K and Ca were estimated using sea water S/Na (0.084), K/Na (0.036) and Ca/Na (0.038) ratios [31]. From this, concentrations of ss-Na stood at 74% and 17% for coarse and fine particulates respectively. While n-ss of S and K accounted for 96% and 97% in coarse fraction respectively. However, sea salt S observed in both fractions was similar to 3% reported [31]. Conversely, average K/Na (<2) and Ca/Na (<3) ratios obtained in fine and coarse fractions showed wide disparity from seawater K/Na (0.036) and Ca/Na (0.038) ratios reported [32]. The wide variation of mass-ratio relative to sodium in both size fractions could be an attestation of multifarious sources of PM in Lagos, been the commercial and industrial nerve center of Nigeria.

Elemental correlations

The results of elemental Pearson correlations for $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ particulate fractions are presented in Tables 2 and 3 respectively. The elements Na to Pb displayed both weak and strong positive as well as negative correlations.

For $\text{PM}_{2.5-10}$ fraction, Na displayed high positive correlation ($r=0.86, 0.76, 0.95, 0.76$ and 0.86) with Mg, S, Cl, K and Br respectively probably due to their association with soil dust. The 100% correlation value ($r=1$) observed for Al and Ti could be a strong indication of similar source origin [33]. Copper displayed strong correlations with many elements; Mg ($r=0.87$), Al ($r=0.83$), Si ($r=0.85$), P ($r=0.73$), S ($r=0.89$), K ($r=0.86$), Ca ($r=0.88$), Ti ($r=0.83$), Ti ($r=0.83$), Cr ($r=0.70$), Mn ($r=0.91$), Fe ($r=0.88$), Zn ($r=0.77$), Br ($r=0.77$), Rb ($r=0.84$), Sr ($r=0.87$), Zr ($r=0.71$) and Pb ($r=0.75$) thus, it could be linked to multiple sources. For $\text{PM}_{2.5}$ fraction (Table 4), correlation ($r=0.57$) registered for Na and Cl was not too strong when compared to 0.95 observed in $\text{PM}_{2.5-10}$ fraction probably due to the influence of other anthropogenic sources. The fact that Al showed negative correlations ($r=-0.02$) with V revealed different emission source origins. V showed strong positive correlation with Ni ($r=0.98$), thus confirming their association with

emissions from petroleum oil combustion activities. The strong positive correlation ($r=0.87$) of P with K could indicate similar source origin probably from biomass or waste burning emissions. Zn correlation with Mn ($r=0.78$) and Cu ($r=0.83$) is appropriate as they could be associated with vehicular or industrial emissions. We also observed positive correlation of Pb with S ($r=0.70$) and Br ($r=0.78$). Prior to ban in importation of leaded gasoline in Nigeria in 2003, the major source of Pb in the atmosphere was reported to be mainly from petroleum products consumption [4], hence concentration of Pb in this fraction could be from local sources. High correlation of S and Br ($r=0.87$) is quite instructive as the two elements are usually used as additives in petroleum products and most of their compounds are used daily in industries.

Time series

In order to obtain prior information of variations in elemental concentrations of some known source markers, we plotted time series graphs. Figure 3a and 3b displayed time series graphs obtained for selected $\text{PM}_{2.5-10}$ markers while Figure 3c and 3d represents time series graphs for identified $\text{PM}_{2.5}$ markers.

Time series graph of Na and Cl detected in $\text{PM}_{2.5-10}$ fraction are shown in Figure 3a. As expected, both elements (markers for sea-spray emissions) portrayed similar time trend even though their concentration values differ. For instance, on 23rd of July 2007, Na and Cl concentrations were both registered as $1.3 \mu\text{g m}^{-3}$. Interestingly, highest concentration of Na ($2 \mu\text{g m}^{-3}$) and Cl ($3.2 \mu\text{g m}^{-3}$) occurred on 9th August 2007. Time series plots (Figure 3b) of soil dust markers (Al, Si, Ca, and Fe) in the $\text{PM}_{2.5-10}$ fraction were also examined. The smoothness of their graphs suggests similar source origin as the same dates; 9th and 16th August 2007 for highest and lowest concentrations. For $\text{PM}_{2.5}$, K/S and V/Ni concentration time series graphs were plotted in Figure 3c and 3d respectively. Potassium and Sulphur displayed similar time trends. For instance, S registered $0.4 \mu\text{g m}^{-3}$ (highest) and 4.0×10^{-4} (lowest) concentration values on 28th July and 17th September 2007 respectively. The same date trend also followed for K ($0.2 \mu\text{g m}^{-3}$) and ($4.5 \times 10^{-3} \mu\text{g m}^{-3}$) highest and lowest concentrations. Conversely, time series graph (Figure 3d) of V and Ni detected in fine fraction showed that their highest and lowest concentrations were registered in different dates.

Comparison of elemental concentrations

In Tables 4 and 5, $\text{PM}_{2.5-10}$ and $\text{PM}_{2.5}$ elemental concentrations were compared with values reported in previous measurements in Nigeria and elsewhere. For $\text{PM}_{2.5-10}$ (Table 4), average concentration ($0.8 \mu\text{g m}^{-3}$) of Na reported for this study were much lower than values ($21.2 \mu\text{g m}^{-3}$ and $2.7 \mu\text{g m}^{-3}$) for Addis Ababa [25] and Kenitra [26] respectively. This could be due to many reasons such as geographical locations, time, height and duration of sampling. Aluminium average concentrations in the coarse particulates were in the order; $3.9 \mu\text{g m}^{-3}$ (Francis Town) $>2.5 \mu\text{g m}^{-3}$ (Addis Ababa) $>2.3 \mu\text{g m}^{-3}$ (Cairo) $>1.8 \mu\text{g m}^{-3}$ (Kenitra) and $0.6 \mu\text{g m}^{-3}$ (this study). Chlorine average concentrations were in the order; $15.9 \mu\text{g m}^{-3}$ (Cairo) $>4.5 \mu\text{g m}^{-3}$ (Dar es Salaam) $>1.1 \mu\text{g m}^{-3}$ (this study, coarse fraction) $>0.5 \mu\text{g m}^{-3}$ (Nairobi) $>0.2 \mu\text{g m}^{-3}$ (Francis Town). High concentration of Cl in Egypt could be due to location of the sampling site; Cairo is situated in delta region of Nile River, hence high impact of sea spray emission to pollutant load in its air-shed is expected. Sulphur average concentration ($0.5 \mu\text{g m}^{-3}$) in this study (coarse fraction) was higher than value for Nairobi but was comparable to value for Abuja, Nigeria. Potassium concentration was highest in Addis Ababa and lowest at Francis Town. Addis Ababa ($40.2 \mu\text{g m}^{-3}$) and Francis Town

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Rb	Sr	Zr	Cs	Pb
Na	1.00																							
Mg	0.86	1.00																						
Al	0.61	0.88	1.00																					
Si	0.60	0.88	0.99	1.00																				
P	0.54	0.62	0.57	0.59	1.00																			
S	0.76	0.92	0.88	0.89	0.61	1.00																		
Cl	0.95	0.86	0.65	0.65	0.51	0.77	1.00																	
K	0.76	0.94	0.93	0.92	0.60	0.96	0.78	1.00																
Ca	0.57	0.86	0.90	0.92	0.54	0.92	0.64	0.90	1.00															
Ti	0.60	0.88	1.00	0.99	0.56	0.88	0.65	0.93	0.90	1.00														
V	0.24	0.38	0.44	0.51	0.36	0.51	0.30	0.39	0.49	0.45	1.00													
Cr	0.40	0.65	0.72	0.71	0.42	0.72	0.43	0.72	0.78	0.71	0.29	1.00												
Mn	0.63	0.90	0.95	0.96	0.61	0.92	0.66	0.91	0.94	0.95	0.53	0.75	1.00											
Fe	0.62	0.89	0.99	1.00	0.60	0.90	0.67	0.93	0.93	0.99	0.52	0.73	0.97	1.00										
Ni	0.35	0.48	0.45	0.53	0.44	0.60	0.42	0.46	0.57	0.46	0.85	0.34	0.58	0.54	1.00									
Cu	0.64	0.87	0.83	0.85	0.73	0.89	0.67	0.86	0.88	0.83	0.52	0.70	0.91	0.88	0.62	1.00								
Zn	0.48	0.61	0.51	0.54	0.68	0.68	0.46	0.60	0.63	0.51	0.39	0.51	0.62	0.57	0.53	0.77	1.00							
Se	0.60	0.72	0.70	0.69	0.37	0.66	0.60	0.70	0.65	0.69	0.29	0.53	0.68	0.68	0.32	0.60	0.24	1.00						
Br	0.83	0.90	0.79	0.79	0.55	0.87	0.87	0.89	0.77	0.79	0.30	0.58	0.79	0.81	0.44	0.77	0.54	0.66	1.00					
Rb	0.63	0.86	0.92	0.93	0.55	0.90	0.67	0.92	0.88	0.93	0.55	0.68	0.92	0.94	0.55	0.84	0.54	0.63	0.78	1.00				
Sr	0.58	0.87	0.90	0.92	0.53	0.90	0.64	0.89	0.98	0.91	0.53	0.75	0.93	0.93	0.58	0.87	0.55	0.66	0.77	0.89	1.00			
Zr	0.49	0.77	0.91	0.89	0.49	0.76	0.53	0.82	0.79	0.92	0.36	0.69	0.86	0.89	0.33	0.71	0.44	0.58	0.66	0.83	0.81	1.00		
Cs	-0.21	-0.27	-0.32	-0.23	-0.03	-0.15	-0.15	-0.32	-0.15	-0.32	0.46	-0.24	-0.16	-0.22	0.51	-0.03	0.00	-0.22	-0.20	-0.20	-0.12	-0.38	1.00	
Pb	0.42	0.63	0.64	0.66	0.49	0.73	0.41	0.68	0.68	0.63	0.43	0.67	0.75	0.69	0.52	0.77	0.83	0.34	0.57	0.66	0.63	0.59	-0.06	1.00

Bolded cells mean that correlation is significant at the 0.05 level (2-tailed)

Table 2: Elemental correlation analysis of PM_{2.5-10} aerosols.

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Rb	Sr	Zr	Cs	Pb
Na	1.00																							
Mg	0.87	1.00																						
Al	0.41	0.60	1.00																					
Si	0.48	0.64	0.97	1.00																				
P	0.54	0.58	0.47	0.56	1.00																			
S	0.84	0.78	0.50	0.58	0.53	1.00																		
Cl	0.57	0.66	0.66	0.74	0.45	0.57	1.00																	
K	0.80	0.77	0.58	0.66	0.87	0.94	0.61	1.00																
Ca	0.19	0.31	0.74	0.75	0.32	0.28	0.47	0.33	1.00															
Ti	0.30	0.40	0.95	0.71	0.39	0.39	0.46	0.46	0.59	1.00														
V	0.05	0.00	-0.02	0.02	-0.11	0.31	-0.10	0.21	0.01	0.10	1.00													
Cr	0.52	0.66	0.66	0.70	0.68	0.52	0.81	0.55	0.40	0.40	-0.08	1.00												
Mn	0.13	0.05	0.26	0.28	-0.03	0.38	0.03	0.32	0.24	0.31	0.49	0.04	1.00											
Fe	0.40	0.54	0.92	0.95	0.45	0.54	0.65	0.61	0.83	0.75	0.13	0.61	0.39	1.00										
Ni	0.35	0.40	0.38	0.42	0.34	0.49	0.40	0.44	0.21	0.27	0.98	0.42	0.43	0.43	1.00									
Cu	0.35	0.30	0.23	0.33	0.43	0.41	0.37	0.36	0.30	0.36	0.15	0.33	0.36	0.38	0.38	1.00								
Zn	0.31	0.24	0.18	0.25	0.41	0.30	0.33	0.25	0.22	0.21	0.62	0.32	0.78	0.25	0.35	0.83	1.00							
Se	0.78	0.80	0.54	0.59	0.65	0.76	0.63	0.73	0.30	0.40	0.06	0.67	0.14	0.51	0.43	0.29	0.24	1.00						
Br	0.66	0.74	0.72	0.57	0.67	0.80	0.78	0.83	0.38	0.46	0.06	0.75	0.18	0.68	0.45	0.30	0.21	0.72	1.00					
Rb	0.58	0.49	0.39	0.46	0.47	0.55	0.47	0.64	0.26	0.37	0.01	0.41	0.30	0.43	0.25	0.37	0.41	0.47	0.44	1.00				
Sr	0.25	0.36	0.53	0.55	0.38	0.40	0.54	0.44	0.54	0.39	0.07	0.41	0.06	0.55	0.31	0.30	0.18	0.33	0.56	0.21	1.00			
Zr	0.42	0.54	0.89	0.84	0.56	0.55	0.66	0.56	0.38	0.41	0.07	0.63	0.11	0.58	0.36	0.25	0.18	0.50	0.72	0.27	0.44	1.00		
Cs	-0.13	-0.21	-0.22	-0.22	-0.33	-0.02	-0.41	-0.13	-0.17	0.02	0.37	-0.35	0.36	-0.16	0.10	0.00	-0.02	-0.15	-0.25	-0.17	-0.19	-0.22	1.00	
Pb	0.33	0.32	0.22	0.29	0.10	0.70	0.17	0.43	0.18	0.21	0.29	0.12	0.44	0.31	0.30	0.23	0.13	0.21	0.78	0.28	0.16	0.31	0.16	1.00

Bolded cells mean that correlation is significant at the 0.05 level (2-tailed).

Table 3: Elemental correlation analysis of PM_{2.5} aerosols.

(0.7 µg m⁻³) represents highest and lowest average concentration of Ca. Iron was highest (3.1 µg m⁻³) in Cairo and lowest (0.6 µg m⁻³) in Dar es Salaam. We observed that Pb concentrations (7 ng m⁻³) in this study was lower than 0.2 and 6.9 µg m⁻³ reported for Kenitra and Cairo

respectively but was comparable to the values of 6, 11, 12, 18 and 29 ng m⁻³ reported for Francis Town, Abuja, Dar es Salaam, Ikoyi and Nairobi respectively.

Elements	This study 2.5<d _{ae} <10 μm	Abiye et al. (2013)	Gebre et al. (2010)	Gatari et al. (2008)	Tahri et al. 2013	Gebre et al. (2010)	Gatari et al. (2008)	Tahri et al. 2013
		Abuja, Nigeria	Addis Ababa, Ethiopia	Nairobi Kenya	Cairo Egypt	Francis Town, Botswana	Dar es Salaam, Tanzania	Kenitra Morocco
		2.5<d _{ae} <10 μm	d _{ae} <10 μm	2.5<d _{ae} <10 μm	d _{ae} <10 μm	2<d _{ae} <10 μm	2<d _{ae} <10 μm	2.5<d _{ae} <10 μm
Na	819	-	21217	-	-	-	-	2707
Mg	235	-	1400	-	-	-	-	-
Al	616	-	2495	-	2333	3900	-	1848
Si	1525	11734	-	2300	7867	< DL	680	-
P	20	-	-	-	-	-	-	-
S	485	833	-	250	-	-	-	-
Cl	1095	-	-	450	15867	230	4500	-
K	281	2249	7687	650	-	350	420	1432
Ca	1789	3528	40167	1000	13083	690	4900	11300
Ti	78	246	67	190	-	110	100	-
V	4	13	18	-	-	-	-	-
Cr	3	89	681	-	-	-	-	61
Mn	12	45	106	180	-	28	27	70
Fe	640	1984	1250	2300	3083	1300	610	2051
Ni	2	24	10	1.8	-	-	-	137
Cu	5	667	113	7.3	-	-	-	144
Zn	42	41	2612	57	-	6.9	40	634
Se	1	-	-	-	-	-	-	-
Br	7	-	-	15	-	1.9	3.1	-
Rb	3	-	33	3	-	-	-	-
Sr	7	-	-	-	-	-	-	-
Zr	3	-	-	-	-	-	-	-
Cs	1	-	-	-	-	-	-	-
Pb	7	11	-	29	6850	5.6	12	196

Table 4: Comparison of PM_{2.5-10} elemental concentrations (ng m⁻³).

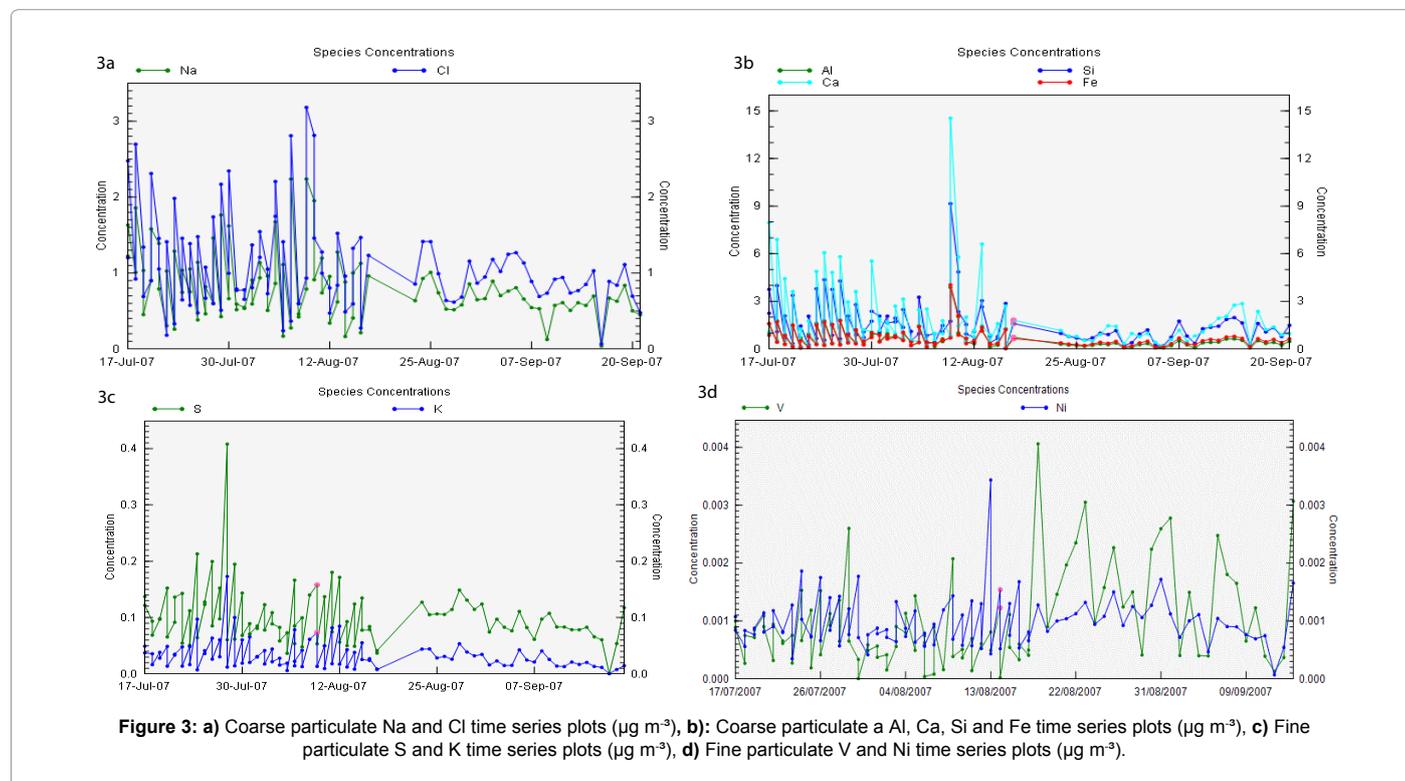


Figure 3: a) Coarse particulate Na and Cl time series plots (μg m⁻³), b): Coarse particulate a Al, Ca, Si and Fe time series plots (μg m⁻³), c) Fine particulate S and K time series plots (μg m⁻³), d) Fine particulate V and Ni time series plots (μg m⁻³).

For PM_{2.5} fraction (Table 5), average elemental concentrations reported in this study were in most cases lower than values for other cities. For instance, S average concentrations in Abuja (0.7 μg m⁻³),

Nairobi (1.3 μg m⁻³), Francistown (0.3 μg m⁻³), and Tanzania (1.0 ng m⁻³) were higher than the 0.1 μg m⁻³ concentration reported in this study.

Elements	This study	Abiye et al. (2013)	Gebre et al. (2010)	Gatari et al. (2008)	Tahri et al. 2013	Gebre et al. (2010)	Gatari et al. (2008)	Tahri et al. 2013
		Abuja, Nigeria	Addis Ababa, Ethiopia	Nairobi Kenya	Cairo Egypt	Francis Town, Botswana	Dar es Salaam, Tanzania	Kenitra Morocco
	2.5<d _{ae} <10 μm	2.5<d _{ae} <10 μm	d _{ae} <10 μm	2.5<d _{ae} <10 μm	d _{ae} <10 μm	2<d _{ae} <10 μm	2<d _{ae} <10 μm	2.5<d _{ae} <10 μm
Na	819	-	21217	-	-	-	-	2707
Mg	235	-	1400	-	-	-	-	-
Al	616	-	2495	-	2333	3900	-	1848
Si	1525	11734	-	2300	7867	< DL	680	-
P	20	-	-	-	-	-	-	-
S	485	833	-	250	-	-	-	-
Cl	1095	-	-	450	15867	230	4500	-
K	281	2249	7687	650	-	350	420	1432
Ca	1789	3528	40167	1000	13083	690	4900	11300
Ti	78	246	67	190	-	110	100	-
V	4	13	18	-	-	-	-	-
Cr	3	89	681	-	-	-	-	61
Mn	12	45	106	180	-	28	27	70
Fe	640	1984	1250	2300	3083	1300	610	2051
Ni	2	24	10	1.8	-	-	-	137
Cu	5	667	113	7.3	-	-	-	144
Zn	42	41	2612	57	-	6.9	40	634
Se	1	-	-	-	-	-	-	-
Br	7	-	-	15	-	1.9	3.1	-
Rb	3	-	33	3	-	-	-	-
Sr	7	-	-	-	-	-	-	-
Zr	3	-	-	-	-	-	-	-
Cs	1	-	-	-	-	-	-	-
Pb	7	11	-	29	6850	5.6	12	196

"d_{ae}" means "aerodynamic diameter"; "< DL" means "less than detection limit"; "-" denotes "not detected"

Table 4: Comparison of PM_{2.5-10} elemental concentrations (ng m⁻³).

S	100	700	1300	320	1000	-	-
Cl	36	-	-	77	1200	10200	-
K	33	878	730	320	350	-	397
Ca	48	952	70	55	270	300	-
Ti	78	69	9	8	8	-	-
V	4	11	3	-	-	-	-
Cr	3	135	-	-	-	-	81
Mn	12	24	12	3	3	-	21
Fe	640	871	130	110	44	933	1939
Ni	2	9	3	-	-	-	161
Cu	5	613	4	-	-	-	240
Zn	42	22	100	5	9	-	1301
Se	-	-	-	-	-	-	-
Br	1	-	36	9	9	-	-
Rb	-	-	2	-	-	-	-
Cs	2	-	-	-	-	-	-
Pb	1	15	76	11	25	2000	303

Table 5: Comparison of PM_{2.5} elemental concentrations (ng m⁻³).

Similarly, K concentration (33 ng m⁻³) was also lower than values reported for other cities. Several factors such as sampling height, time and period as well as types of samplers could contribute to these differences. For instance, in Francistown Botswana, PM_{2.5} was sampled at 1.5 m above ground level while in Nairobi; PM_{2.5} was sampled at an elevation of 25 m. However, average concentration of Ca in this fraction was close to 70 and 55 ng m⁻³ values for Nairobi and Francistown respectively but differs considerably with 1.0 μg m⁻³ for Abuja. Average concentrations for heavy oil combustion related elements (V and Ni) were close to values for other cities (Table 5). On the other hand, average concentration recorded for Zn (42 ng m⁻³) in this study was

comparable to values for other cities. Average concentration (1 ng m⁻³) of Pb in this fraction was the lowest among the cities compared. This low concentration of Pb in Lagos air shed is probably due to low industrialization and ban in use of leaded gasoline.

Positive matrix factorization (PMF)

PMF model was run in default robust mode to decrease the influence of extreme values on its solution. To ensure that appropriate number of factors was chosen, scaled residuals and ratio of PMF-modeled residual to input uncertainty were examined for each fraction. For final examination, PMF was applied to each data using 4 to 7 factors

and robustness of the outputs with further examination of rotational parameter, FPEAK [34]. The result showed that a five-factor solutions gave the best options for coarse and fine fractions respectively. The resolved source profiles and contributions are discussed herein.

For fine ($PM_{2.5}$) fraction (Figure 4), first factor displayed high loadings of K (84%) and Br (43%) as well as S (33%) and was identified as emissions emanating from biomass burning activities [33]. The insignificant (~ 0%) contribution of the factor to overall $PM_{2.5}$ mass loads are quite strange as open burning of waste dumps is prevalent in Lagos. Furthermore, biomass is a major source of energy by most inhabitants of Lagos. Unfortunately, literature on source apportionment of size segregated particulates are limited in Nigeria for comparison purposes, therefore further investigations are imminent. The next factor registered high loadings of Cl (64%), Cr (63%), P (67%), Sr (46%), Mg (44%) and Na (40%). We termed it “mixed” source because it was difficult to pin down a specific source for the profile. For instance, Na, Cl and Mg are markers for sea spray emissions while Ni and Cr are markers for petroleum products combustions and smelting emissions respectively. The factor accounted for 24% of total $PM_{2.5}$ mass loads. Factor 3 three with high loadings of Zn (70%) and Cu (35%) could be emissions emanating from industrial activities [35]. The fact that PMF apportioned 0.4% of total PMF mass load to the factor is disturbing as we expected higher contribution of industrial emissions in Lagos which hosts for over 40% of industries in Nigeria. However, the result requires further investigation. The influence of soil dust on $PM_{2.5}$ aerosols was observed in the fourth factor as it displayed high loadings of Al (41%), Si (34%), Ca (65%), and Fe (48%). About 28% of total $PM_{2.5}$ mass fraction was apportioned to this factor. High percentage of total $PM_{2.5}$ contribution attributed to the factor could be due to entrained and re-suspended dust from poorly maintained road networks and unpaved workways in Lagos. The fifth factor with high loadings of V (80%), Ni (48%), S (36%), Mn (60%) and Pb (39%) was identified as emissions from gasoline oil combustion emissions [36].

The significant loadings of Mn and Pb could be an artifact from industrial and local sources as Nigerian banned use of leaded gasoline since 2004. PMF apportioned 48% of the overall $PM_{2.5}$ mass load to the factor. This conjecture is further supported by the fact that Lagos accounts for over 30% of petroleum products consumed in Nigeria [2].

For coarse fraction (Figure 5), the first factor with high loadings of Al (54%), Si (47%), Fe (40%), Ti (60%), and Zr (68%), is a typical soil dust profile [37]. Interestingly, the overall percentage contribution (22%) of $PM_{2.5-10}$ mass apportioned to the factor is less than apportioned 28% recorded in the $PM_{2.5}$ fraction. This phenomenon calls for further investigation (with different variant of receptor models) as we expected higher soil dust contribution in the $PM_{2.5-10}$ fraction. Moreover, particle size analysis of soil dust revealed larger aerodynamic diameter in the range of 2.5 to 10 μm aerodynamic diameter. The next PMF resolved factor was similar to first factor but showed high profile of Ca. Hence, we attributed it to emissions related to physical construction activities probably from road construction and cement factories located about 150 km away from sampling sites. It showed high loadings of Ca (75%) and Sr (69%) with significant loadings of soil dust markers (Al, Si, Fe and Ti). The third factor could be from emissions emanating from industrial activities. It has high loadings of Zn (57%) and Pb (46%) and it contributed about 10% to $PM_{2.5-10}$ total mass loads.

However, Zn could also indicate vehicular emissions as it is considered as an indicator element for emissions from two-stroke vehicles due to its usage as an additive in lubricating oils. The fourth factor was identified to be contributions from biomass burning emissions [33]. Its profile is characterized with S (31%), K (28%) and Se (26%) and contributed about 21% of total PM mass loads. The high percentage estimate apportioned to the factor contradicted the near zero percent registered in the $PM_{2.5}$ fraction. Owing to the particle size of biomass source emissions (aerodynamic diameter $\leq 2.5 \mu m$), we expected higher contribution estimate in $PM_{2.5}$. Again, the scenario calls for further studies. The fifth factor is a typical profile of emissions

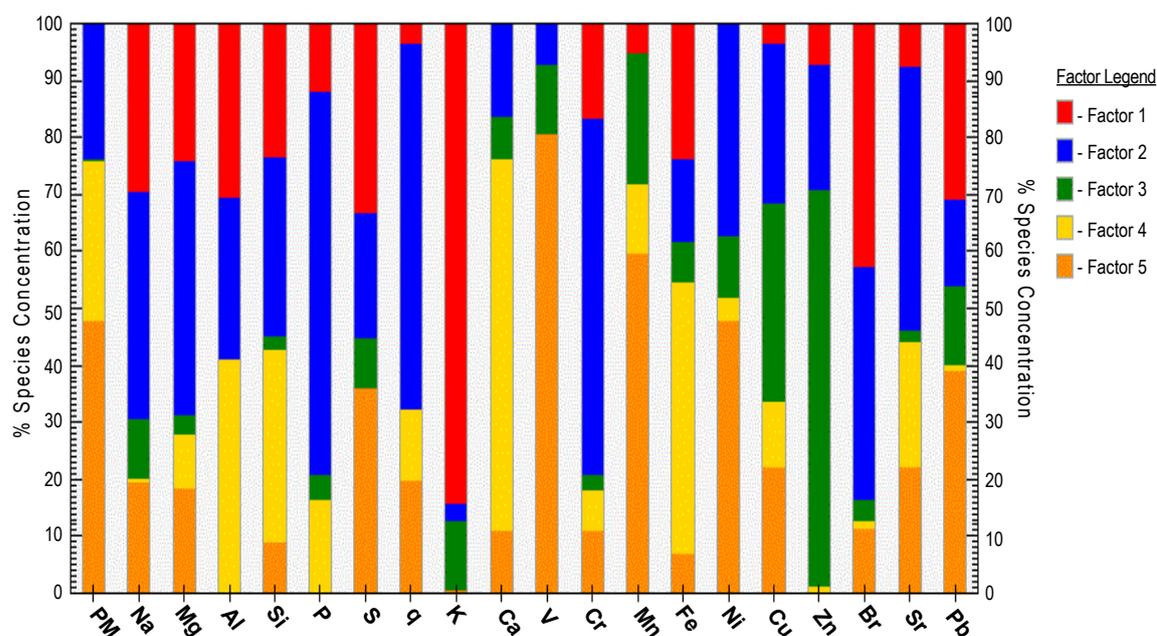


Figure 4: PMF results of $PM_{2.5}$ fraction.

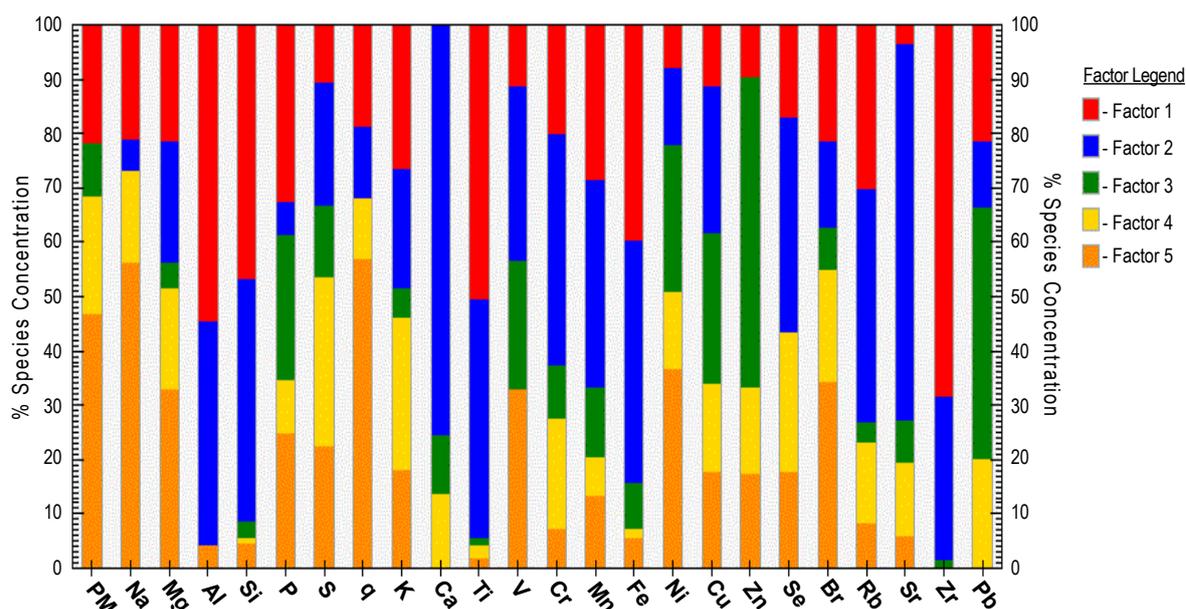


Figure 5: PMF results of PM_{2.5-10} fraction.

from marine/sea spray [37]. It displayed high loadings of Na (56%), Cl (57%), Mg (33%) and Br (34%) which markers for sea spray. Interestingly, 47% of the PM_{2.5-10} overall mass was contributed by the factor probably due to location of sampling points which were situated few kilometers to the shores of Atlantic Ocean.

Conclusions

This study on source apportionment and identification of size segregated atmospheric particulates has produced a new set of more robust data of PM_{2.5} and PM₁₀ concentrations in Lagos air-shed. The lowest and highest mean mass concentration of PM_{2.5} stood at 4 µg m⁻³ and 16 µg m⁻³ respectively while PM₁₀ recorded 32 µg m⁻³ (lowest) to 75 µg m⁻³ (highest). An improved speciated set of data for elemental concentration (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Zr, Cs and Pb) of PM_{2.5} and PM_{2.5-10} have also been established using the PIXE analytical technique in an external ion beam set-up. The concentration of S was most pronounced in fine fraction while crustal elements (Al, Si, Ca and Fe) concentrations were more prominent in the coarse fraction. Although, there are no standard guideline thresholds for most elements, continuous exposure to some of these elements could be toxic even at low concentration values. Enrichment factor calculation of elements revealed that S, Cl, Br and Pb were highly enriched (EF>100) in both fractions while PIs results grouped S, Cl and Br in highly pollution class for coarse fraction. The element in both fractions displayed both positive and negative correlations while time series plots revealed similar patterns for two or more markers of specific source origin. PMF resolved five for both PM_{2.5} and PM_{2.5-10} fractions of which the percentage contributions estimate for gasoline oil combustion (PM_{2.5}) and sea spray emissions contributed to over 40%. High percentage estimates resolved for anthropogenic petroleum oil combustion and sea-spray calls for stringent abatement options. This work presents first known major application of PMF for source apportionment and identifications of atmospheric aerosols at receptor locations in Nigeria.

Acknowledgements

The authors are grateful to International Atomic Energy Agency (I.A.E.A.) Vienna Austria, for the NIR 12022 Postgraduate Fellowship granted to Ezeh G.C. We also acknowledge the contributions of Profs' Chiari, Nava, Calzolari and Lucarelli; all of Department of Physics and Astronomy, University of Florence and I.N.F.N., Via Sansone 1, 50019 Sesto Fiorentino (FI), Italy for facilitating the NIR 12022 programme at Florence.

Conflict of Interest

No conflict of interest was declared by the authors

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