

Elemental Concentrations and Source Apportionment of Atmospheric Air Particulates from two Functional Sites in the Metropolitan City of Ibadan, Nigeria

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Abstract Ambient concentrations of size-segregated fractions of $PM_{2.5}$ and $PM_{2.5-10}$ were investigated for chemical compositions and pollution sources at two functional receptor sites (industrial and residential areas) in the metropolitan city of Ibadan, Nigeria between March 2014 and February, 2015. Seventy four fractions (37 each) were collected on quartz filter media using a low volume Gent sampler equipped with double-staged stacked filter unit. Elemental characterizations of both fractions were carried out using Particle Induced X-ray Emission (PIXE) technique in an external ion beam analysis set-up. Elements such as K, Na, P, S and Cl which were evidences of burning activities correlated well in the $PM_{2.5}$, while the relationship observed between Al, Si, K, Ca and Fe suggested crustal material source for the elements in the $PM_{10-2.5}$. Results of the seasalt estimation of some naturally occurring elements (Na, K, Ca and S) in the ambient air suggested their sources in Ibadan as either of crustal or anthropogenic. Source apportionment study with Positive Matrix Fractionalisation (PMF) receptor model identified five sources with stable profiles in $PM_{2.5}$; tail pipe/industrial emissions (48.5%), suspended road dust (13.1%), ferrous metal smelting (34.6%), fine brake (0%), and vegetative/biomass burning (3.8%). Six were in $PM_{2.5-10}$. They are petroleum products combustion plus smelting (9.3%), biomass burning (5.2%), exhaust and non-exhaust mobile (0%), airborne/re-suspended soil (23.4%), fuel oil combustion (24.5%), and municipal incineration plus solid waste combustion (37.6%). This study resolved high values for anthropogenic vehicular emission and solid waste burning, thus call for routine monitoring by regulatory agencies and stringent abatement options to control the possible untold hazards on health and environment.

Keywords: ambient, fractions, PIXE, source apportionment

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1. Introduction

Over the past few decades, Urban Air Pollution (UAP) informed by the unprecedented population growth and increasing industrialisation especially in the modern day developmental processes of the third world countries has been a global atmospheric chemistry issue. The pollution problems are results of combined effects of gaseous air pollutants such as sulphur dioxide, oxides of nitrogen, ozone and particulate matter (PM). The air-borne particulate size fractions with aerodynamic diameter of less than 2.5 μm are referred to as fine ($PM_{2.5}$) fraction while the fractions with aerodynamic diameter ranging between 2.5 and 10 μm are referred to as the coarse ($PM_{2.5-10}$). It has been estimated that in developing countries, increasing urban atmospheric pollution (UAP) has resulted in more than two million deaths per annum along with various cases of respiratory illnesses [1]. PM has been shown to

have negative impacts on human health, atmospheric visibility, and radiative forcing [2]. Quantifying the relative source contribution to observed ambient PM concentrations and atmospheric deposition are critical to emission mitigation and local environmental impact management. To achieving this, receptor modeling provides a method to distinguish the relative contributions of sources based upon measurements at receptor sites. Positive Matrix Factorization (PMF) receptor model was developed in 1994 [3]. The model was modified overtime and widely used to identify sources and provide the source contribution towards mitigation measure. It has been shown to be a powerful alternative to other traditional receptor modeling methods as it incorporates the variable uncertainties associated with measurements of environmental samples and forces the values in the solution profiles and contributions to be nonnegative, though also with its own shortcomings among which is large number requirement of data to run [4,5].

So far nationwide, a combination of wavelength-dispersive X-ray fluorescence (WDXRF) and atomic

absorption spectroscopy (AAS) techniques was used for elemental characterisation of PMs collected from three sites in Lagos where five sources were identified with percentage contributions in ranges using chemical mass balance (CMB) [6]. Furthermore, an instrumental neutron activation analysis (INAA) assay of particulates from four sites in Lagos was conducted and same common sources ascribed to both the PM_{2.5} and PM_{2.5-10} fractions using the principal component analysis (PCA) [7]. In addition, PMF was applied to PM composition data at a scrap iron and steel smelting industry located along the Ile-Ife - Ibadan expressway road where same four sources were identified for each of the two fractions [8]. A chemical characterization of coarse particulates collected from four sites in Abuja, Nigeria was undertaken with PIXE therein three sources were identified with the aid of PMF [9]. Lately, PIXE was complimented with Proton Induced Gamma-ray Emission (PIGE) technique in the study of the characterisation of PMs in Lagos where five sources in both fractions were identified along with their contributions using PMF [10]. PMF has been successfully used in such many cities of the world for assessment of source contributions as Atlanta in US [11], Mavi Mumbai in India [12], Beijing in China [13], Bangkok in Thailand [14] and Alberta in Canada [15].

Towards a holistic approach to tackling the increasing threats to the air quality however, a robust data base for the country is highly expedient. A comprehensive and robust data base for the country in PIXE multi-elemental characterization of the PM fractions in Ibadan using the bilinear multivariate Positive Matrix Factorisation (PMF) receptor model is therefore expedite. Application of PMF motivated this study, thereby eliminating the unnecessary headache of a prior knowledge of local source fingerprints, the input data in traditional receptor model like CMB which are even not yet in existence for Ibadan. In addition, the uncertainties in the estimations in traditional receptor models culminating in ranges in the percentage contributions for example, are adequately eliminated.

This study attempts to present results of the elemental constituents of the atmospheric PM_{2.5} and PM_{2.5-10} fractions in the metropolitan city of Ibadan and identifies the natural and anthropogenic factor contributions to each of the PM fractions. Thus, the specific objective of this study is to identify PM sources and then estimate their contributions to the particle mass concentrations across the two site classes of the metropolis thereby affording availability of reliable robust air quality data base for researches and agencies.

2. Sampling, Sample Preparation Methods and Data Pre-treatment

2.1. Particulate Sampling

Two sampling locations each characterised by its typical urban features of residential and industrial classes were identified for the 1-year study taking into consideration the diurnal and seasonal variations of wind direction and speed. The two locations are the Saro Lifecare (07.36624° N/003.85471° E) within Oluyole industrial Estate and the Fun Factory Event Centre (07.42171° N / 003.90510° E)

within Bodija residential Estate both in Ibadan metropolis. Oluyole industrial estate, located within the Ibadan South West Local Government Area (LGA) is a designated industrial estate hosting a number of manufacturing and industrial outfits which includes plastic recycling, detergent, food, packaging, household, beverages industries and iron smelting. The estate shares boundary northwards with Oluyole residential estate and southwards with Odo-ona residential area. On other hand, the Bodija residential estate is located in Ibadan North LGA, though well planned has overtime lost its low density features now assumes some commercial outlook as business outlets, offices, event and recreational centres remain its prominent features. The second greatest urban sprawl after the Ojoo - Lagos expressway is the Ojoo - Apata expressway which transverses the city westwards from northern part of the city. Figure 1 shows the map of Oyo State in Nigeria indicating the sampling locations.

PM_{2.5} and PM_{2.5-10} samples were collected with a "Gent" stacked filter unit sampler. The filter holder was placed at the height of about 1.6 m (the average nose height) above the ground in such a way that air circulation around it was not hindered while a total of 74 samples (37 of each fraction) were collected on pre-weighed and pre-conditioned quartz filter media at a flow rate between 16 and 18 L⁻¹ min [16,17]. Sampling on each day was varied between 7 - 20 hrs over the 24 hr of the day to avoid clogging of filter and as well ensure that the flow rate employed throughout the process is within the prescribed limits of the sampler. This control process was geared towards proper size fractionation and effective collection. The filter media were previously conditioned at about 25°C and 50% constant humidity for 24 hr before weighing. The exposed filters were then stored in a desiccator prior to elemental analysis of the collected PM fractions via a PIXE facility available at the Centre for Energy Research and Development (CERD) of the Obafemi Awolowo University, Ile-Ife, Nigeria.

2.2. PIXE Analysis

The conditioned filter media were energy-analyzed by Particle Induced X-ray Emission (PIXE) facility at external ion beam analysis (IBA) set-up of 2 - 3 MeV Tandem nuclear accelerator at the Centre for Energy Research and Development (CERD) of the Obafemi Awolowo University, Ile-Ife. PIXE is a multi-elemental, non-destructive analytical technique well suited for well suited for quantifying elemental content in ambient PM and aerosol filter analysis. Calibration of the system was performed by irradiating suitable thin target standards in the similar experimental conditions while X-ray spectra obtained from the measurements were analyzed with GUPIXWIN[®] software developed at Guelph University [18] for their net peak areas. Elemental concentrations of the PM samples were obtained in ng cm⁻² on the filter and then converted to ng m⁻³ of air sampled by multiplying by the exposed filter area (in cm²) and dividing by the volume of air sampled in 24 hr (in m³). The 27 elements detected, quantified along with their average values are as follows; Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Nb, Mo, Pb and Bi.

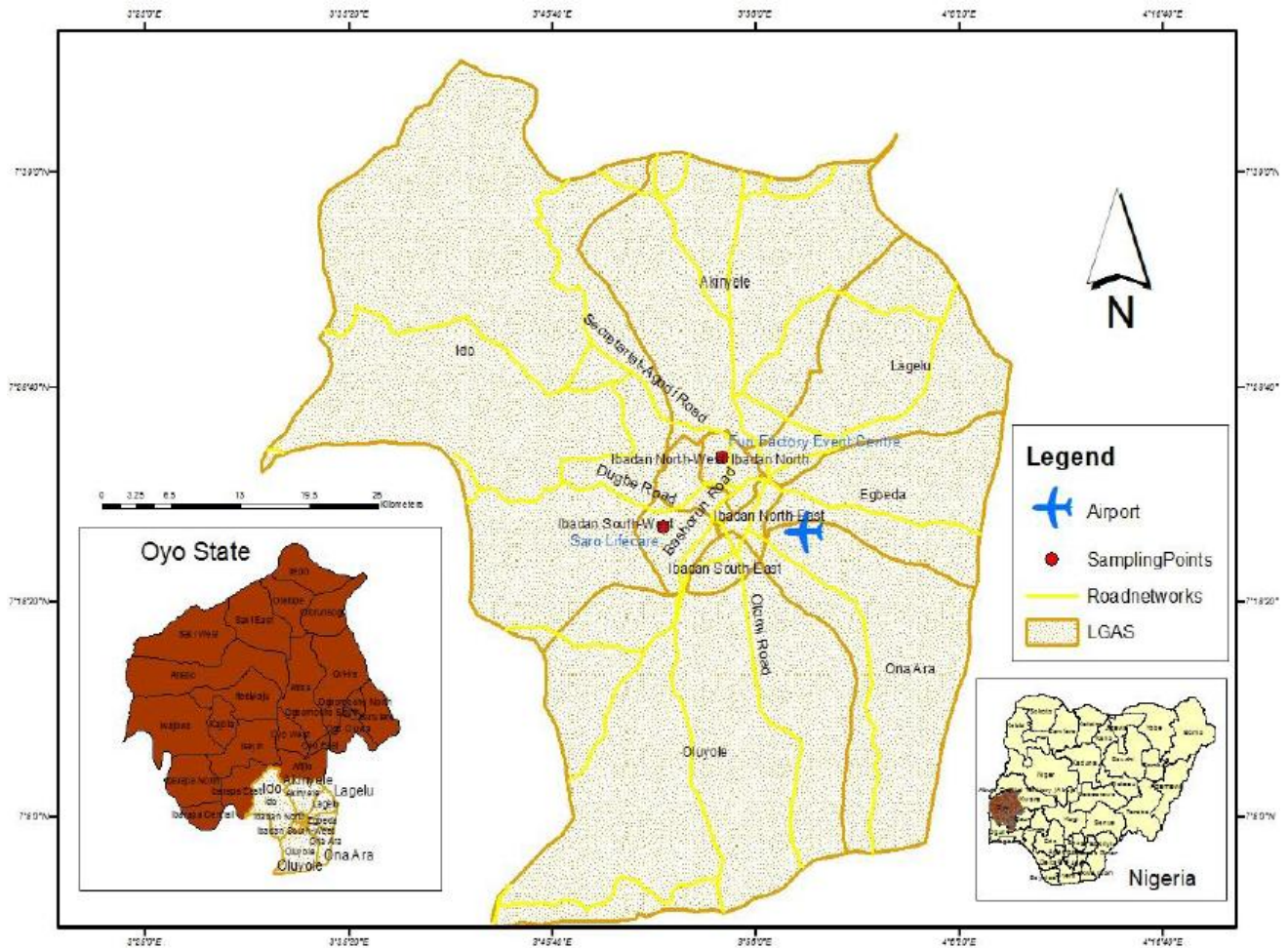


Figure 1. A map of Nigeria and Oyo State showing Ibadan metropolis and the sampling points

2.3. Statistical Analysis

Elemental concentrations of the $PM_{2.5}$ and $PM_{2.5-10}$ fractions from the two sampling points of residential and industrial area were subjected to statistical analysis for the Pearson distance correlation matrix of the elements [19]. This was with the view to determine the chemical similarity, an indication of a common source or otherwise of the elements in the fractions. The matrix of the elements in the fractions was obtained with the aid of the SPSS 10.0 statistical software ($p < 0.05$) at two tailed. The correlation coefficient value r , otherwise known as the critical value was obtained with $n = 96$, at 98%.

2.4. Estimation of the Seasalt and Non-Seasalt Contributions to Na, Ca, K and S Concentrations

Being a transit point between the coastal Lagos and the Sahara, the estimation of the seasalt and non-seasalt components of some naturally occurring elements in Ibadan aerosol was desirable. Thus, Na, Ca, K and S seasalt (ss) and non-seasalt (n-ss) components were estimated. Starting with, the two components of Na in the $PM_{2.5}$ and $PM_{2.5-10}$ fractions which were each contributed by the sea and crustal sources at the receptor sites were estimated using expressions (1) and (2), respectively and the crustal Na/Al ratio of 0.348 [20].

$$n - ssNa = cAl \times c \frac{Na}{Al} (\text{crustal}) \quad (1)$$

$$cNa(\text{Total}) = ssNa + n - ssNa \quad (2)$$

where c indicate measured concentrations. Earlier studies on S, Na, K and Ca associated with sea spray in the fine fraction concluded that $S/Na = 0.092 \pm 0.085$, $K/Na = 0.032 \pm 0.013$ and $Ca/Na = 0.038 \pm 0.025$ [21]. In this study, we estimated the n - ssS in the aerosol in the same way with an earlier study [22] and came up with the values in the fractions at the 2 receptor sites using the following expressions;

$$n - ssS = cNa(ssNa) \times c \frac{S}{Na} (\text{seawater}) \quad (3)$$

$$n - ssS = cS(\text{Total}) - ssS \quad (4)$$

Thus, using the earlier four expressions, in addition to the following two;

$$ssK = cNa(ssNa) \times c \frac{K}{Na} (\text{seawater}) \quad (5)$$

$$ssCa = cNa(ssNa) \times c \frac{Ca}{Na} (\text{seawater}) \quad (6)$$

the percentage contributions of the seaspray and non-seasalt sources to the observed values of Na, Ca, S and K were obtained.

2.5. Source Apportionment Study and PMF Receptor Model

Source apportionment is the process of identification and quantification of impact of different pollutants at the receptor sites based on the measured ambient air pollutant data with receptor models. The models are based on linear algebra principle; hence they are good example of statistical model. For this study, the source apportionment technique was performed using the U.S. Environmental Protection Agency's (EPA) Positive Matrix Factorization (PMF) model (Version 3.0). Details of the model are as described elsewhere [23]. Briefly, the corresponding matrix to the general receptor modeling problem is

$$X = GF + E \quad (7)$$

where X is an $n \times m$ data matrix with n measurements and m is the number of elements; E is an $n \times m$ matrix of residuals; G is an $n \times p$ source contribution matrix with p sources; and F is a $p \times m$ source profile matrix [10]. Similar approach as used by some earlier workers was adopted in the procedure for data treatment and then subsequently used for treatment of concentrations and the associated uncertainties data which serves as input for the PMF model [24].

Sources in PMF are constrained to have non-negative species concentrations, none of the samples can have a negative source contribution and error estimates for each observed data point are therefore used as point-by-point weights, such that missing and below detection limit data which is a characteristic feature of environmental sample data can be accommodated [25]. This feature cannot however be said of any known multivariate data analysis method. For improved resolution of sources, the modeling was performed by combining all the data obtained from the two sites and a data matrix of 74 (samples) \times 27

(variables) and 74 (samples) \times 37 (variables) were used for $PM_{2.5}$ and $PM_{2.5-10}$ respectively. The optimum number of factors and the rotation were evaluated by a set of statistical tools [26]. Thus, optimum number of factors and rotation was evaluated in line with a previous work [27] and thus selected on trial and error analysis of the solutions by the user and by comparison of the factor profiles with previous profiles of sources. We then run the model in the robust method by varying the factors from 2 to 20 with an $\alpha = 0.4$ using the error model “-12” (that uses observed values) and 20 runs per configuration. The FPEAK parameter was varied from -0.2 to 1 to refine the source profiles [28]. The optimum solution was chosen to be that with FPEAK = -0.2 based on G-space edges showing no correlations among the resolved sources. A five factor model with a rotation with FPEAK = -0.2 was selected for $PM_{2.5}$ while a six factor model with a rotation with FPEAK = -0.2 was selected for $PM_{2.5-10}$.

3. Results and Discussion

3.1. Elemental Concentrations

The mean elemental concentrations of the $PM_{2.5}$ and $PM_{2.5-10}$ across the two sampling sites of the metropolis are shown in Table 1 which displayed the detected and quantified twenty-seven (27) elements. The concentration of the elements ranged from 25 ± 38 to $117,743 \pm 208 \text{ ng m}^{-3}$ and from 25 ± 27 to $2,856 \pm 161 \text{ ng m}^{-3}$ in the coarse and fine fractions respectively in the industrial area and ranged from 19 ± 17 to $13,424 \pm 218 \text{ ng m}^{-3}$ and from 17 ± 16 to $1,437 \pm 195 \text{ ng m}^{-3}$ in the coarse and fine fractions respectively in the residential area. In Table 2, comparison of the guideline values of the select elements was carried out with standard limits [29,30].

Table 1. Mean elemental concentrations (ng m^{-3}) of $PM_{2.5-10}$ and $PM_{2.5}$ fractions across the two sampling points

Element	Crustal rocks (Mason,1966)	Industrial		Residential		Crustal/anthropogenic derived
		$PM_{2.5-10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{2.5}$	
Na	23,600	952 ± 31	660 ± 3	511 ± 35	252 ± 28	crustal
Mg	23,300	136 ± 46	160 ± 5	140 ± 55	150 ± 60	crustal
Al	82,300	1399 ± 94	897 ± 111	$1,005 \pm 102$	457 ± 114	crustal
Si	28,150	$6,092 \pm 182$	$2,856 \pm 161$	$4,036 \pm 170$	$1,339 \pm 154$	crustal
Ca	41,500	$2,393 \pm 100$	801 ± 89	$2,029 \pm 108$	668 ± 94	crustal
Ti	5,700	$117,743 \pm 208$	808 ± 61	$13,424 \pm 218$	39 ± 51	crustal
Mn	950	560 ± 28	98 ± 19	730 ± 33	28 ± 19	crustal
Fe	56,300	$1,774 \pm 42$	663 ± 29	$1,405 \pm 41$	464 ± 30	crustal
P	-	248 ± 127	194 ± 156	298 ± 148	196 ± 200	anthropogenic
S	260	$2,991 \pm 186$	$1,428 \pm 176$	$2,610 \pm 203$	$1,437 \pm 195$	anthropogenic
Cl	130	$7,053 \pm 22$	$1,201 \pm 167$	$7,889 \pm 282$	805 ± 178	anthropogenic
K	20,900	$1,193 \pm 100$	401 ± 104	$1,173 \pm 106$	176 ± 111	crustal
V	135	167 ± 52	25 ± 27	217 ± 64	23 ± 30	anthropogenic
Cr	100	97 ± 23	93 ± 22	115 ± 26	109 ± 26	anthropogenic
Ni	75	25 ± 38	27 ± 14	19 ± 17	27 ± 10	anthropogenic
Cu	55	177 ± 24	107 ± 27	173 ± 26	120 ± 23	anthropogenic
Zn	70	190 ± 27	49 ± 19	112 ± 27	17 ± 16	anthropogenic
As	-	25 ± 38	34 ± 35	26 ± 39	34 ± 43	anthropogenic
Se	0.05	38 ± 40	29 ± 40	28 ± 46	32 ± 36	anthropogenic
Br	2.5	57 ± 49	59 ± 4	37 ± 58	49 ± 58	anthropogenic
Rb	90	77 ± 83	87 ± 82	128 ± 110	69 ± 84	anthropogenic
Sr	375	111 ± 115	134 ± 115	86 ± 121	134 ± 122	crustal
Zr	175	142 ± 165	173 ± 178	278 ± 240	192 ± 214	anthropogenic
Nb	-	192 ± 214	270 ± 244	162 ± 243	211 ± 224	anthropogenic
Mo	-	291 ± 302	134 ± 292	357 ± 361	296 ± 308	anthropogenic
Pb	12.5	129 ± 169	77 ± 132	100 ± 233	126 ± 183	anthropogenic
Bi	-	110 ± 107	75 ± 99	167 ± 145	77 ± 110	anthropogenic

Table 2. Comparison of the guideline values (ng m⁻³) of the WHO and EU limits for some elements with this study

Element	WHO	EU**	This study (for PM _{2.5} only)
Mn	5	5	28 - 98
Ni	-	20	27
Pb	0.5	0.5	77 - 126
V*	1	-	23 - 25
As	6.6 x 10 ⁻⁷	6.6 x 10 ⁻⁶	34
Cr	x 10 ⁻⁸	-	93 - 109

*Mean 24-hr value

**Annual mean of 24-hr value established by the European Council Directive the outcome of which informs that there was a high level of emission of some of these elements in the metropolis which calls for urgent attention.

3.2. Correlation Analysis

Results of the Pearson elemental correlation analysis are summarised in Table 3 and Table 4. The matrices show the elements displaying negative and positive correlations.

Among the elements in the PM_{2.5}, the correlation values were observed between the anthropogenic elements like Pb and P ($r = 0.65$), S ($r = 0.68$), Cl ($r = 0.65$), Rb ($r = 0.82$) as well as As ($r = 0.82$) which showed clearly that they were related in terms of their source, possibly vehicular exhaust source as the elements are important tracers for petrol combustion in the automobiles. In addition, a linear dependence was exhibited by the following metals; Mo, Zn and Fe by being well positively correlated indicating vehicular sources in the fraction. The fact that a negatively correlation was observed between Pb and K ($r = -0.59$) might suggest that they were not related in the fraction. The highly correlation values observed between the typical crustal metals like Mn and Fe ($r = 0.98$), Al and Fe ($r = 0.97$) and Fe and Ti ($r = 0.98$) suggested that air borne or re-suspended soil was an important factor contribution to the fraction in the metropolis. Notice was also made of the 100% correlation between Ti and Mn ($r = 1.00$), an indication of a strong correlation in terms of source. Furthermore, the relationship between K which is a biomass marker element and crustal Na ($r = 0.86$) as well as some anthropogenic elements like S ($r = 0.62$) was a strong indication of combustion processes in the fine particulates, a prevailing situation in the metropolis [31]. The Na was also correlated though weakly with P ($r = 0.10$), and strongly with Cl ($r = 0.95$) which are anthropogenically derived. A strong indication that Na and P might not have common source, while Na and Cl were well related in source. Furthermore, the high correlation value between Ni and V ($r = 0.96$) can be interpreted to mean that the 2 elements were related to industrial emissions like pyrometallurgical processes such as those in steel plants and non-ferrous metal industries [32] or related by emissions from petroleum oil combustion. The correlation observed between Mo and Zn ($r = 0.59$) and Fe and Zn ($r = 0.80$) can be interpreted to mean that they are related especially in brake linings [33,34].

Some typical crustal elements (namely Al, Fe, Ca, Mn and Si) in the coarse mode exhibited high correlation within themselves; thus Al and Fe ($r = 0.97$), Si and Al ($r = 0.99$), Mn and Si ($r = 0.99$) suggesting that they were closely related to crustal sources. The high correlation value ($r = 0.76$) observed between Na and Cl suggested

that they were either related to marine sources or better still related in source. A similar observation was made of the relationship between Si and K ($r = 0.99$) which could be explained by suggesting that they were of same source. The negative correlation ($r = -0.08$), though very small between Cl and K, could be explained that the 2 elements were not related, though may be weakly related in a way especially in solid waste combustion. Anthropogenic elements Sn and Pb with correlation factor ($r = 0.78$) indicating that the elements were closely related in the vehicular sources as Pb is a good tracer for vehicular exhaust. However, Pb correlated with Cl ($r = 0.81$), but weakly with S ($r = 0.31$) and P ($r = 0.38$) indicating that S and P might had other sources apart from vehicular sources. Conversely, Pb was negatively correlated with the crustal metal Mg ($r = -0.11$) suggesting that the Pb was anthropogenic and therefore not of crustal sources. Observation we made between Na and S where there was a very strong correlation value ($r = 0.96$) informed that they may be related in crustal sources. Also, K which is a biomass burning marker element was more strongly correlated with majority of crustal elements like Mg ($r = 0.83$), Al ($r = 0.92$), Si ($r = 0.90$) and moderately correlated with Mn ($r = 0.51$) and negatively correlated with P ($r = -0.20$) and S ($r = -0.24$) in the coarse fraction. These observations suggested that the coarse K may have multiple sources apart from crustal S source with crustal elements and therefore originated only from natural (crustal) sources or better still the S might have multiple sources or origin in the metropolis. It may have emanated from storage tanks from boilers as well as residual oils combustion in the boilers of some industrial facilities employed in the industries [35]. There might also be a relationship between coarse K and Mn which might be anthropogenic in nature.

3.3. Seasalt and Non-seasalt Contributions to Na, Ca, K and S Concentrations

The result of the estimated percentage contributions of the seaspray and non-seasalt sources to the observed values of Na, Ca, S and K is presented in Table 5. The percentage contributions of the seaspray sources to Na estimated in the PM_{2.5} and PM_{2.5-10} fractions of atmospheric aerosol at the industrial receptor sites were 53 and 49 respectively while they were 37 and 32 at the residential receptor site area. At the industrial site, we established that Na value was almost of equal and half each of marine and crustal origin in the industrial site, the percentage value being however higher in the PM_{2.5} than in the PM_{2.5-10} fraction. Similarly, the percentage values were discovered to be higher in the corresponding PM_{2.5} fractions at the residential site than in the PM_{2.5-10} fraction though seasalt percentage contributions of 37% and 32% in PM_{2.5} and PM_{2.5-10} fractions respectively were lower than what were obtained at the industrial site. For the total S in the aerosol, only very little and therefore insignificant seasalt contributions of 2% and 1.3% in the PM_{2.5} and PM_{2.5-10} fractions respectively at the industrial receptor site along with the 0.5% contributions for each of the 2 fractions at the residential site were obtained. These observed low percentage contributions to S in the PM_{2.5} fractions across the receptor sites of less than 3% were in

line with an earlier work [22]. This observation was an indication of only anthropogenic source for the total S as against the suggestion that it might have being of sea

spray. Similar observation was made where between 1-3% contributions were observed at the Cheju Island site between 1996 and 1997 [36,37].

Table 3. Correlation coefficients of elements in PM_{2.5} collected from the industrial and residential areas

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn
Na	1.00												
Mg	0.92	1.00											
Al	0.89	0.81	1.00										
Si	0.86	0.74	0.99	1.00									
P	0.84	0.57	0.23	0.16	1.00								
S	0.91	0.92	0.70	0.65	0.39	1.00							
Cl	0.87	0.81	0.98	0.97	0.21	0.73	1.00						
K	0.86	0.71	0.98	0.99	0.10	0.62	0.95	1.00					
Ca	0.88	0.80	0.97	0.97	0.15	0.77	0.98	0.95	1.00				
Ti	0.89	0.76	0.99	0.99	0.13	0.64	0.98	0.98	0.95	1.00			
V	0.87	0.66	0.80	0.80	0.09	0.57	0.79	0.79	0.78	0.84	1.00		
Cr	0.23	0.38	0.04	0.13	-0.11	0.61	0.47	-0.10	0.52	-0.15	-0.03	1.00	
Mn	0.92	0.89	0.99	0.99	0.60	0.75	0.99	0.97	0.97	1.00	0.85	0.18	1.00
Fe	0.86	0.74	0.97	0.98	0.08	0.69	0.96	0.96	0.97	0.98	0.79	0.74	0.98
Ni	-0.19	-0.01	-0.15	-0.14	-0.14	0.13	-0.09	-0.19	-0.05	-0.23	0.96	0.67	-0.20
Cu	0.06	0.12	0.00	-0.05	0.18	0.24	0.08	-0.09	0.09	-0.05	0.10	0.18	0.05
Zn	0.86	0.67	0.70	0.67	0.24	0.67	0.68	0.74	0.70	0.77	0.76	0.23	0.74
As	0.66	0.53	0.61	0.62	0.33	0.50	0.62	0.61	0.62	0.83	0.91	0.16	0.81
Se	0.78	0.17	-0.28	0.03	-0.20	0.17	-0.02	0.15	-0.14	0.39	0.47	0.30	0.25
Br	0.95	0.46	0.66	0.68	-0.04	0.51	0.69	0.73	0.71	0.69	0.67	0.14	0.83
Rb	-0.27	-0.16	0.17	-0.03	-0.15	-0.13	0.17	0.08	0.12	0.76	0.27	-0.27	-0.46
Sr	0.18	0.31	0.13	0.07	0.54	0.32	0.12	0.03	0.17	0.01	-0.03	0.42	0.16
Zr	-0.34	-0.41	-0.48	-0.36	-0.13	-0.29	-0.27	-0.29	-0.24	-0.81	0.34	-0.29	-0.21
Nb	0.27	0.12	0.17	0.19	-0.02	0.15	0.15	0.20	0.18	0.23	0.33	0.18	0.22
Mo	0.75	0.68	0.45	0.42	0.67	0.60	0.46	0.40	0.48	0.63	0.67	0.41	0.67
Pb	0.19	0.83	0.57	0.29	0.65	0.68	0.65	-0.59	0.41	0.60	0.27	0.09	0.58
	Fe	Ni	Cu	Zn	As	Se	Br	Rb	Sr	Zr	Nb	Mo	Pb
Na													
Mg													
Al													
Si													
P													
S													
Cl													
K													
Ca													
Ti													
V													
Cr													
Mn													
Fe	1.00												
Ni	-0.03	1.00											
Cu	-0.03	0.03	1.00										
Zn	0.70	0.06	0.16	1.00									
As	0.60	-0.29	0.32	0.31	1.00								
Se	0.10	0.41	-0.17	-0.32	1.00	1.00							
Br	0.64	-0.17	0.19	0.80	0.80	-0.56	1.00						
Rb	-0.14	-0.03	0.26	-0.05	0.53	-0.21	0.35	1.00					
Sr	0.08	0.19	0.22	-0.03	-0.14	0.22	0.14	-0.17	1.00				
Zr	-0.54	-0.64	0.11	-0.63	0.52	-0.48	0.68	0.18	-0.29	1.00			
Nb	0.16	0.04	-0.29	0.12	0.05	0.43	0.23	-0.51	0.48	-0.63	1.00		
Mo	0.47	0.06	0.21	0.59	0.27	0.68	-0.08	-0.01	0.79	-0.53	0.10	1.00	
Pb	0.13	0.38	0.33	0.34	0.72	0.58	-0.24	0.82	0.16	-0.69	-0.49	0.27	1.00

Table 4. Correlation coefficients of elements in PM_{2.5-10} collected from industrial and residential areas

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn
Na	1.00												
Mg	-0.37	1.00											
Al	-0.55	0.88	1.00										
Si	-0.48	0.89	0.99	1.00									
P	0.77	-0.16	-0.39	-0.34	1.00								
S	0.96	-0.35	-0.37	-0.29	0.67	1.00							
Cl	0.76	-0.02	-0.31	-0.26	0.70	0.72	1.00						
K	-0.18	0.83	0.92	0.90	-0.20	-0.24	-0.08	1.00					
Ca	0.27	0.50	0.81	0.86	0.03	0.13	0.09	0.77	1.00				
Ti	0.90	-0.40	-0.53	-0.45	0.82	0.85	0.79	-0.39	-0.01	1.00			
V	0.53	-0.46	-0.34	-0.27	0.65	0.64	0.50	-0.31	0.05	0.77	1.00		
Cr	0.30	0.08	0.06	0.09	0.35	0.40	0.26	0.15	0.27	0.39	0.38	1.00	
Mn	-0.46	0.53	0.42	0.36	-0.17	-0.49	0.04	0.51	0.15	-0.33	-0.32	-0.19	1.00
Fe	-0.47	0.84	0.99	0.98	-0.36	-0.31	-0.29	0.90	0.84	-0.48	-0.29	0.17	0.37
Ni	0.19	-0.22	-0.21	-0.20	0.04	0.21	0.02	-0.26	-0.22	0.16	0.82	0.03	-0.25
Cu	0.84	-0.36	-0.29	-0.22	0.63	0.80	0.72	-0.16	0.13	0.81	0.60	0.36	-0.31
Zn	0.29	0.14	0.14	0.16	0.29	0.24	0.27	0.20	0.22	0.19	-0.03	0.19	0.15
As	-0.15	0.65	0.13	0.11	-0.05	-0.32	-0.27	0.11	0.12	-0.18	-0.18	0.55	0.02
Se	0.27	-0.03	-0.21	-0.19	0.22	0.25	0.30	-0.19	-0.11	0.21	0.29	-0.14	-0.21
Br	0.30	0.07	0.46	0.46	-0.16	0.14	0.02	0.52	0.44	-0.09	-0.14	0.12	0.14
Rb	0.26	-0.10	-0.29	-0.31	0.48	0.20	0.55	-0.06	-0.02	0.48	0.38	0.48	0.07
Sr	-0.14	0.22	-0.09	-0.13	-0.17	-0.17	-0.22	-0.06	-0.17	-0.23	-0.33	-0.11	0.00
Zr	0.36	-0.56	-0.26	-0.22	0.71	0.47	0.36	-0.23	-0.02	0.69	0.78	0.22	0.17
Nb	0.46	-0.31	-0.15	-0.11	0.15	0.47	0.32	-0.19	0.04	0.31	0.28	0.21	-0.32
Mo	0.01	-0.65	-0.34	-0.31	0.35	0.47	0.43	-0.40	-0.16	0.55	0.43	0.32	-0.60
Pb	0.42	-0.11	-0.25	-0.23	0.38	0.31	0.28	-0.17	-0.16	0.36	0.27	0.28	-0.17
	Fe	Ni	Cu	Zn	As	Se	Br	Rb	Sr	Zr	Nb	Mo	Pb
Na													
Mg													
Al													
Si													
P													
S													
Cl													
K													
Ca													
Ti													
V													
Cr													
Mn													
Fe	1.00												
Ni	-0.17	1.00											
Cu	-0.24	0.26	1.00										
Zn	0.16	0.16	0.34	1.00									
As	0.19	-0.29	-0.25	-0.01	1.00								
Se	-0.20	0.24	0.34	0.05	-0.10	1.00							
Br	0.49	0.20	0.26	0.51	-0.38	-0.09	1.00						
Rb	-0.22	0.31	0.50	-0.07	-0.46	-0.45	0.15	1.00					
Sr	-0.11	-0.02	-0.01	0.38	-0.37	-0.10	0.37	0.47	1.00				
Zr	-0.27	0.34	0.46	0.00	-0.40	-0.37	0.05	0.40	-0.26	1.00			
Nb	-0.15	-0.56	0.16	-0.35	-0.59	0.42	-0.27	-0.57	-0.25	-0.07	1.00		
Mo	-0.31	0.23	0.14	-0.50	-0.03	0.34	-0.43	-0.16	-0.64	0.30	0.48	1.00	
Pb	-0.20	0.67	0.26	0.48	0.12	-0.43	0.11	0.45	0.04	0.54	-0.28	-0.12	1.00

Table 5. Estimates of the concentration and percentage contribution of the salt and non-seasalt components of Na, S, K and Ca

Elemental comp.	Industrial				Residential			
	PM10 (ng m ⁻³)	% Contribution	PM2.5 (ng m ⁻³)	% Contribution	PM10 (ng m ⁻³)	% Contribution	PM2.5 (ng m ⁻³)	% Contribution
NssNa	486.852	51	312.156	47	349.74	68	159.036	63
SsNa	465.148	49	347.844	53	161.260	32	92.964	37
NssS	2951.00	98.7	639.312	98	2596	99.5	1429.191	99.5
SsS	39.072	1.3	29.218	2	13.545	0.5	7.809	0.5
NssK	1176.255	98.6	388.478	97	1167.195	99.5	172.933	98.1
SsK	16.745	1.4	12.522	3	5.805	0.5	3.347	1.9
NssCa	2375	99.3	787.782	98.4	2022.872	99.7	664.467	99.47
SsCa	17.675	0.7	13.218	1.6	6.128	0.3	3.533	0.53

Furthermore, the non-seasalt component of both K and Ca were estimated not to be less than 97% of their total metal in the aerosol in both fractions across the sites indicating that the seasalt contributions were very low. This observation was in line with a previous study where 95% was estimated to be of non seasalt for the K and Ca [38]. Majority of fine K was therefore suggested to be of biomass burning or crustal source [22]. Same observations were made of Ca which suggested that

the fine Ca in the study was mainly of crustal origin majority of which resulting from long-range transported aerosols.

3.4. PMF Analysis Result

The result showed in Figure 2 that five-factor solution gave the best options for PM_{2.5} while six-factor solution was adequate for the PM_{2.5-10} as shown in Figure 3.

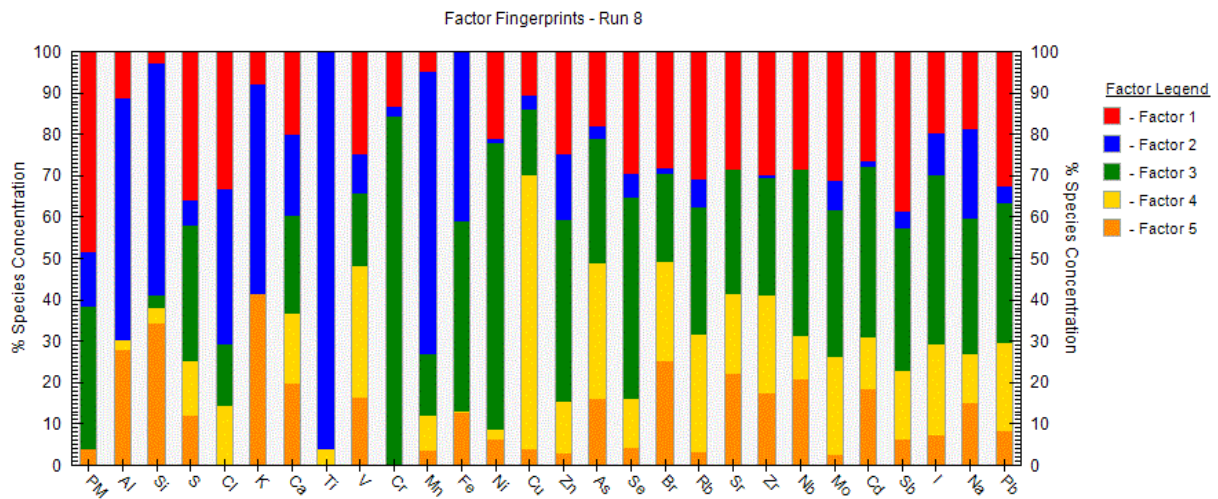


Figure 2. Result of PMF analysis of PM_{2.5}

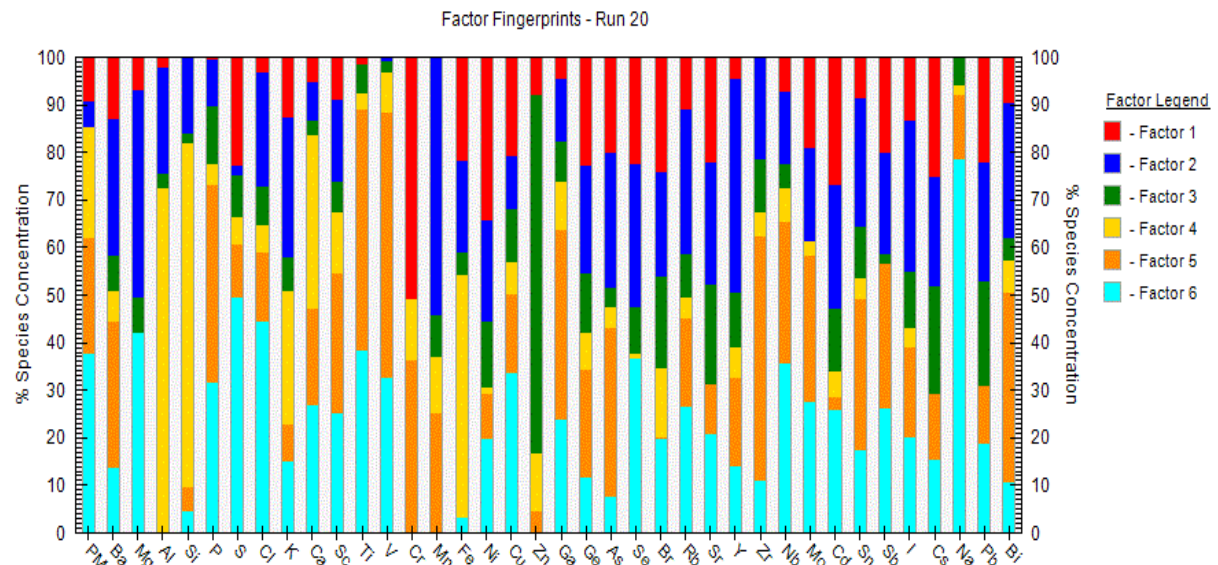


Figure 3. Result of PMF analysis of PM_{2.5-10}

For the PM_{2.5} fraction, the first source was indicated by the factor profile shown in Table 6 and was characterised by high loadings of such elements as Pb (32.7%), Rb (31.1%), S (36.0%), Mo (31.3%), Cl (33.3%), Se (29.7%), Zr (30.1%) and Br (28.1%) suggesting tail pipe exhaust source. An earlier study used Pb and S as marker elements for vehicular emissions [39]. The observed high loading for Pb in the fine is in line with the fact that it shows higher tendency to be associated more with the fine fraction than the coarse fraction [40]. This is borne out of the fact that Pb particles tend to form at high temperature from where it becomes part of the vehicle exhaust. Mo could be attributed to industrial emission [7]. The PMF analysis revealed that this mixture of source accounted for as much as 48.5% of fine fraction in the metropolis. The second source was characterised by high loadings of such major crustal elements as Ti (96.3%), Mn (68.3%), Al (58.6%), Si (55.8%) as well as Fe (40.9%) in the fine fraction. These elements are marker elements for re-suspended road dust [13,41]. This source is a peculiar feature of the metropolis and accounted for about 13.1% to the PM_{2.5}. This observed level of re-suspended road dust indicated that the source is an important pollution source in the metropolis on account of the numerous unpaved road network and walkways giving rise to entrained and re-suspended dust that characterises the metropolis. The third source in the fine was characterised by significant high loadings of trace elements which included Cr (84.2%), Fe (46.2%), Ni (69.2%), Zn (43.9%), Se (49.0%), S (32.5%) and Pb (33.8%). Given that Zn and Cr contents were high; this source was thought to be relevant to smelters and metallurgical industries [42]. Cr was once used as a marker element for smelting emissions source [10]. In this study, PMF analysis revealed that ferrous smelting source accounted for 34.6% of PM_{2.5} in the metropolis. The fourth source revealed that Cu had the highest loading of 66.1% followed by V (31.9%) and As (32.9%). The observed high loading of Cu revealed that the factor is traffic related [43,44]. PMF analysis revealed that fine car brake contribution to PM_{2.5} fractions in the metropolis was insignificant. This insignificant amount of brake in the fine is expected as a substantial amount of brake was expected only in PM_{2.5-10} fractions. The fifth source was suggested to be of biomass burning as it was characterised by high loadings of K (41.3%), Si (34.2%), Al (28.0%) and Br (25.2%) in the fifth factor profile of the PM_{2.5}. K is a marker element for vegetation and biomass burning and it was associated with contributions from continuous open burnings of vegetative materials in the metropolis. Furthermore, loadings of such metal elements like K and Na (15.2%) along with elements like Br were observed to be in high concentrations and therefore attributed to biomass burning [39]. PMF analysis revealed that biomass burning source accounted for 3.8% to PM_{2.5} in the metropolis. However, a much higher percentage contribution of biomass mass burning was expected as a substantial number of people employ open air burning of solid fuels as means of energy in their homes coupled with forest fire episodes during the dry season. This staggering contribution of biomass burning to the fine fraction was surprising and calls for a further investigation.

For the PM_{2.5-10} fraction, the factor profile of which is as indicated in Table 6. The first source was characterised

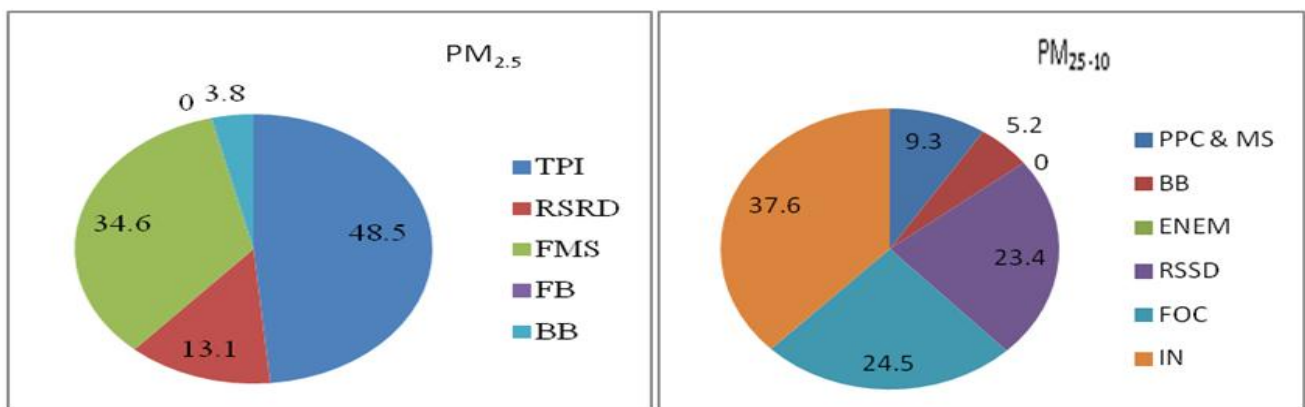
based upon the loadings of Cr (50.9%), Ni (34.4%), Se (22.5%), Br (24.3%) and Cs (25.1%) and certain amount of Fe (21.6%). Ni and Cr are markers for petroleum products combustions and metal smelting emissions respectively [10]. We termed this source to be mixture of source of petroleum products combustions and smelting emissions. This mixture of sources contributed 9.3% to the coarse fraction in the metropolis. This observed little contribution of combustion products to coarse particulate was in line with our expectation as a substantial amount of combustion products was being expected only in fine particulates. For the second source in PM_{2.5-10}, the profile was characterised by high loadings of Mn (54.2%), Mg (43.7%), Rb (30.5%), Se (30.0%), As (28.3%), Ba (28.7%), K (29.3%) and Cl (24.0%) suggesting that the source was of biomass and vegetative burning, though with presence of some crustal elements like Mn and Mg. K is an excellent tracer of municipal/biomass burning aerosols [45]. This factor profile included substantial amounts of Mn, Mg and Rb as well. The PMF analysis showed that this source contributed about 5.2% to PM_{2.5-10} in the metropolis. The third source had a very high loading of Zn (75.4%) followed by Cs (22.7%), Pb (21.7%) and Sr (20.9%). Zn is encountered in the wear and tear of brake line and tyres. Tyre wear is likely to result some quantities of metals, especially Zn due to the use of zinc compounds in rubber production [46]. Zn is also known to be one of the indicators of emission from fossil fuel combustion process, in particular the vehicle exhaust [47]. Vehicular emissions are associated with high concentrations of Zn and so therefore Zn is widely used as a chemical fingerprint for tyre wear [48]. In addition, Zn suggests source contribution from motor vehicles, especially the 2-stroke engines like motorcycles (*Okada* in local parlance) and motor scooters that were popular commercial transportation means in the metropolis. In 2-stroke engines especially, lubricants are often used as additives to fuel and therefore burnt together in the piston chambers, with the emission of Zn. Lubricants are introduced into the cylinders separately in four-stroke engines therefore leading to subsequent emission of Zn [49]. This factor was therefore identified as a mobile source factor comprising of the exhaust and non-exhaust mobile sources contributing an insignificant amount to the coarse fractions. The fourth source was characterised by high factor loadings of some major crustal elements like Al (72.4%), Si (72.4%) and Fe (51.0%) as well as Ca (36.2%) and K (28.2%). These elements are major constituents of airborne soil and road dust which is an important metropolitan feature of Ibadan and borne out of the consequence of the unpaved and damage road infrastructure in the metropolis. Airborne and soil dust usually makes important contribution to the coarse aerosol [33]. We discovered that K/Ca = 0.78 and Al/Si > 1, implying a significant contribution of Sahara Dust to the airborne soil dust during the dry season months [50, 51]. Interestingly, PMF showed that airborne or re-suspended soil dust contributed a substantial amount of 23.4% to PM₁₀ fraction in the metropolis. This amount was expected as unpaved road network and walkways are prominent features of the metropolis. The fifth source had loadings of V (55.5%), P (41.6%), Sn (31.7%), Cr (36.2%), Bi (39.7%) and As (35.5%) in the profile. This source was characterised by high loading of V, marker

element for fuel combustion. Fuel oil is used for heating of boilers and furnaces in industrial activities. Elevated V and As are usually attributed to fuel oil combustion [48]. Fuel oil combustion contributed about 24.5% to PM_{2.5-10} in the metropolis. The sixth source was characterised by such loadings of Na (78.6%), Cl (44.5%), S (49.6%), Mg (42.2%), Cu (33.6%), Ti (38.3%), Nb (35.5%), Se (36.5%), P (31.6%) and Pb (18.9%). Na, Cl and Mg are markers for sea spray emissions. Source profiles (Table 6) with dominant Na and Cl, as identified in various source apportionment studies conducted in coastal areas have been classified as seasalt [10,52,53]. However, it might be very difficult to pinpoint and ascribe this source to sea spray on account of the amounts of seasalt Na earlier estimated in this study which were relatively small and affirmed not to be of marine source; 49% and 53% for the coarse and fine particulate fractions respectively at the

industrial area and 32% and 37% for the coarse and fine particulate fractions respectively at the residential areas. Furthermore, Se is found impurely in metal sulphide ores, where it partially replaces sulphur. A substantial loading of Se was also observed. The Se could be from emissions associated to smelting activities, glass factories or from electronic waste due to its usage as semi-conductors. It could also be suggested to be emitted by municipal incinerators, one of such facilities is the one currently being operated by a tertiary Teaching Hospital. In addition, there are a number of high heat plastic recycling facilities in Oluyole industrial estate. Pb and Cl were used as markers of incinerator in a number of works [48,54,55]. We nevertheless suggested this source to be waste incinerator due to the loading of Pb and presence of some Pb-related industries in the metropolis along with substantial loadings of Cl and K [56].

Table 6. Profile of particulate sources resolved by PMF analysis for the metropolis

Sources	Tail pipe exhaust	Road dust	Ferrous smelting	Fine car brake	Biomass burning	Petroleum Products combustion/Smelting	Biomass & vegetative Burning	Exhaust & Non-exhaust mobile	Re-suspended soil dust	Fuel oil combustion	Waste incineration	
Element	PM _{2.5}					PM _{2.5-10}						
Al	11.2	58.6	-	2.3	28.0	2.1	22.6	3.0	72.4	-	-	
As	18.1	3.0	30.1	32.9	15.9	20.0	28.3	4.1	4.5	35.5	7.6	
Br	28.1	1.6	21.3	23.8	25.2	24.3	21.8	19.1	14.6	0.4	19.7	
Ca	20.1	19.7	23.7	16.9	19.7	5.2	8.1	3.3	36.2	20.4	26.9	
Cl	33.3	37.5	14.9	14.4	-	3.2	24.0	8.1	5.7	14.4	44.5	
Cr	13.2	2.6	84.2	-	-	50.9	-	-	12.9	36.2	-	
Cu	10.6	3.3	16.1	66.1	3.9	20.7	11.0	11.3	6.8	16.5	33.6	
Fe	-	40.9	46.2	0.2	12.6	21.6	19.3	5.0	51.0	-	3.1	
K	8.0	50.7	-	-	41.3	12.7	29.3	7.1	28.2	7.6	15.0	
Mn	4.9	68.3	15.0	8.2	3.6	-	54.2	8.9	11.8	25.1	-	
Mo	31.3	7.2	35.5	23.6	2.5	19.1	19.5	-	3.1	30.7	27.6	
Na	18.8	21.4	33.0	11.6	15.2	-	-	6.1	1.8	13.6	78.6	
Nb	28.6	-	40.0	10.7	20.7	7.2	15.4	4.9	7.3	29.8	35.5	
Ni	21.1	1.1	69.2	2.6	6.1	34.4	21.3	13.8	1.4	9.3	19.8	
Pb	32.7	3.8	33.8	21.4	8.2	22.1	25.1	21.7	-	12.1	18.9	
Rb	31.1	6.6	30.6	28.5	3.2	11.0	30.5	9.2	4.3	18.5	26.5	
S	36.0	6.2	32.5	13.5	11.8	22.9	1.8	8.9	5.9	10.9	49.6	
Se	29.7	5.4	49.0	11.6	4.3	22.5	30.0	9.6	1.3	-	36.5	
Si	3.0	55.8	3.0	3.9	34.2	-	16.1	2.0	72.4	5.0	4.5	
Sr	28.5	-	30.2	19.1	22.2	22.0	25.9	20.9	-	10.3	20.8	
Ti	-	96.3	-	3.7	-	1.5	-	6.1	3.2	50.9	38.3	
V	24.8	9.5	17.5	31.9	16.3	0.1	0.7	2.4	8.5	55.6	32.7	
Zn	24.8	15.9	43.9	12.6	2.8	8.0	-	75.4	11.9	4.6	-	
Zr	30.1	0.5	28.4	23.6	17.5	-	21.4	11.2	5.3	51.3	10.9	



TPI -Tail pipe & Industrial, RSRD - Re-suspended road dust, FMS - Ferrous metal smelting, FB - Fine car brake, BB - Biomass burning, ENEM - Exhaust & Non-exhaust mobile, RSSD - Re-suspended soil dust, FOC - Fuel oil combustion, IN - Incineration.

Figure 4. Percentage contributions of each source identified with PMF analysis of PM_{2.5} and PM_{2.5-10}

Interestingly, the PMF analysis apportioned a substantial amount of 37.6% to PM₁₀ in the metropolis. Open and uncoordinated air burnings of solid waste are common practices in the four designated waste dump sites in Ibadan in addition to the various backyard burning activities in various neighbourhoods, this amount was in line with the expectations in Ibadan.

Percentage contributions to the fractions by the various sources identified is shown in Figure 4.

4. Conclusion

In this study, positive matrix fractionalization (PMF) model was applied to identify possible emission sources and evaluate the percentage contribution of each emission source to PM_{2.5} and PM_{2.5-10} fractions in two functional areas of Ibadan metropolis. The elements in both fractions displayed both positive and negative correlations. Thus, typical crustal elements such as Al, Fe, Ca, Mn and Si displaying high correlations in the coarse fraction have common source, which is air borne or windblown soil source in the metropolis. K and S were negatively correlated, indicating that they were not of a common origin in the coarse fractions. In the fine fraction, K, Na, P, S and Cl were highly correlated. The seasalt estimation of aerosol indicated that there were insignificant seasalt contributions of 2% and 1.3% of S in fine (PM_{2.5}) and coarse (PM_{2.5-10}) fractions respectively at the industrial receptor site along with 0.5% for each of the fractions in residential area. Non-seasalt component of K and Ca were estimated not to be less than 97% of their total metal in the aerosol in both fractions across the two functional areas of the metropolis indicating that the seasalt contributions were very low, same with Na thereby confirming that seaspray influence in Ibadan air-shed was very negligible and unimportant. This was an indication that they were of a similar or common source, a combustion source probably.

PMF resolved five sources for PM_{2.5} while six sources were resolved for PM_{2.5-10} fractions. The percentage contributions estimate for tail pipe emission/gasoline oil combustion to PM_{2.5} was 48.5% while solid waste combustion/incineration contributed 37.6% to the PM_{2.5-10} in the Ibadan metropolis. These high percentage values resolved for anthropogenic tail pipe emission and solid waste burning calls for a step-up in compliance and routine monitoring activities of regulatory agencies on one hand and stringent abatement options on the other to control the possible untold hazards on health and environment.

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