RECEPTOR MODELING OF ATMOSPHERIC AEROSOLS IN FEDERAL CAPITAL TERRITORY (FCT), NIGERIA

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ABSTRACT

The air quality of Abuja urban air shed was investigated with a view to establishing sources of pollution in the city. Forty samples of coarse atmospheric particulates ($PM_{2.5-10}$) were collected at different categories of spatially distributed receptor locations; high (High-dra) and low (Low-dra) density residential, commercial (Comm-1&2) and institutional (Institute) areas with a sequential double stage sampler for eight non-sequential months. Positive matrix factorization (PMF) receptor model was used for source apportionment of aerosols' inorganic chemical species characterized using an ion beam analysis (IBA) technique with incident particle energy of 2.5 MeV. A data matrix of 40 by 20 species (Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Cd, Sn, Ta, Pb and PM) was used to run the model. Mean mass concentration in High-dra, Low-dra, Comm-1, Comm-2 and Institute were 21 μg/m^3 (range, 10 - 49 μg/m^3), 66 μg/m^3 (range, 7 - 287 μg/m^3), 42 μg/m^3 (range, 7 – 91 μg/m^3), 63 μg/m^3 (range, 10 - 183 μg/m^3), and 60 μg/m^3 (range, 4 – 167 μg/m^3) respectively. Three distinct sources; Crustal 4.2%, Biomass/Fuel burning 8.8%, Vehicular 87.0% were identified and apportioned by the PMF model. On site measured concentrations and model predicted concentrations of PM in this study were related by equation $y = (0.59 \pm 0.07)x + (14.73 \pm 5.38)$ with a good coefficient of determination $r^2 = 0.67$ The study concluded that traffic-related pollution posed a great hazard to the atmospheric environment of Abuja and likewise on human receptors in the study areas.

Keywords: $PM_{2.5-10}$, PIXE, Trace Elements, Receptor Model

INTRODUCTION

A number of urban cities across Nigeria, including Abuja (The Federal Capital Territory) are known to experience elevated levels of particulate matter (PM) pollution (Obioh *et al.,* 2005). Within the Abuja metropolis for instance, myriads of sources contribute to the air quality mix and are complex in nature. In the neighboring rural areas, the sole dependence on biomass burning for energy and other related agricultural activities have increased the pollution strength within the local regions and have also contributed to the Abuja urban ambient concentrations (Abiye *et al.,* 2013). All these factors form a web of pollution sources that either emanate from or arrive at the Federal Capital Territory. However, exposure to elevated levels of PM has long been associated with adverse human health impacts and is a major source of morbidity and mortality worldwide especially from the particulate fractions with an aerodynamic diameter of less than 10 μm (Afroz *et al.,* 2003; Liew *et al.,* 2011). The adverse effects are intensified even more on the population living in urban environment influenced by high traffic density or industry (Dongarra *et al.,* 2010). A World Health Organization (WHO, 2007) workshop on the health relevance of PM from various sources suggested that future research should, among other things, consider the contributions of different emission sources to population exposure. For these reasons, airborne particulate matter has been considered world over the most significant criteria to indicate air quality (Singh and Sharma, 2011). This is of particular importance because research into the sources of high PM levels is needed to understand and regulate the factors that contribute to reduce ambient air quality (*Jeong et al., 2011).* Since urban areas are influenced by multiple sources of aerosols, it is important to undertake source-receptor relations to establish source contribution. Such source analyses could indentify key sources which may be important when designing pollution abatement strategy to enhance air quality management for the city. In order to achieve this, chemical specie of sampled PM is required. Different methods of

characterizing airborne particles have been developed and applied worldwide. Among the techniques available, particle induced X-ray emission (PIXE) is a powerful, relatively simple and economic technique that is capable of non destructive multi-elemental analysis in a single run (Romo-kroger, 2010). The focus of this study is therefore to identify natural and anthropogenic sources of $PM_{2.5-10}$ and apportion their contributions by applying PMF receptor model to the characterized aerosol samples with a view to providing air quality indices needed for air quality management in Abuja.

MATERIALS AND METHODS

Description of Abuja and Receptors Sampling Location

The five categories of sampling sites as indicated in Table 1 and the Districts (Figure 1) were located in FCT Abuja (9°4′N, 7°31′E), which is situated in north-central part of Nigeria. Abuja has an approximate land area of 770km^2 and like the rest of the country experiences two seasons annually: the rainy season from April to October, characterized by moderate temperatures and precipitation, and the dry season, from November to March, characterized by extreme temperatures and low levels of precipitation. It is a new city and one of Africa's purpose-built cities, designed to be an urban non-industrial Federal Capital Territory of Nigeria. Pollution sources in Abuja appear to be mainly dominated by road transportation, which span all classes of vehicles. Other sources may be associated with residential, commercial and public institutions, as well as those arising from urban service delivery, especially waste management, road expansion and construction activities and fuel combustion. The selected receptor locations are situated within three districts namely Maitama, Wuse II and Garki. Maitama District is to the north of the city with Wuse lying to its southwest. This area is home to the top bracket sections of the society and corporate business, and has the reputation of being very exclusive, expensive and generally a low density residential area. Wuse is prominently known as a commercial area having Abuja's principal market located within it. Garki is a suburb of the city mainly for residential purpose. The population in Garki is dense compared to others and accommodates some low income earners. Institute and Low-dra sampling spot are both located within the rich district of Maitama, a mix of low density residential and institutional area with paved roads and walkways. Receptors at the Institute location experience a traffic pattern that changes from peak level during morning rush hour to moderate at noon time and then peaks up at closing time in the evening. Unlike Institute, Low-dra is located a little bit inwards from the main roads and has more of residential structure than institutional. Installation of industrial size power plant in each compound is a characteristic feature of Low-dra. These power plants supply the energy demand for home lightening and driving domestic gadgets. While the inhabitants of the compounds enjoy the comfort of their homes, pollution plume from the plants' exhaust continue to impact on the ambient air of the surroundings'. Garki district is less expensive compared to Maitama and Wuse making it more affordable for low and average income earners. It has a network of unpaved streets in its interiors leading to enhanced dust generation by both pedestals and motorist. According to National Population Commission (2006), the FCT had a population of 1,406, 239.

***Table 1: Sampling Locations**
*(table is adapted from Abiye *et al.,* 2013)

Site_Id	District	Sampling spot	Coordinates
Low-dra	Maitama	NIMET Office, Gana Street.	9° 4 ′ 48.83"N, 7° 30 ′ 1.36"E
Institute	Maitama	Federal Ministry of Environment	9° 4 ′ 50.43"N, 7° 29 ′ 31.78"E
High-dra	Garki	Nsukka Street	9° 1 ′ 39.43"N, 7° 29 ′ 41.81"E
Comm-1	Wuse II	Wuse main market	9° 4 ′ 0.00"N, 7° 28 ′ 59.99"E
Comm-2	Wuse II	Banex Plaza	9° 4 ′ 7.14"N, 7° 27 ′ 57.54"E

Aerosol Sampling and Measurement

Forty samples of airborne $PM_{2.5-10}$ aerosols filters were deployed and collected at five locations once every month for a total of eight non sequential months in 2009 and 2010. *Gent" Stacked Filter Unit (SFU)* sampler (Hopke *et al.,* 1997) equipped with an impactor for $PM_{2.5-10}$ cut-off inlet was used for the particulate sampling. Nucleopore polycarbonate filters (diameter 47mm) with 8 μm pore size were used as media for collecting the particulates. The SFU impactor was installed face-down at a height of about 1.6 m above ground level to represent the nose-level of an average height person and at such position where free air circulation is not hindered. The sampler was operated at a flow rate of 18 L/min. Average sampling duration of about 10hr commencing from 08:00-18:00 hr was observed as a protocol. All the filters used for sampling were pre-weighed and pre-conditioned in a dessicator. Pre-conditioning consisted of an exposure of filters for 24 h at 25 ^{0}C and constant humidity around 50% in a dessicator and post-weighed to determine the gravimetric mass using Sartorius Microbalance with sensitivity of 0.1 μg. The micro-weighing balance was calibrated using automated *isoCAL* function and measurements were taken in quadruple to ensure accuracy.

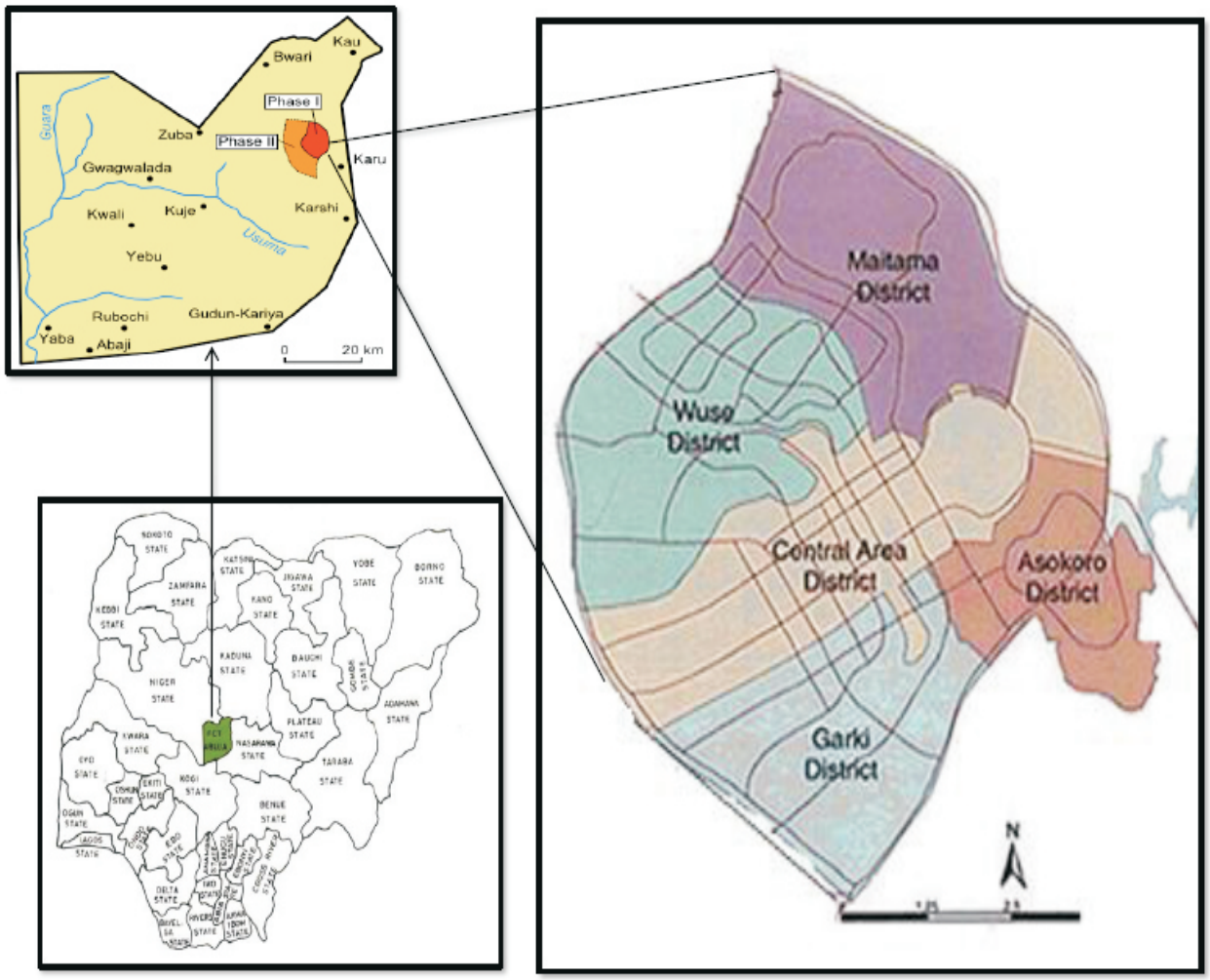

Figure 1: Map Showing Phase I of Abuja Municipal Area Council (AMAC) and Districts of Sampling Location

Ion Beam Analysis

Accelerator based ion beam technique was used for the elemental characterization of the particle laden filters collected from the urban environment of Abuja. This was achieved using Particle Induced X-ray Emission (PIXE) technique from a highly sensitive 1.7 MV Tandem 5SDH Accelerator available at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. One quarter of each filter was cut out and mounted on a metallic sample holder maintained at not less than 3×10^{-6} Torr in a vacuum chamber. An 8 mm beam collimator diameter and charged helium ($^{4}He^{+}$) particle of 2.5 MeV was used for sample irradiation. A Si-Li detector (model ESLX 30-50, -500V) equipped with a 90 μm Kapton filter absorber was employed for the PIXE signals. Spectra acquisition was taken for a 30 000 counts of 3.0 μC lasting for an average of 1200 s. Elemental concentrations were obtained in $ngcm^{-2}$ and then converted to ngm^{-3} by considering the filter area (in cm^{2}) exposed to the incident beam and the specific volume of air sampled. GUPIXWIN computer code (Maxwell *et al.,* 1995; Campbell, 2008) was used for fitting the experimental PIXE spectra. Subsequently, GUPIXWIN was used to calculate the corresponding elemental concentrations in the samples analyzed. The details of the PIXE method have been described by Saliba *et al.* (2007).

Quality Control and Quality Assurance

Analyses of six standard reference materials, Fe (19202), Cu (19205), Ni (19204), Si (19197), V (19201) and Ti (19200) all provided by MICROMATTER, were carried out in order to check the analytical accuracy and precision of the

analytical procedure. The results of reference standards showed deviations of ±2.8% or less for all elements analyzed (Abiye *et al.,* 2013).

Source Identification and Apportionment

Source identification and apportionment was performed using an advanced receptor model known as Positive Matrix Factorization (PMF version 3.0.2.2) to assess particulate matter source contribution. PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles. Multivariate methods are based on the assumption that each aerosol source type has unique chemical properties, hence highly correlated chemical compounds originate from the same source (Jeong *et al.,* 2011). The model solves the general receptor modeling problem using constrained, weighted, least-squares. The general model assumes there are *p* sources, source types or source regions (termed factors) impacting a receptor, and linear combinations of the impacts from the *p* factors give rise to the observed concentrations of the various species. Mathematically stated,

$$x_{ij} = \sum_{i=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

Where x_{ij} is the concentration at a receptor for the j^{th} species on the i^{th} day, g_{ik} is the contribution of the k^{th} factor to the receptor on the i^{th} day, f_{kj} is the fraction of the k^{th} factor that is species j, and e_{ij} is the residual for the j^{th} species on the i^{th} day. The corresponding matrix equation is

$$X = GF + E \quad (2)$$

where X is a $n \times m$ matrix with n measurements and m number of elements. E is an $n \times m$ matrix of residuals; *G is* $n \times p$ source contribution matrix with p sources and F *is a* $p \times m$ source profile matrix. A non-negative constraint is applied to source contributions and mass fractions. Chemical species with lots of uncertainty are also not allowed to influence the estimation of the contributions and profile as much as those with small uncertainty, hence weighted. The PMF methodology has been described in detail by its developers (Paatero and Tapper, 1994) and has been well adopted in several studies for receptor modeling of airborne PM and particle source contributions (Almeida *et al.,* 2005; Abu-Allaban *et al.,* 2007; Aldabe *et al.,* 2011; Begum *et al,* 2013). In this study, we have strictly used sample-specific uncertainties obtained by analyzing the PIXE spectra using GUPIX code. Signal-to-noise ratio analysis (Table 4) was performed to validate each elemental species based on technique and procedure for specie categorization suggested by Paatero *et al.* (2003).

RESULTS AND DISCUSSION

Mass Concentration Levels

The mean, range and standard deviation of mass concentration for coarse fractions sampled are given in Table 2 and the temporal variation presented in Figure 2. Generally, $PM_{2.5\text{-}10}$ concentrations were low in the year 2009 with concentrations less than the overall mean (51 μgm^{-3}). However, the later part of the year 2009 and early 2010 recorded elevated mass levels above the mean concentration. A peak value of 287 μgm^{-3} was obtained at Low-dra, during the hamattan haze which occurred across the country in the first quarter of 2010. More than 95% of the measurements at sampling sites exceeded 25 μgm^{-3}. Abuja is expected to be less impacted by dust particles considering that it is a well planned city but we found that its location at a less humid and arid region of the country, influence of seasonal harmattan occasioned by the north-east trade wind with characteristic dust haze, intensified dryness and the extensive construction of buildings and urban infrastructure development have contributed to the high levels recorded in this study. The values obtained in this study are comparable to those of other cities in Nigeria (Obioh *et al.,* 2013)

Table 2: Summary Result of Coarse PM Concentration (μgm^{-3})

Site	Comm-1	Institute	Comm-2	High-dra	Low-dra	All sites
Mean	42	60	64	21	66	51
Range	7 - 91	4 - 167	10 – 183	10 - 49	7 – 287	4 - 287
StDev	36	61	62	15	100	61

Elemental Compositions

Table 3 shows the mean values of $PM_{2.5-10}$ chemical species at the five sampling locations. For all the sites, crustal elements Si, K, Ca and Fe have the highest concentrations (range: 1 100 -3 6000 ngm^{-3}) in the order Si > Ca > K > Fe (Comm-1 and High-dra) and Si > K > Ca > Fe (Institute, Low-dra and Comm-2). These values are generally higher than those reported for Lagos, 900 – 4 000 ngm^{-3}(Ezeh *et al.,* 2012). High-dra has a high percentage of residents depending on biomass burning for energy and could justify the highest value of K obtained at the location. The mean concentrations of Cd vary between 63 and 940 ngm^{-3}. These ranges of values are 7 – 105 and 13 - 188 times higher than the values obtained by Ezeh *et al.* (2012) at Ikoyi, Lagos and WHO guideline for European countries respectively. Cadmium is used for electroplating of steel and is released into the environment as a by-product in the extraction zinc of and copper. Chronic exposure to cadmium can result in renal and epithelial cell damages (Yuzo, 2005).

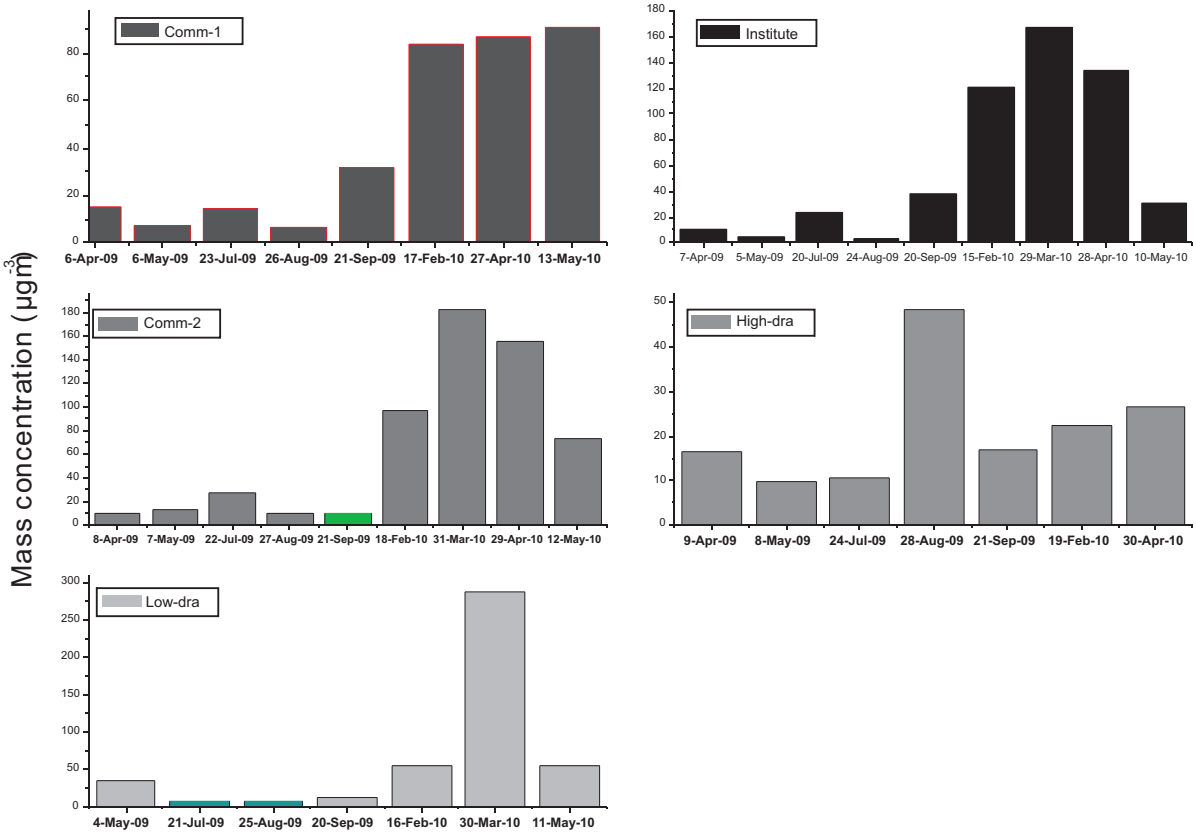

Figure 2: Time Series of PM Mass Variation During the Sampling Period

Atmospheric transport of particulates from industrial processes in the states around Abuja may account for the high cadmium concentration. Tracers for heavy oil combustion (Ni and V) varied moderately in concentration at the five sites but were all higher than those obtained for Lagos (Ezeh *et al.,* 2012). Pb, Zn, Mn, Cu, Br, have the highest mean values of 56 ngm^{-3}, 64 ngm^{-3}, 66 ngm^{-3} (High-dra), 852 ngm^{-3}(Comm-2), and 61 ngm^{-3}(Institute) respectively. The range of values obtained for elemental composition of particulate matter in Abuja are comparable with those reported for similar urban cities such as Cairo (Abu-Allaban *et al.,* 2007), Spain (Aldabe *et al.,* 2011) , Bangladesh (Begum *et al.,* 2013) and Western European coast (Almeida *et al.,* 2005).

Table 3: Mean Elemental Concentration (ng/m^3) of Coarse PM at Each Location

	Comm-1(*StDev)	Institute (StDev)	High-dra(StDev)	Low-dra (StDev)	Comm-2 (StDev)
Si	8 358(609)	13 958(422)	18 435(656)	22 746(386)	35 968(699)
P	224(114)	133(59)	**nd**	189(176)	148(82)
S	865(411)	834(385)	966(93)	756(307)	873(646)
K	1 503(309)	2 226(370)	3 619(239)	2 633(475)	3 213(843)
Ca	1 860(458)	2 154(487)	6 103(513)	2 630(276)	2 983(410)
Ti	147(112)	240(165)	422(412)	352(367)	448(491)
V	15(5)	23(5)	14(5)	11(7)	12(10)
Cr	118(115)	35(41)	43(37)	56(66)	82(87)
Mn	33(22)	44(20)	66(68)	64(46)	63(62)
Fe	1 416(60)	1 887(182)	3 096(524)	2 606(360)	2 684(932)
Co	5(3)	9(6)	21(15)	39(24)	29(17)
Ni	18(13)	13(7)	14(8)	20(6)	21(12)
Cu	598(184)	709(261)	721(217)	596(53)	852(145)
Zn	28(15)	33(14)	64(46)	56(48)	31(21)
Br	49(32)	61(47)	30(15)	42(11)	29(10)
Cd	66(42)	125(52)	940(1386)	63(45)	181(48)
Sn	126(41)	106(71)	265(248)	101(29)	125(78)
Ta	84(32)	148(61)	126(56)	100(6)	130(61)
Pb	19(11)	32(7)	56(28)	11(2)	27(6)

***StDev** = standard deviation, **nd** = not detected

PMF Source Apportionment

PMF receptor model requires a large matrix of chemical species for better performance (Norris and Vendatham, 2008). Source apportionment was therefore performed by combining all the data from the five locations with a data matrix of 40 (samples) × 20 (variables) as input, a data size comparable with Saliba *et al.* (2010). The particulate mass concentration and inorganic chemical species were considered as individual variable. Except for cadmium that was categorized as "weak" based on the signal to noise ratio, other variables were strong (Table 4). All the species have scaled residuals between ±2 and were normally distributed except for Pb. Rotational ambiguity (Paatero *et al.,* 2005) in the PMF solution was analyzed using Fpeak tool (Fpeak strength between -2 and +2 at 0.1 intervals). In order to scale down the uncertainty associated with the spatial-temporal distribution of the collected samples, the model was executed with extra modeling uncertainty of 5% for twenty base runs at a random seed to examine the solutions for three, four and five factors. Four-factor solution has a complex mixture of elements that are difficult to separate into possible sources and did not apportion the $PM_{2.5-10}$ fraction to the source. Five-factor solution merges marker elements of vehicular and dust particles into a single source without apportioning the PM mass. It was observed that the three-factor solution gives the best option and is discussed as follows:

Source profiles of the modeled factors are shown in Figure 3. The first factor apportioned was

characterized by high loadings of Si (72.8%), Ca (86.6%), Ti (84.6%), Fe (85.8%). This factor represents contributions from soil dust referred to as crustal source (Oluyemi and Asubiojo, 2001). 4.2% of the PM mass was apportioned to this source. Sahara dust (locally known as hamattan dust), re-suspension of road dust by vehicles, wind and construction are the major origin of this factor. The crustal factor containing Si, Ca, Ti and Fe may have arisen partly from the well known Sahara dust in Africa and re-suspension of soil dust. Construction of buildings and massive roads expansion were also common in year 2009/2010 when this work was carried out. Hamattan is characterized by dry soil conditions, low relative humidity, scanty rainfall and north-easterly prevailing winds. These sources are either natural or anthropogenic and contribute majorly to the crustal loading in the urban environment. Ca is a marker element for construction materials such as cement (Cohen *et al.,* 2009). Time series of contribution (Figure 4) show that

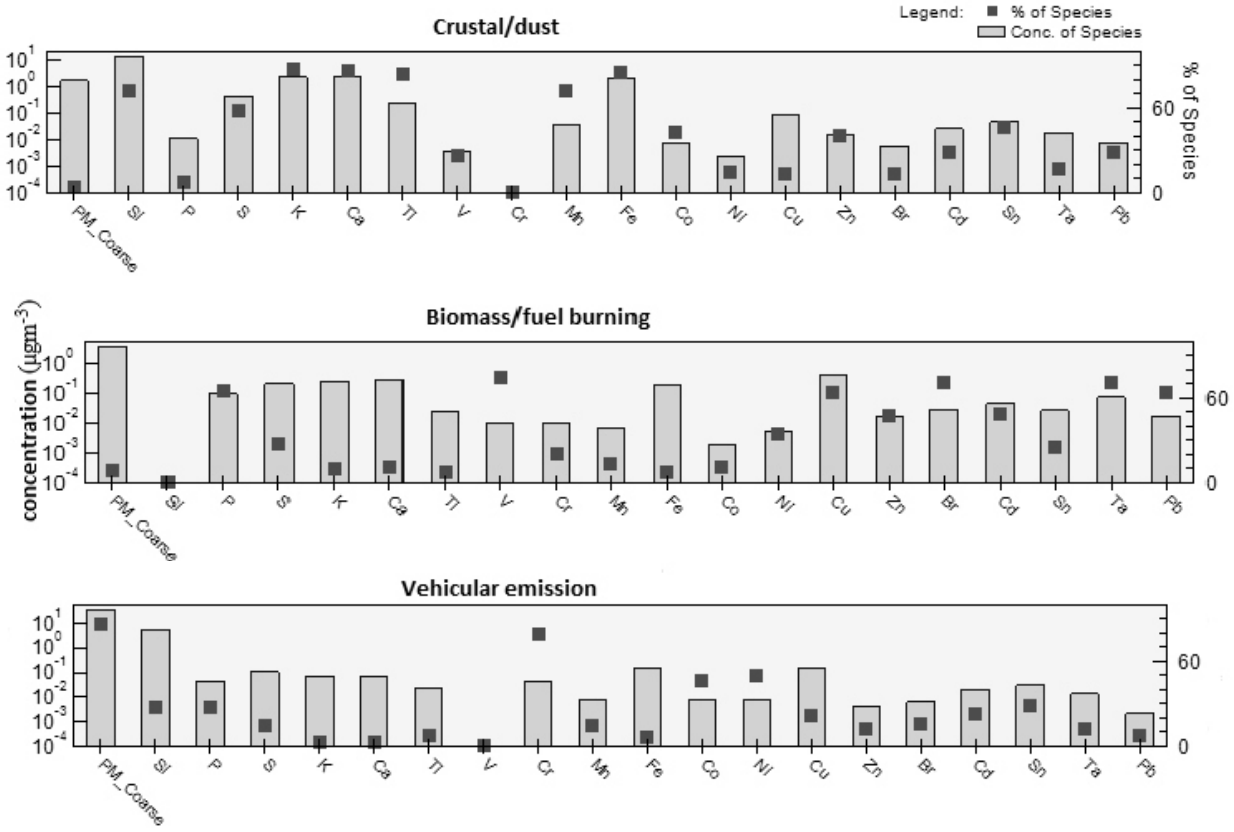

Figure 3: Source Profile of $PM_{2.5-10}$ for Abuja Urban

crustal sources are most pronounced in the dry months of late 2009 and early 2010. 8.8% of PM mass was attributed to the second factor containing marker elements V (74.1%), Cu (64.4%), Zn (47.2%), Sn (25.5%), Br (70.6%), Cd (49.2%), Pb (63.9) with a combination of P and S). These combinations of elements are fingerprints for fuel burning (biomass, traffic, industrial and high temperature). Cu is a characteristic of emission from diesel use by road vehicles (Kothai *et al.,* 2008). Cd is a typical marker for emission due high temperature combustion of fossil fuel (Liu *et al.,* 1998). Mobile sources constitute the larger fraction of fuel consumption in Abuja. As an estimate, the number of used vehicle imported into Nigeria in year 2000 is above 30, 000 and it is projected that more than 45, 000 will be imported between 2001 and 2005 (Ajayi and Dosunmu, 2002). By proportional analysis and assumed implication, it can be said that the city of Abuja have experienced an upward trend of vehicle population since then.

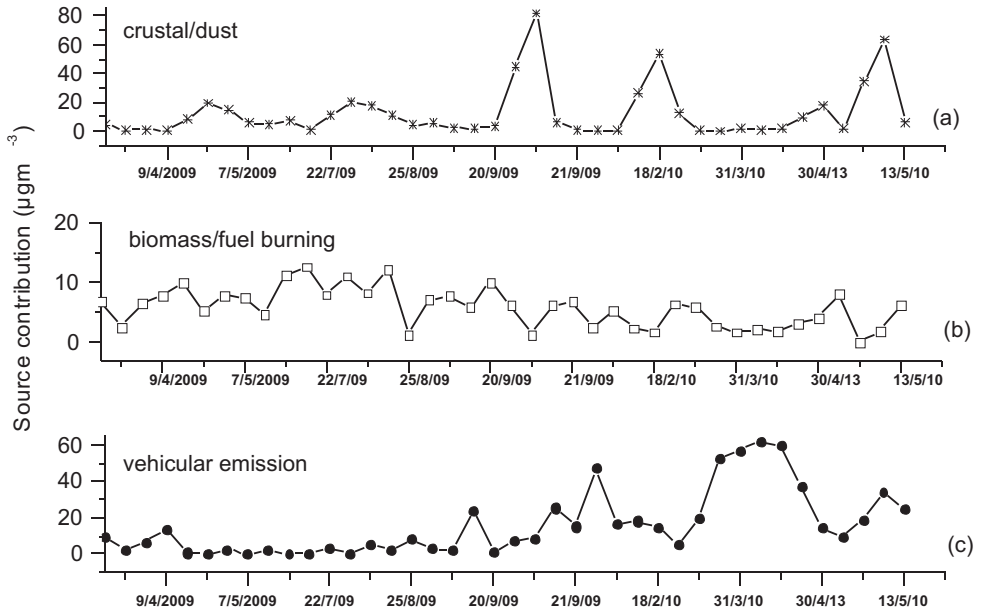

Figure 4: Time Variation of Source Contributions to the Pollution Load

Power plants also contributed significantly to fuel burning emission as discussed in section 2.1 above. Automobiles are known to be major sources of atmospheric lead due to the use of leaded anti-knock additives in gasoline (Pacyna *et al.,* 2009; Kummer *et al.,* 2009). The effort to phase out of Pb in gasoline started worldwide during the 70s and 80s and many countries have seen a dramatic decrease in concentration of airborne Pb but there is no clear definition how Nigeria is engaged in the process. In Nigeria, gasoline still contains lead in the range of 0.65 to 0.74 g/L (Galadima and Garba, 2012). Orisakwe (2009) have earlier shown that the Clean Air Initiative which aims to reduce lead content of gasoline has been ineffective due to negligence of the Nigerian government. Phosphorous is a marker element for waste disposal and incineration. It may be due to municipal waste containers located some distance away from some of the sampling spots. Zn and Sn are mainly from industrial processes (Marcazzan *et al.,* 2001). Abuja is a non-industrial urban centre surrounded by neighboring states with significant mining and industrial activities. For instance, non-ferrous metals like tin, lead and zinc are mined in almost all the states surrounding or sharing borders with the city. Tin has been mined since colonial times and is one of the most versatile metals commonly used in industry. Tin ore (cassiterite, SnO_2) is obtained mostly from younger granites in the northern parts of the country and has been largely won from placers on the Jos Plateau and around younger granite masses in Bauchi, Kaduna and Benue States. Lead and zinc ores occur in commercial quantities in the Benue Trough, a narrow belt over 560 km stretching from Ishiagu in the south-east to Bauchi State. This indicates that long trans-boundary transport of dust and air dispersion may be responsible for this factor in Abuja. Cr, Ni - fingerprints for vehicular emission (Isakson *et al.,* 2001) and PM contribute 80%, 50% and 87 % respectively to the third factor. The contribution of each factor to PM mass loading and percentage of each specie apportioned is listed in Table 4. The goodness

Table 4: Contribution to Factors by Individual Modeled Variable

	% of specie apportioned to each factor			
	Crustal/dust	Biomass/fuel burning	Vehicular emission	Signal/noise ratio
Si	72.8	----	27.2	0.706
P	7.3	64.7	28.0	0.634
S	57.8	27.9	14.3	0.511
K	87.6	9.6	2.7	0.710
Ca	86.6	10.9	2.5	0.692
Ti	84.6	7.7	7.7	0.776
V	25.9	74.1	-----	0.605
Cr	----	20.5	79.5	0.732
Mn	7.2	13.0	14.9	0.639
Fe	85.8	7.9	6.3	0.823
Co	43.3	10.7	45.9	0.619
Ni	15.0	34.9	50.2	0.570
Cu	14.0	64.4	21.6	0.997
Zn	40.8	47.2	12.0	0.699
Br	13.9	70.6	15.5	0.832
Cd	28.2	49.2	22.5	0.211
Sn	46.2	25.5	28.3	0.930
Ta	16.2	70.6	12.5	0.548
Pb	28.3	63.9	7.8	0.658
PM	**4.2**	**8.8**	**87.0**	0.917

of fit by the PMF model is shown in Figure 5. The one to one line is a reference for a perfect line of fit. Relationship of the regression line is $y = (0.59 \pm 0.07)x + (14.73 \pm 5.38)$, with the coefficient of determination $r^2 = 0.67$ indicating a very good correlation between the measured and the predicted values.

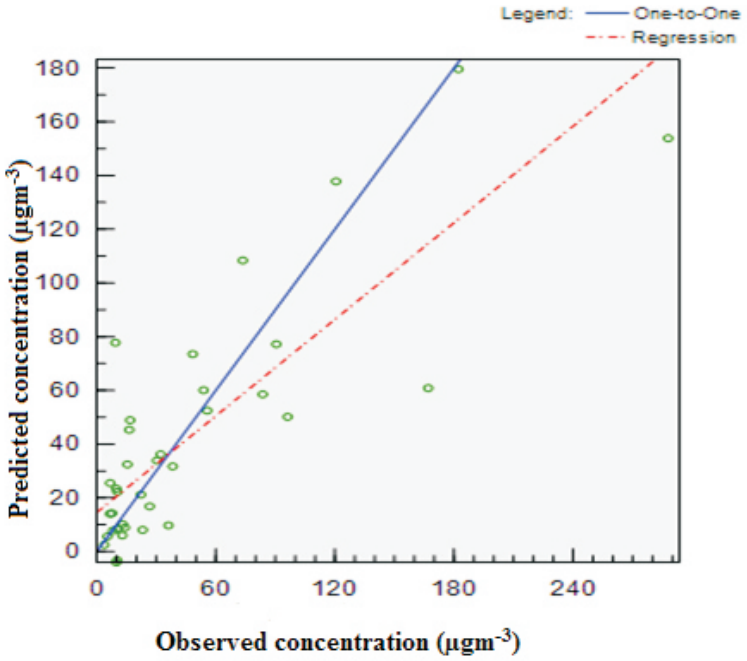

Figure 5: Plot of predicted PM mass and measured (observed) PM mass

CONCLUSIONS

Coarse fractions of air borne aerosols have been monitored and the chemical species characterized using an Ion Beam Analysis technique. PMF model was used to identify and apportion sources contributing to $PM_{2.5-10}$ pollution load in Abuja urban. Crustal/dust, biomass/fuel burning and vehicular emissions were found to be the major sources contributing to the pollution strength in the city of Abuja. This study showed that transport-related pollution in Abuja was highly significant with possible severe health implications.

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