

# ELEMENTAL CHARACTERIZATION AND SOURCE IDENTIFICATION OF FINE PARTICULATE MATTER(PM<sub>2.5</sub>) IN AN INDUSTRIAL AREA OF LAGOS STATE, NIGERIA.

## Abstract

Fine particles (PM<sub>2.5</sub>) are mainly generated by combustion processes including emissions from motor vehicles, combustion of fossil fuel for power generation and large industrial processes such as ore and metal smelting. They may also include natural emissions such as fine windblown soils, sea spray and smoke from biomass burning. Based on the field study conducted, the concentrations of PM<sub>2.5</sub> at the different locations vary with respect to anthropogenic activities. The PM<sub>2.5</sub> levels obtained ranged from 14.00 to 32.67 µg/m<sup>3</sup> during wet season and 18.67 to 34.67 µg/m<sup>3</sup> during dry season. Trace elements especially heavy metals are significant components of PM<sub>2.5</sub> in industrial environments. The heavy metals are of particular concern due to their persistence in the environmental media and their human toxicity. The particulate matter concentration was obtained using Casella cel-712 microdust pro-real time dust monitor and flame atomic absorption spectrophotometer was used to determine the elemental content. The Enrichment Factor (EF) analysis showed very high enrichment for the elements; Pb, Cd, Cr, Cu, Ni, Na, K, Mg, and Ca in the fine fraction (PM<sub>2.5</sub>). The Principal Component Analysis explained three common contributing sources of fine particulates (PM<sub>2.5</sub>) such as entrained soil, sea salt and combustion. Spatial variation was performed and mean concentration of some of the elements in the various locations showed significant difference at P<0.05. Correlation matrix was also determined and some of the elements were strongly correlated while some were not. Seasonal variation for the elemental concentration also revealed that the mean values for some of the elements were statistically significant at P<0.05 for both seasons.

**Key Words:** Fine particulate, Anthropogenic, Heavy Metal, Spatial and Season

## INTRODUCTION

Gaseous pollutants and particulate matter are released into the atmosphere at concentrations above their normal ambient level. This is caused by the increasing human activities which eventually have a measurable effect on humans, animals and plants. Particulate matter (PM) which is inhaled into the human respiratory system is related to most serious health effects

including pulmonary and cardiovascular illnesses. The size of particles is directly linked to their potential for causing health problems. Environmental Protection Agency (EPA) agencies such as Federal Ministry of Environment and United State Environmental Protection Agency are concerned about particles that are 2.5 micrometer in diameter ( $PM_{2.5}$ ) or smaller because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health problems (FMEN, 2015; US EPA, 2013). The source of airborne particulates includes natural and anthropogenic processes. The most noteworthy anthropogenic source with regards to quantity stem from incomplete combustion processes, such as fossil fuel and biomass burning (Seinfeld and Pankow, 2003). The rate of increase of air pollutant concentrations in developing countries such as Nigeria are higher than those in developed countries and hence atmospheric pollution is often severe in cities of developing countries all over the world. There has been remarkable industrial progress in Nigeria over the last three decades with the establishment of many cottage industries. This rapid industrialization has not been matched with proper planning for the control of environmental pollution problems that are usually associated with such industrial development (Owoade *et al.*, 2013).

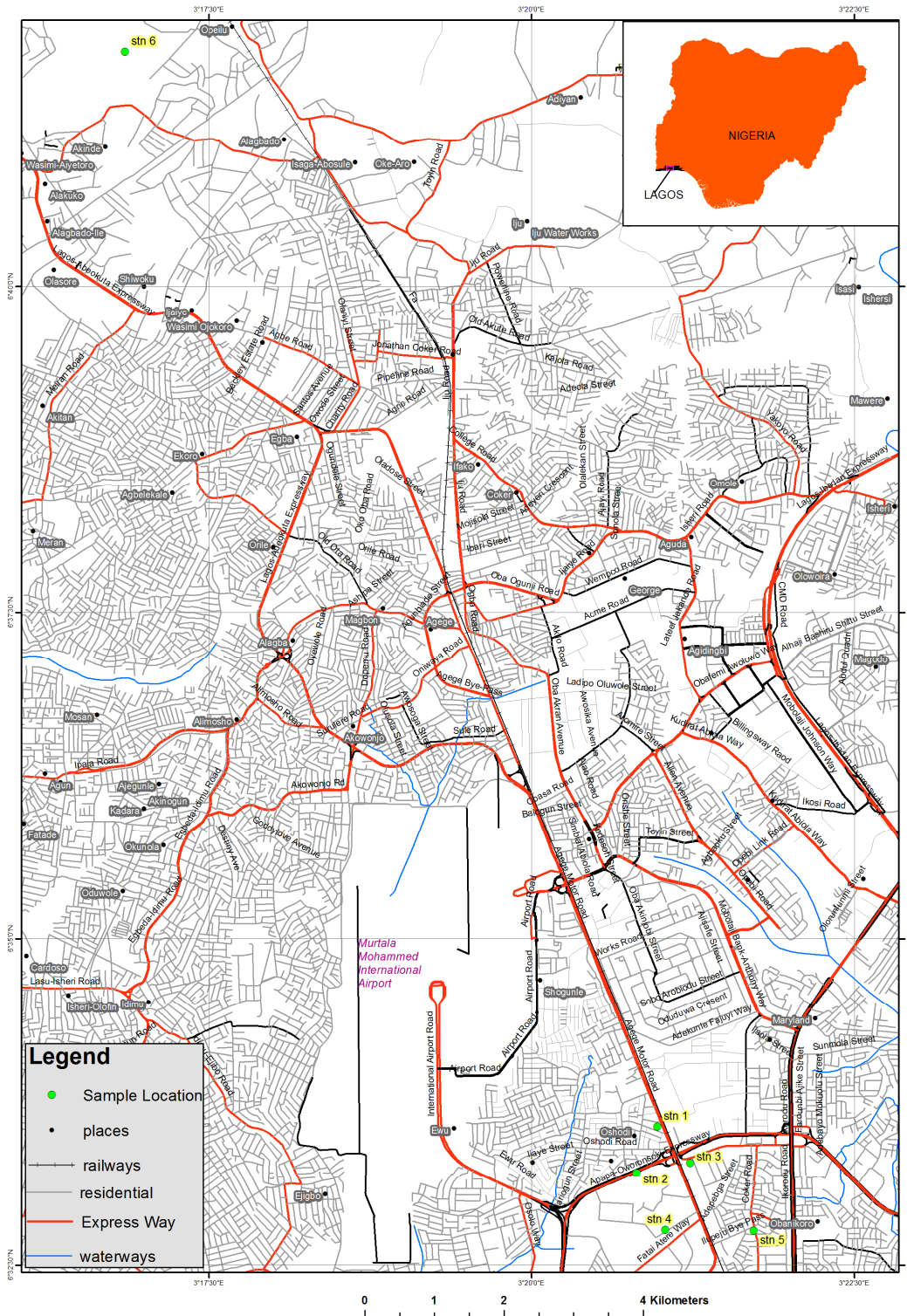
Severe air pollution has been identified in overcrowded cities in Nigeria such as Lagos, Port Harcourt, Kaduna, Kano, and Abuja (Ifeanyichukwu, 2002). Both gaseous pollutants and atmospheric particulate matter contribute to the deterioration of air quality (Casse *et al.*, 2013). Thus this research is aimed at evaluating the status of  $PM_{2.5}$  and provides a base line information and data with respect to heavy and light metals (alkali and alkali-earth metals) in those study locations.

## MATERIALS AND METHODS

**Sample Locations:** Sampling of  $PM_{2.5}$  was conducted in six (6) locations within the Lagos metropolitan area. The sampling was done for both wet and dry seasons between July 2016 and April 2017. Table 1 shows the site codes, coordinates and site descriptions. Locations 1 to 5 are busy industrial areas while location 6 which is a busy non industrial area was used as the control site.

62 **Table 1. Site codes, Coordinates and Site Description**

| S/N | SITE CODE | COORDINATES                  | SITE LOCATIONS/DESCRIPTION    |
|-----|-----------|------------------------------|-------------------------------|
| 1   | LTN1      | 6° 33' 35.8"N, 3° 20' 58.4"E | Bolade-Oshodi area            |
| 2   | LTN2      | 6° 33' 14.6"N, 3° 20' 48.9"E | Apapa-Oworonshoki express way |
| 3   | LTN3      | 6° 33' 19.2"N, 3° 21' 13.8"E | Town Planning way             |
| 4   | LTN4      | 6° 32' 48.2"N, 3° 21' 02.1"E | Ilupeju Industrial Avenue     |
| 5   | LTN5      | 6° 32' 47.9"N, 3° 21' 43.3"E | Oshodi-Ilupeju by-pass        |
| 6   | LTN6      | 6° 41' 50"N, 3° 16' 51"E     | Alagbado-Alakuko axis         |



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64 **Figure 1. Map of Lagos State Showing the Sampling Sites**

**Sample Collection:** The fine particulate matter (PM<sub>2.5</sub>) was collected using Casella Cel-712 Microdust Pro Real-time Dust Monitor with a polyurethane foam (PUF) and a glass fiber filter (GFF). The sampler was placed at heights of 1.5 m above ground level and within the human breathing zone. The glass fiber filter (GFF) was used to collect the fine particulate matter. The sampler was connected to a pump with a flow rate of 2 L/min for a sampling period of 8 hours/day. A size selective polyurethane foam (PUF) fixed in the sampler probe served as a collecting medium and a glass fiber filter also fitted in the probe collected PM<sub>2.5</sub> screened through the PUF as described by Gaita *et al.*, (2014). Meteorological parameters such as humidity and temperature were simultaneously measured using thermo-hygrometer during the period of sampling. At the end of each sampling day, samples were carefully wrapped in a polyethene bag and kept in a plastic container to avoid contamination prior to metal analysis. Samples were collected in triplicates.

**Sample Preparation and Measurement:** In order to determine the concentrations of the metallic elements, a mixture of hydrochloric (HCl) and nitric acid (HNO<sub>3</sub>) was used to extract the metals from the glass fiber filters. Each glass fiber filter was cut into smaller pieces (0.5 mm × 2 mm) and put into a 200 ml beaker and 20 ml of Aqua Regia (mixture of HCl and HNO<sub>3</sub> in the ratio of 3:1) was added and digested by heating the beaker containing the glass fibre filter (GFF) and 20 ml aqua regia on a heating mantle at 70 °C for 2 hours before digestion is complete. The digested samples were analysed for Pb, Cd, Cr, Ni, Fe and Cu, using Shimadzu Atomic Absorption Spectrophotometer (SHIMADZU-GFA 7000A), a single beam type. Air-acetylene flame and hollow cathode lamps with background correction were used for the instrumental analysis and the blank content duly subtracted from the analysis. The alkali and alkali-earth metals (Na, K, Mg and Ca) were analyzed using Sherwood Model 410 Flame Photometer.

## RESULTS AND DISCUSSION

The PM<sub>2.5</sub> levels obtained ranged from 14.00 to 32.67 µg/m<sup>3</sup> during wet season and 18.67 to 34.67 µg/m<sup>3</sup> during dry season. Variation in anthropogenic activities in these locations could be a major contributing factor to the observed differences in particulate matter levels in the various locations.

95 **Table 2. PM<sub>2.5</sub> Concentration (µg/m<sup>3</sup>) in the different Sampling Locations for Wet Season**

|      | LOCATION 1 | LOCATION 2 | LOCATION 3 | LOCATION 4 | LOCATION 5 | CONTROL    |
|------|------------|------------|------------|------------|------------|------------|
| DAY1 | 30         | 20         | 22         | 23         | 23         | 10         |
| DAY2 | 33         | 12         | 14         | 23         | 25         | 15         |
| DAY3 | 35         | 18         | 19         | 19         | 22         | 17         |
| MEAN | 32.67±5.03 | 16.67±4.16 | 18.33±4.04 | 21.67±2.31 | 23.33±1.53 | 14.00±3.61 |

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97 **Table 3. PM<sub>2.5</sub> Concentration (µg/m<sup>3</sup>) in the different Sampling Locations for Dry Season**

|       | LOCATION 1 | LOCATION 2 | LOCATION 3 | LOCATION 4 | LOCATION 5 | CONTROL    |
|-------|------------|------------|------------|------------|------------|------------|
| DAY I | 33         | 25         | 27         | 29         | 28         | 18         |
| DAY 2 | 35         | 19         | 16         | 27         | 30         | 17         |
| DAY 3 | 36         | 21         | 23         | 21         | 25         | 21         |
| MEAN  | 34.67±1.53 | 21.67±3.06 | 22.00±5.57 | 25.67±4.16 | 27.67±2.52 | 18.67±2.08 |

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99 Trace elements especially heavy metals are significant components of PM<sub>2.5</sub> in industrial  
100 environments. These elements are of particular concern due to their persistence in the  
101 environmental media and their human toxicity. In particular, non-biodegradability of heavy  
102 metals leads to their accumulation in the environment.

103 **Table 4. Concentrations of the Heavy Metals in PM<sub>2.5</sub> ( µg/m<sup>3</sup>) During Wet Season**

| SAMPLES | Pb        | Cd        | Ni  | Fe        | Cu  | Cr        |
|---------|-----------|-----------|-----|-----------|-----|-----------|
| LTN1    | 0.89±0.10 | NDL       | NDL | 0.75±0.20 | NDL | 0.47±0.19 |
| LTN2    | 0.85±0.16 | 0.85±0.18 | NDL | 0.47±0.06 | NDL | 0.38±0.13 |
| LTN3    | 0.36±0.13 | 0.34±0.06 | NDL | 0.20±0.12 | NDL | NDL       |
| LTN4    | 0.35±0.05 | 0.44±0.25 | NDL | 0.59±0.22 | NDL | 0.54±0.15 |
| LTN5    | 0.34±0.12 | NDL       | NDL | 0.54±0.01 | NDL | NDL       |
| CONTROL | NDL       | NDL       | NDL | NDL       | NDL | NDL       |

104 LTN1, 2, 3, 4 and 5 represent different sampling locations

105 NDL= Not within detection limit of the instrument used

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**Table 5. Concentrations of the Heavy Metals in PM<sub>2.5</sub> (µg/m<sup>3</sup>) During Dry Season**

| SAMPLES | Pb        | Cd        | Ni        | Fe        | Cu        | Cr        |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| LTN1    | 0.91±0.07 | 0.21±0.02 | 0.11±0.01 | 0.87±0.19 | 0.11±0.02 | 0.51±0.19 |
| LTN2    | 0.88±0.11 | 0.93±0.15 | 0.19±0.02 | 0.61±0.16 | 0.19±0.03 | 0.46±0.12 |
| LTN3    | 0.56±0.23 | 0.50±0.19 | 0.13±0.01 | 0.33±0.08 | 0.11±0.01 | 0.11±0.01 |
| LTN4    | 0.51±0.25 | 0.54±0.19 | 0.22±0.02 | 0.69±0.18 | 0.18±0.03 | 0.60±0.12 |
| LTN5    | 0.55±0.23 | 0.16±0.05 | 0.13±0.02 | 0.64±0.14 | 0.16±0.04 | 0.12±0.02 |
| CONTROL | NDL       | NDL       | NDL       | NDL       | NDL       | NDL       |

The elemental concentration of PM<sub>2.5</sub> in the different locations for both wet and dry seasons was depicted on Tables 4 and 5 respectively. Pb was found to be more in location 1 followed by Fe and then Cr. This may be as a result of the high vehicular activity and industrial emission in that area. The use of Pb containing anti knocking gasoline additives played a dominant role in the buildup of atmospheric Pb levels. The presence of paint and stainless steel industries in the study area added to the elevated levels of Pb, Fe and Cr observed. The concentration of Pb and Cd was higher in location 2 and 3 followed by Fe and then Cr. This may be as a result of high vehicular activities and industrial fume discharge in those areas. Comparing locations 1 and 2 it was observed that the concentrations of Pb in both locations are very close. This implies that the activities resulting in Pb emission in location 1 are almost the same to that of location 2. The concentration of Pb in locations 3, 4 and 5 are within the same range while the concentration of Fe in locations 4 and 5 are also close. In location 4, the concentration of Fe is higher followed by Cr, Cd and then Pb. This could however be due to reason(s) earlier referred to. In location 5 with Fe being the dominant metal present is an indication that fumes were emitted from several units such as sinter/pellet plant and blast furnace in iron and steel industries present in that area. The concentrations of all the heavy metals in the control site for both wet and dry seasons were below detection limit. This suggests that there are no activities taking place in that location that involves the emission of particulate matter with heavy metals contamination.

**Table 6. Concentration of the Light Metals in PM<sub>2.5</sub> (µg/m<sup>3</sup>) During Wet Season**

| SAMPLE  | Na           | K            | Mg           | Ca           |
|---------|--------------|--------------|--------------|--------------|
| LTN1    | 300.80±64.11 | 108.43±16.03 | 164.39±80.14 | 108.43±73.70 |
| LTN2    | 322.81±42.54 | 143.86±77.59 | 133.33±48.62 | 63.16±45.88  |
| LTN3    | 539.22±42.45 | 213.59±21.87 | 164.57±53.90 | 154.41±42.42 |
| LTN4    | 578.48±60.17 | 158.73±69.39 | 229.28±60.17 | 363.32±16.16 |
| LTN5    | 653.32±64.10 | 270.46±74.01 | 221.29±58.67 | 347.73±65.81 |
| CONTROL | 136.41±72.70 | 101.43±59.67 | 332.28±57.79 | 682.02±58.42 |

**Table 7. Concentration of the Light Metals in PM<sub>2.5</sub> (in µg/m<sup>3</sup>) During Dry Season**

| SAMPLE  | Na           | K            | Mg           | Ca           |
|---------|--------------|--------------|--------------|--------------|
| LTN1    | 309.55±55.43 | 117.17±19.25 | 169.64±71.91 | 113.68±61.69 |
| LTN2    | 329.82±36.87 | 149.12±62.24 | 138.60±43.87 | 68.42±38.10  |
| LTN3    | 546.22±32.55 | 220.59±21.01 | 173.32±44.44 | 110.29±76.54 |
| LTN4    | 584.49±47.47 | 163.22±66.74 | 214.22±42.00 | 366.84±17.60 |
| LTN5    | 662.10±49.61 | 275.73±66.45 | 224.80±50.61 | 351.25±52.33 |
| CONTROL | 139.98±58.89 | 106.74±53.71 | 337.71±52.06 | 689.42±58.95 |

Tables 6 and 7 show the concentration of the light metals obtained from the different locations for both wet and dry seasons. It was observed that the concentration of Na in locations 1 to 5 for both seasons was more than the other elements. This could be traced to both crustal and sea spray and also it is an indication that the concentration of Na is dependent on both natural and anthropogenic sources. However, the control site has the highest levels of Ca. The high concentration of Ca in the control site is attributed to local construction activities in the area, where concrete was being mixed in the vicinity of the site as at the time of sampling. Preparation of road surfaces for new pavements also produced an increase in the observed calcium concentrations. The high concentration of elements typical of marine aerosol (Na and K) and soil-related (Ca and Mg), may be as a result of persistent sea salt breeze, road construction, agricultural, cooking and frying activities in those areas. These light metals are easily introduced into the particulate matter and can be transported through a long distance as a result of their smaller molecular weight as compared to the heavy metals.

## ENRICHMENT FACTOR

In order to determine the different pollution sources and trace down the extent of anthropogenic contribution, a fundamental study of the chemical composition is necessary (Okuo and Ndiokwere, 2005). Soil and anthropogenic sources were delineated using computations of enrichment factor (EF). EF is widely used to identify the anthropogenic source of metallic elements and it is generally applied to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material or Sea salt (Gao *et al.*, 2002). EFs were calculated to discriminate the crustal source from the anthropogenic sources of atmospheric heavy and light metals. (Petaloti *et al.*, 2006; Yongming *et al.*, 2006; Ayrault *et al.*, 2010).

The Enrichment Factor (EF) is commonly defined by the following relation:

$$EF = \frac{\left(\frac{E}{R}\right)_{sample}}{\left(\frac{E}{R}\right)_{crustal}} \quad (1)$$

Where E represents considered element, and R is the reference element for crustal material.

$\left(\frac{E}{R}\right)_{sample}$  is the concentration ratio of E to R in the particulate matter sample, and

$\left(\frac{E}{R}\right)_{crustal}$  is the mean concentration ratio of E to R in the crust.

The EF values close to unity indicate crustal origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas  $EF > 1.0$  indicates that the element is of anthropogenic origin (Huang *et al.*, 2010). Five contamination categories are recognized and interpreted as suggested by Birth (2003). In this study Fe was used as a reference element to determine the EF with respect to crustal abundance.

173 **Table 8. Enrichment Factor Analysis during Wet Season**

| Elements | location1 | location 2 | location 3 | location4 | location 5 | Control |
|----------|-----------|------------|------------|-----------|------------|---------|
| Pb       | 2799.07   | 4244.84    | 4305.96    | 1407.47   | 1492.13    | -       |
| Cd       | 0.00      | 282965.17  | 264982.46  | 117526.10 | 0.00       | -       |
| Fe       | 1.00      | 1.00       | 1.00       | 1.00      | 1.00       | -       |
| Cr       | 324.20    | 426.60     | 0.00       | 486.53    | 0.00       | -       |
| Na       | 1996.67   | 3375.62    | 13283.63   | 4850.43   | 5900.00    | -       |
| K        | 255.85    | 542.92     | 1898.96    | 481.02    | 881.49     | -       |
| Mg       | 687.88    | 892.34     | 2594.62    | 1232.13   | 1278.97    | -       |
| Ca       | 307.94    | 286.89     | 524.57     | 1325.19   | 1364.12    | -       |

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175 **Table 9. Enrichment Factor Analysis during Dry Season**

| Elements | Location1 | Location 2 | Location3 | Location4 | Location 5 | Control |
|----------|-----------|------------|-----------|-----------|------------|---------|
| Pb       | 2468.56   | 3427.78    | 7712.58   | 1963.45   | 2005.36    | -       |
| Cd       | 38389.33  | 242121.04  | 463890.03 | 90128.22  | 39548.27   | -       |
| Ni       | 95.90     | 237.50     | 556.11    | 238.03    | 155.57     | -       |
| Fe       | 1.00      | 1.00       | 1.00      | 1.00      | 1.00       | -       |
| Cu       | 130.06    | 326.46     | 670.42    | 285.64    | 269.39     | -       |
| Cr       | 303.13    | 394.49     | 335.21    | 456.85    | 100.30     | -       |
| Na       | 1740.50   | 2663.78    | 15814.43  | 4147.78   | 5064.44    | -       |
| K        | 237.77    | 434.66     | 2304.94   | 418.03    | 761.17     | -       |
| Mg       | 610.45    | 716.39     | 3211.55   | 972.92    | 1100.47    | -       |
| Ca       | 277.65    | 240.04     | 1387.13   | 1130.83   | 1167.07    | -       |

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Tables 8 and 9 show that the majority of these metals in the air came from the emissions of non crustal sources. Extremely severe enrichment of Pb, Cd, Cr, Cu, Ni, Na, K, Mg, and Ca is an indication that the atmosphere in the various sampling locations were heavily polluted by these metals and that the pollution is more of anthropogenic source than the crustal origin. The high enrichment factor of Na, K, Ca and Mg, could be as a result of suspension from road dust and the pronounced effect of sea breeze in the region. The high enrichment of Pb, Cd, Cu, Ni and Cr could be due to vehicular and industrial emissions, break pad and tyre wears, and municipal waste incineration in the area. In particular, Cd in PM<sub>2.5</sub> had extremely high EF values of 117526.10 – 282965.17 and 38389.33 - 463890.03 for both wet and dry season respectively indicating extreme contamination by anthropogenic Cd sources. High Cd concentration in these locations may be associated with industrial emissions especially from steel production units because a large amount of Cd plated steel scraps are recycled in these areas. Other possible sources include open burning of municipal waste containing Cd batteries and plastics containing Cd pigments, vehicular emissions including tyre abrasions and cigarette smoking. In addition locations 1 to 5 are industrial areas where a lot of anthropogenic activities leading to industrial fume emission, vehicular and automobile exhaust emission, municipal waste incineration, cooking, frying, biomass/wood burning and agricultural practices etc, are prevalent. The high enrichment factor of the light metals also suggests that the pollution source is not only of natural origin but a combination of natural and anthropogenic origin.

## **PRINCIPAL COMPONENT ANALYSIS**

Source identification analysis of particulate matter was performed based on the principal component analysis method which is widely used to factorize the input concentration data of different species having a linear relationship between total mass concentration and the individual concentrations, (Artkinson *et al.*, 2010; Stanek *et al.*, 2011). Principal Component Analysis (PCA) with varimax rotation was used in order to identify the possible sources contributing to heavy and light metals in ambient air particles in the study areas for wet and dry seasons. Factors with eigen values greater than 1.0 were used to identify major elements associated with different sources. The factor loadings from PCA analysis at the sampling sites for PM<sub>2.5</sub> particles were identified. From the PCA, two factors were extracted which explained 78.74 % and three factors which explained 81.53 % of the total variance for both wet and dry seasons respectively. In addition, those metals with high positive loads further indicate that the degree of pollution with

208 these metals was affected not only by the intrinsic properties of fine particulate matter but also,  
 209 more importantly, by human activities.

## 210 SPATIAL VARIATION

211 Spatial variation in PM<sub>2.5</sub> was investigated for distribution over the various locations of chemical  
 212 constituents.

213 **Table 10. Spatial Variation During Wet Season**

|    | Location1                  | Location 2                 | Location 3                 | Location 4                 | Location 5                 | Control Site              | P     |
|----|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------|-------|
| Pb | 0.89±0.10 <sup>a</sup>     | 0.85±0.16 <sup>a</sup>     | 0.36±0.13 <sup>b</sup>     | 0.35±0.05 <sup>b</sup>     | 0.34±0.12 <sup>b</sup>     | ND                        | 0.000 |
| Cd | ND                         | 0.85±0.18 <sup>a</sup>     | 0.34±0.06 <sup>b</sup>     | 0.44±0.25 <sup>ab</sup>    | ND                         | ND                        | 0.030 |
| Fe | 0.75±0.20 <sup>a</sup>     | 0.47±0.06 <sup>ab</sup>    | 0.20±0.12 <sup>b</sup>     | 0.59±0.22 <sup>ab</sup>    | 0.54±0.14 <sup>ab</sup>    | ND                        | 0.019 |
| Cr | 0.47±0.19 <sup>a</sup>     | 0.38±0.13 <sup>a</sup>     | ND                         | 0.54±0.15 <sup>a</sup>     | ND                         | ND                        | 0.505 |
| Na | 300.80±64.11 <sup>a</sup>  | 322.81±42.54 <sup>a</sup>  | 539.22±42.45 <sup>b</sup>  | 578.48±60.17 <sup>b</sup>  | 653.32±64.10 <sup>b</sup>  | 136.41±72.70 <sup>a</sup> | 0.000 |
| K  | 108.43±16.03 <sup>a</sup>  | 143.86±77.59 <sup>ab</sup> | 213.59±21.87 <sup>ab</sup> | 158.73±69.39 <sup>ab</sup> | 270.46±74.01 <sup>b</sup>  | 101.43±59.67 <sup>a</sup> | 0.029 |
| Mg | 164.39±80.14 <sup>ab</sup> | 133.33±48.62 <sup>b</sup>  | 164.57±53.90 <sup>ab</sup> | 229.28±60.17 <sup>ab</sup> | 221.29±58.67 <sup>ab</sup> | 332.28±57.79 <sup>b</sup> | 0.020 |
| Ca | 108.43±73.70 <sup>a</sup>  | 163.16±45.88 <sup>a</sup>  | 154.41±42.45 <sup>a</sup>  | 363.32±16.16 <sup>b</sup>  | 347.73±65.81 <sup>b</sup>  | 682.06±58.42 <sup>c</sup> | 0.000 |

214 Means with different superscript are statistically significant at p<0.05

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216 **Table 11. Spatial Variation During Dry Season**

|    | Location1                  | Location 2                 | Location 3                 | Location 4                 | Station 5                 | Control Site              | P     |
|----|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------|---------------------------|-------|
| Pb | 0.91±0.07 <sup>a</sup>     | 0.88±0.11 <sup>a</sup>     | 0.55±0.23 <sup>bc</sup>    | 0.58±0.25 <sup>bc</sup>    | 0.55±0.24 <sup>c</sup>    | ND                        | 0.003 |
| Cd | 0.21 ±0.02 <sup>ab</sup>   | 0.94±0.15 <sup>c</sup>     | 0.50±0.19 <sup>b</sup>     | 0.40±0.19 <sup>ab</sup>    | 0.16±0.05 <sup>a</sup>    | ND                        | 0.000 |
| Ni | 0.11±0.01 <sup>a</sup>     | 0.19±0.02 <sup>b</sup>     | 0.13±0.01 <sup>a</sup>     | 0.22±0.02 <sup>b</sup>     | 0.13±0.02 <sup>a</sup>    | ND                        | 0.000 |
| Fe | 0.87±0.19 <sup>a</sup>     | 0.61±0.16 <sup>b</sup>     | 0.17±0.08 <sup>c</sup>     | 0.69±0.18 <sup>ab</sup>    | 0.64±0.14 <sup>ab</sup>   | ND                        | 0.004 |
| Cu | 0.11 ±0.02 <sup>a</sup>    | 0.19±0.03 <sup>b</sup>     | 0.11±0.01 <sup>a</sup>     | 0.19±0.03 <sup>b</sup>     | 0.17±0.04 <sup>b</sup>    | ND                        | 0.000 |
| Cr | 0.51 ±0.19 <sup>a</sup>    | 0.46±0.12 <sup>a</sup>     | 0.11±0.01 <sup>b</sup>     | 0.60±0.12 <sup>a</sup>     | 0.12±0.02 <sup>b</sup>    | ND                        | 0.000 |
| Na | 309.55±55.43 <sup>a</sup>  | 329.82±36.87 <sup>a</sup>  | 546.22±32.55 <sup>b</sup>  | 584.49±47.47 <sup>bc</sup> | 662.10±49.61 <sup>c</sup> | 539.98±58.89 <sup>b</sup> | 0.000 |
| K  | 117.17±19.25 <sup>ab</sup> | 149.12±62.24 <sup>ab</sup> | 220.59±21.01 <sup>bc</sup> | 163.22±66.75 <sup>ab</sup> | 275.73±66.45 <sup>c</sup> | 106.74±53.71 <sup>a</sup> | 0.000 |
| Mg | 169.64±71.91 <sup>a</sup>  | 138.60±43.87 <sup>a</sup>  | 173.32±44.44 <sup>a</sup>  | 214.22±42.00 <sup>a</sup>  | 224.80±50.61 <sup>a</sup> | 337.71±52.06 <sup>b</sup> | 0.000 |
| Ca | 113.68±61.69 <sup>a</sup>  | 98.42±38.10 <sup>a</sup>   | 110.29±76.54 <sup>a</sup>  | 366.84±17.60 <sup>b</sup>  | 351.25±52.33 <sup>b</sup> | 689.42±58.95 <sup>c</sup> | 0.000 |

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218 Means with different superscript are statistically significant at p<0.05

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NOTE: The superscripts a,b,c,ab and bc denote that the mean values are statistically NOT significant with the same superscript and statistically significant with different superscripts.

Tables 10 and 11 describe the spatial variation for both wet and dry seasons respectively. From Table 10, Pb, Cd, Fe, Na, K, Mg, and Ca showed significant spatial variation with P-value  $\leq 0.05$  while Cr showed no significant spatial variation ( $P \geq 0.05$ ). Table 11, showed that there are significant variations for Pb, Cd, Ni, Fe, Cu, Cr, Na, K, Mg and Ca with P-value  $\leq 0.05$ .

## CORRELATION MATRIX

**Table 12. Correlation Matrix Analysis during Wet Season**

|    | Pb       | Cd      | Fe     | Cr     | Na     | K      | Mg      | Ca |
|----|----------|---------|--------|--------|--------|--------|---------|----|
| Pb | 1        |         |        |        |        |        |         |    |
| Cd | 0.798**  | 1       |        |        |        |        |         |    |
| Fe | 0.498    | 0.213   | 1      |        |        |        |         |    |
| Cr | -0.300   | -0.563  | 0.014  | 1      |        |        |         |    |
| Na | -0.828** | -0.669* | -0.171 | 0.122  | 1      |        |         |    |
| K  | -0.474   | -0.058  | -0.256 | -0.109 | 0.711* | 1      |         |    |
| Mg | -0.498   | -0.618  | 0.228  | -0.055 | -0.251 | -0.222 | 1       |    |
| Ca | -0.606*  | -0.304  | 0.217  | 0.457  | -0.275 | -0.150 | 0.777** | 1  |

\*\* . Correlation is significant at the 0.01 level (2-tailed).

\* . Correlation is significant at the 0.05 level (2-tailed).

**Table 13. Correlation Matrix Analysis During Dry Season**

|    | Pb       | Cd      | Ni      | Fe     | Cu     | Cr       | Na       | K      | Mg      | Ca |
|----|----------|---------|---------|--------|--------|----------|----------|--------|---------|----|
| Pb | 1        |         |         |        |        |          |          |        |         |    |
| Cd | 0.296    | 1       |         |        |        |          |          |        |         |    |
| Ni | 0.41     | 0.366   | 1       |        |        |          |          |        |         |    |
| Fe | 0.515**  | -0.242  | 0.187   | 1      |        |          |          |        |         |    |
| Cu | -0.043   | 0.256   | 0.704** | 0.298  | 1      |          |          |        |         |    |
| Cr | 0.061    | 0.028   | 0.569*  | 0.472* | 0.377  | 1        |          |        |         |    |
| Na | -0.589** | -0.489* | 0.094   | -0.242 | 0.083  | -0.390   | 1        |        |         |    |
| K  | -0.315   | -0.192  | -0.152  | -0.293 | -0.252 | -0.528** | -0.710** | 1      |         |    |
| Mg | -0.387*  | -0.487* | -0.097  | -0.138 | -0.123 | -0.310   | -0.290   | -0.204 | 1       |    |
| Ca | -0.401*  | -0.488* | 0.253   | 0.1541 | 0.340  | 0.045    | -0.270   | -0.137 | 0.783** | 1  |

\*\* Correlation is significant at the 0.01 level (2-tailed).

\*. Correlation is significant at the 0.05 level (2-tailed).

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234 The association pattern among the heavy and light metals can be displayed by a correlation  
 235 matrix of these metals. The correlation matrix is constructed based on the Pearson correlation  
 236 coefficients obtained from a correlation analysis of related components. A correlation analysis  
 237 was performed between all variables for the different locations to see if some of the metals are  
 238 interrelated with each other as shown on Tables 12 and 13. Both positive and negative  
 239 correlations were observed for wet and dry seasons. A correlation coefficient of 0.05 was taken  
 240 as significant. Some of these elements were highly correlated positively in both seasons. The  
 241 negative correlation observed suggests that the changes in the level of one of these metals,  
 242 affects the concentration of the other in the same location and the positive correlation indicates  
 243 that there is no significant influence of one metal on the other.

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## Seasonal Variation of Elemental Composition

Seasonal variation for the elemental concentration of source contribution to the PM<sub>2.5</sub> for both wet and dry seasons was carried out using ANOVA as shown on Table 14. The mean concentration of some of the elements for both seasons is statistically significant at P< 0.05. The seasonal variation of heavy metals in aerosols could be affected by the sources, transportation, and meteorological conditions. It was observed that the mean values obtained during dry season were higher than those obtained during wet season which may be attributed to meteorological factors like humidity, temperature, cloudy weather and rainfall. Thus the concentrations of these metals are higher at lower humidity and elevated temperature.

**Table 14. Mean comparison of heavy and light metals based on Season**

|            |    | Wet          | Dry          | P     |
|------------|----|--------------|--------------|-------|
| Location 1 | Pb | 0.89±0.10    | 0.94±0.03    | 0.489 |
|            | Cd | -            | 0.21±0.02    |       |
|            | Ni | -            | 0.11±0.01    |       |
|            | Fe | 0.75±0.20    | 1.00±0.06    |       |
|            | Cu | -            | 0.11±0.02    | 0.110 |
|            | Cr | 0.47±0.19    | 0.55±0.22    |       |
|            | Na | 300.80±64.11 | 318.29±57.79 |       |
|            | K  | 108.43±16.03 | 125.92±20.99 |       |
|            | Mg | 164.39±80.14 | 174.89±80.14 | 0.880 |
|            | Ca | 108.43±73.70 | 118.92±63.25 |       |
| Location 2 | Pb | 0.85±0.16    | 0.92±0.03    | 0.469 |
|            | Cd | 0.85±0.18    | 1.03±0.02    | 0.154 |
|            | Ni | -            | 0.19±0.02    | 0.003 |
|            | Fe | 0.47±0.06    | 0.75±0.04    |       |
|            | Cu | -            | 0.19±0.03    |       |
|            | Cr | 0.38±0.13    | 0.53±0.06    |       |
|            | Na | 322.81±42.54 | 336.84±37.95 | 0.692 |
|            | K  | 143.86±77.59 | 154.39±59.86 | 0.861 |
|            | Mg | 133.33±48.62 | 143.86±48.62 | 0.804 |
|            | Ca | 63.16±45.88  | 73.68±37.95  |       |
| Location 3 | Pb | 0.36±0.13    | 0.75±0.07    | 0.012 |
|            | Cd | 0.34±0.06    | 0.67±0.05    | 0.002 |
|            | Ni | -            | 0.13±0.01    | 0.443 |
|            | Fe | 0.20±0.12    | 0.14±0.02    |       |
|            | Cu | -            | 0.11±0.01    |       |
|            | Cr | -            | 0.11±0.01    |       |

|              |    |              |              |       |
|--------------|----|--------------|--------------|-------|
| Location 4   | Na | 539.22±42.45 | 553.22±26.43 | 0.653 |
|              | K  | 213.59±21.87 | 227.59±21.87 | 0.477 |
|              | Mg | 164.57±53.90 | 182.07±42.45 | 0.681 |
|              | Ca | 49.02±42.45  | 171.57±39.77 | 0.022 |
|              | Pb | 0.35±0.05    | 0.80±0.03    | 0.000 |
|              | Cd | 0.44±0.25    | 0.36±0.14    | 0.652 |
|              | Ni | -            | 0.22±0.02    |       |
|              | Fe | 0.59±0.22    | 0.80±0.03    | 0.169 |
|              | Cu | -            | 0.19±0.03    |       |
|              | Cr | 0.54±0.15    | 0.66±0.07    | 0.272 |
|              | Na | 578.48±60.17 | 590.50±43.64 | 0.793 |
| Location 5   | K  | 158.73±69.39 | 167.71±79.14 | 0.890 |
|              | Mg | 229.28±60.17 | 199.16±10.48 | 0.441 |
|              | Ca | 363.32±16.16 | 370.37±21.82 | 0.676 |
|              | Pb | 0.34±0.12    | 0.75±0.07    | 0.008 |
|              | Cd | -            | 0.16±0.05    |       |
|              | Ni | -            | 0.13±0.02    |       |
|              | Fe | 0.54±0.14    | 0.74±0.05    | 0.081 |
|              | Cu | -            | 0.17±0.04    |       |
|              | Cr | -            | 0.12±0.02    |       |
|              | Na | 653.32±64.10 | 670.88±42.59 | 0.713 |
|              | K  | 270.46±74.01 | 281.00±74.01 | 0.870 |
| Control Site | Mg | 221.29±58.67 | 228.31±54.07 | 0.886 |
|              | Ca | 347.73±65.81 | 354.76±49.80 | 0.890 |
|              | Na | 136.41±72.70 | 143.56±57.85 | 0.900 |
|              | K  | 101.43±59.67 | 112.04±59.73 | 0.838 |
|              | Mg | 332.28±57.79 | 343.14±57.85 | 0.829 |
|              | Ca | 682.06±58.42 | 696.78±71.50 | 0.796 |

## CONCLUSION

Fine particulate matter (PM<sub>2.5</sub>) is mainly generated through natural and anthropogenic sources. The PM<sub>2.5</sub> levels obtained ranged from 14.00 to 32.67 µg/m<sup>3</sup> during wet season and 18.67 to 34.67 µg/m<sup>3</sup> during dry season and the samples were analysed and trace elements such as Pb, Cd, Cr, Ni, Fe, Cu, Na, K, Mg and Ca were determined. The enrichment factor analysis showed very high enrichment for the elements; Pb, Cd, Cr, Cu, Ni, Na, K, Mg, and Ca in the fine fraction (PM<sub>2.5</sub>). Principal component analysis explained three common contributing sources of fine particulates (PM<sub>2.5</sub>) such as entrained soil, sea salt and combustion. Spatial variation revealed that the mean concentration of some of the elements in the various locations showed significant difference at P<0.05. Correlation matrix justified that some of the elements were strongly

correlated while some were not. Seasonal variation for the elemental concentration of the PM<sub>2.5</sub> for both seasons shows the mean values for some of the elements were statistically significant at P<0.05 for both seasons.

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