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Assessment of Heavy Metal Concentrations in Particulate Matter (PM10) in the Ambient Air of Selected Roadsides in the Accra Metropolis of Ghana, West Africa.

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ABSTRACT

This study assessed the concentrations of heavy metals in particulate matter (PM10) in the ambient air at four roadside locations (Weija, Mallam, Kaneshie First Light and Graphic Road) in the Accra Metropolis of Ghana, West Africa. The Mini Vol. air sampler was used to collect the PM10 particles from the ambient air. PM10 concentrations ranged from 219.20 - 236.00 μg/m^3, 189.80 - 232.20 μg/m^3, 150.70 - 182.70 μg/m^3 and 158.70 - 213.90 μg/m^3 for Weija, Mallam, Kaneshie First Light and Graphic Road respectively. The level of PM10 pollution was very high in the ambient air across the four sampling sites with mean concentrations exceeding WHO and Ghana EPA guidelines. A flame atomic absorption spectrometry was used to investigate the heavy metals: Cu, Mn, Zn, Pb and Cd in the particulate matter. Mean metal concentrations of Cu, Mn, Zn, Pb and Cd across the four sampling sites ranged from 0.15 – 0.63 ng/m^3, 0.86 - 7.22 ng/m^3, 1.79 – 7.34 ng/m^3), 0.08 - 0.69 ng/m^3, and 0.01 - 0.19 ng/m^3 respectively. There was no significant variation between metal concentrations at the various sampling sites except for cadmium which was significantly different. This may probably be due to the burning of cadmium containing electronic-waste close to the sampling site.

Introduction

In cities of most developing world, rapid economic growth together with ineffective transportation system is causing a rise in vehicular ownership and subsequent vehicular traffic, which is a main source of emissions of particulate matter pollution (Kinney *et al.* 2011). In Ghana for instance, the number of vehicles registered increased from 52,881 in the year 2000 to 1,073,206 in the year 2012, the number of registered vehicles in Accra however increased from 23,021 in the year 2000 to 425,804 in 2012: a percentage increase of 1749.63% (DVLA, 2013). This increase in vehicular fleet coupled with majority of the population depending on road transport has serious economic, social and environmental

implications especially for those who live and work along roadways. The composition of inhalable particulate matter is complex and differs depending on the source and location.

In Accra, Ghana, for instance, the Environmental Protection Agency (EPA) established air quality monitoring sites at road sides, residential and commercial areas in Accra for the monitoring of pollutants like particulate matter (PM10), lead, manganese, carbon monoxide, ozone amongst others. This monitoring network was the result of collaborative support from the United States Environmental Protection Agency (USEPA), United States Agency for International Development (USAID) and United Nations Environment Programme (UNEP) in 2005 to develop air monitoring network in two sub-Sahara Africa cities: Accra, Ghana and Dar Es Salaam, Tanzania. Reports from the monitoring programme in Accra revealed high levels of particulate matter in the city particularly at roadside locations (Nerquaye-Tetteh 2009).

Particulate air pollution is a major issue in Accra especially along roadsides with heavy traffic. The concentrations of particulate matter in Accra's ambient air has been investigated and found to be very high at roadside locations. (Nerquaye- Tetteh, 2009: Dionisio *et al.* 2010). The occurrence of toxic metals such as Pb, Zn, Cu, and Ni in inhalable particulates may contribute to substantial health effects (Safo-Adu *et al.* 2014). Some of these heavy metals in particulates are strong triggers of carcinogenesis, teratogenesis and mutagenesis (Awan *et al.* 2011). Due to the occurrence of particulate matter related deaths, attention has focused on the routine monitoring of particulate matter in most cities (Yang *et al.* 2013).

The adverse health effects caused by particles have often been associated with particles of size fraction less than or equal to 10μm in diameter, or to the chemical composition. The chemical composition of fine particulate matter can reveal the hazards of this air pollutant for human health which is very important concerning the number of people at risk and the continuous nature of exposure (Talebi and Tavakoli-Ghinani 2008).

Since the occurrence of toxic heavy metals in PM10 is assumed

to contribute to substantial health effects (Talebi and Tavakoli-Ghinani 2008), it is of particular interest to investigate the levels of heavy metals such as cadmium, lead, copper, zinc and manganese in particulate matter in the ambient air of selected roadside locations (Weija, Mallam, Kaneshie First Light and Graphic Road) in the Accra Metropolis of Ghana, West Africa.

Measurement of Pm10

Air was sampled at four roadsides (Weija, Mallam, Kaneshie First Light and Graphic Road) for particulate matter (PM_{10}) using MiniVol Tactical Air Samplers. Quartz filter papers of diameter 47 mm which have high purity and efficiency were used to trap the particles. Prior to and after sampling, the quartz filter papers on which the particles were trapped were stabilized in a desiccator for a minimum of twenty-four (24) hours, so as to get rid of any moisture in them. The quartz filter papers were weighed before and after sampling, and the difference in weight (W2-W1) was used to calculate the concentrations of the particulate matter in $\mu g/m^3$ using the USEPA method for calculating PM_{10} (USEPA, 1999).

$$(PM_{10})\mu g/m^3 = \frac{(W_2 - W_1)}{Q \times T} \times 10^6 \times 10^3 \qquad \text{equation 1}$$

Where:
W_1 = initial weight of clean filter paper (g)
W_2 = final weight of exposed filter paper (g)
Q = average sampling rate (flow rate), m^3/min
T = Time (hours).
10^6 = conversion from g to $\mu g/m^3$
10^3 = conversion of l to m^3

Flow rates of the miniVol samplers were set at 5 l/min. Sampling was done every six days for a twenty-four-hour period on each monitoring day from October to November**.** A total of twenty-seven (27) samples were collected for determination of PM_{10} concentrations during the sampling period. Analyses for heavy metals were carried out at the Metal Laboratory of the Water Research Institute in Accra.

Extraction and Determination of Heavy Metals in PM_{10}

Concentrations of heavy metals in PM_{10} were determined using an Atomic Absorption spectrophotometer (model AA-200 Series Agilent Technologies). The USEPA method IO-3.1 (USEPA 1999) was used for the extraction process.

The PM_{10} loaded filters were extracted in an acid mixture to remove heavy metals. This acid mixture was made of hydrochloric acid and nitric acid in a ratio of 3:1. Each filter paper was carefully placed in Teflon tubes and 10 ml of the acid mixture was slowly added to cover the samples. The Teflon tubes were closed and placed in stainless steel bombs which were in turn placed on a hot plate and heated at 150°C for six (6) hours. The digested samples were allowed to cool to room temperature, filtered and transferred into polypropylene graduated tubes. The Teflon tubes were rinsed three times with deionised water, filtered and the content added to the digested sample in the polypropylene tubes. The resulting solution was diluted with deionized water to a 30 ml mark. This was then used for heavy metals analysis with the flame atomic absorption spectrophotometer (FAAS). An unexposed filter paper was prepared as a blank using the same method described for the exposed filter paper. The limit of detection of the FAAS for cadmium and copper were < 0.001 mg/l and < 0.010 mg/l respectively. Lead, zinc and manganese had limit of detection < 0.005 mg/l. The units of metal concentrations were converted from mg/l to $\mu g/m^3$ using the following equation:

$$\text{Metal Concentration } (\mu g/m^3) = \frac{(C_1 - C_2) \times V}{Wt} \times 10^{-6} \quad \text{equation 2}$$

Where:
C1 = metal concentration in solution of sample (mg/l)
C2 = metal concentration in solution of the blank filter (mg/l)
V = sample solution volume (ml)
Wt = weight of particles on quartz filter paper (g).
10-6 = conversion from grams (g) to microgram (µg).

Data Analysis

Analysis of Variance (ANOVA) was used to compare the Mean PM10 and metal values of the various sampling sites so as to determine whether they were significantly different or not. Normality test was carried out on the data collected in order to determine whether the distributions of the groups whose means were to be compared had normal distributions or not. The normality test proved the presence of outliers which were detected and removed. It is worth noting that these outliers were not bad values but came about as a result of conditions (e.g. burning of waste) around the sampling area which influenced the values. Also, in situations where the air sampler failed to sample for more than twenty (20) hours, the values were omitted in order to get accurate results. The outliers were not included in statistical analysis as these may affect the results. However, the reasons for getting such results were explained in the discussion part.

Results

PM_{10} Concentrations

The Fig 1 below shows the mean PM_{10} concentrations at the various sampling sites compared with guideline values from WHO and EPA-Ghana.

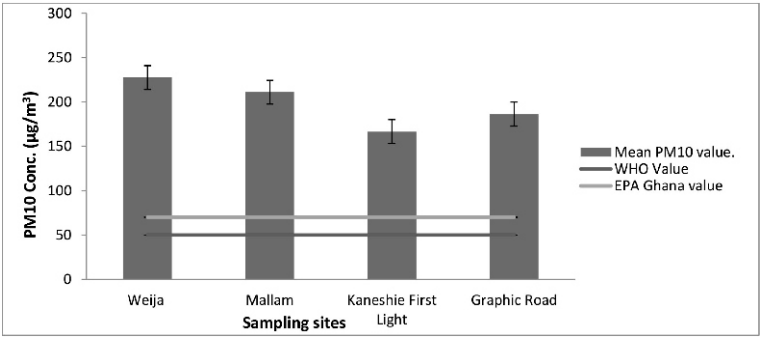

Fig 1: Mean PM_{10} Concentrations at the Sampling Sites

Pm_{10} values recorded at all four sampling sites exceeded the 24-hour guideline values of 50 µg/m^3 from WHO and 70 µg/m^3 from EPA-Ghana.

Weija recorded the highest mean PM_{10} concentrations (227.60 $\mu g/m^3$) followed by Mallam (211.00 $\mu g/m^3$), Graphic Road (186.25 $\mu g/m^3$) and Kaneshie First Light (166.67 $\mu g/m^3$).

Environmental Factors on PM_{10} Concentrations

The table below shows the daily PM_{10} concentrations measured at the various sampling sites with environmental factors such as burning and rainfall having an effect on PM_{10} values that are marked with asterisks.

Table 1: Daily PM_{10} concentrations at the sampling sites

SAMPLES	SAMPLING SITE			
	WEIJA Site 1	MALLAM Site 2	KANESHIE 1st LIGHT- Site 3	GRAPHIC RD. Site 4
Sample 1	250	236	153	236
Sample 2	97*	56*	56*	69*
Sample 3	208	264	222	217
Sample 4	236	1182*	153	-
Sample 5	236	139	139	111
Sample 6	208	222	208	181
Sample 7	708*	194	125	56*

* = values were not included in statistical analysis due to environmental effects of burning and rainfall on PM_{10} or sampling not lasting for 24hours.

Due to the environmental effect of rainfall, PM_{10} concentrations recorded across all four sampling sites for second sample were lower than those recorded on other days except for the sixth sample which also recorded a low PM_{10} value at Graphic Road. Also due to the effect of burning close to the sampling area, PM_{10} concentrations recorded at Mallam and Weija for the fourth and sixth samples respectively were far higher than those recorded for the other samples.

Without the influence of these environmental factors (rainfall and burning), PM_{10} concentrations ranged between 219.20-236.00 $\mu g/m^3$, 189.80-232.20 $\mu g/m^3$, 150.70-182.70 $\mu g/m^3$, 158.70-213.90

µg/m^3 for Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively.

Metal Concentrations at Various Sampling Sites

The concentrations of metals recorded at the various sampling sites were compared with guideline values from the CPCB, MassDEP, EPA-Ghana and WHO.

Table 2:
Lead (Pb) concentrations in ng/m^3 at the various sampling sites

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija-Site 1	0.14 - 0.23	0.18 ± 0.12	1000 ng/m^3 (24-hour average) CPCB, 2009 140 ng/m^3 (24-hour average) MassDEP, 1990
Mallam-Site 2	0.08 - 0.11	0.09 ± 0.04	
Kaneshie First Light-Site 3	0.19 - 0.39	0.29 ± 0.23	
Graphic Road-Site 4	0.23 - 0.69	0.47 ± 0.57	

Concentrations of lead ranged between 0.14 - 0.23 ng/m^3, 0.08 - 0.11 ng/m^3, 0.19 - 0.39 ng/m^3, 0.23 - 0.69 ng/m^3 at for Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively. The highest mean concentration of lead was recorded at Graphic Road-Site 4 (0.47ng/m^3) and the lowest mean at Mallam-Site 2 (0.09 ng/m^3). Lead values recorded at the various sampling sites were all below the Central Pollution Control Board (CPCB) and the Massachusetts Department of Environmental Protection (MassDEP) guideline value of 1000 ng/m^3 and 140 ng/m^3respectively.

Table 3:
Manganese (Mn) concentrations in ng/m^3 at the various sampling sites

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija-Site 1	2.09 - 3.55	2.82 ± 1.93	1000 ng/m^3 (24-hour average) EPA Ghana
Mallam-Site 2	0.86 - 1.23	1.05± 1.93	
Kaneshie First Light-Site 3	1.66 - 2.94	2.30 ± 1.69	
Graphic Road-Site 4	2.34 - 7.22	4.78 ± 5.45	

Concentrations of manganese ranged between 2.09 - 3.55 ng/m^3, 0.86 - 1.23 ng/m^3, 1.66 - 2.94 ng/m^3, 2.34 - 7.22 ng/m^3 at Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively. Graphic Road-Site 4 recorded the highest mean concentration (4.78 ng/m^3) whilst Mallam-Site 2 recorded the lowest mean concentration (1.05 ng/m^3). Manganese values recorded at the four sampling sites were all below the EPA Ghana guideline value of 1000 ng/m^3.

Table 4:
Zinc (Zn) concentrations in ng/m^3 at the various sampling sites

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija-Site 1	1.79 - 2.39	2.09 ± 0.79	100-500 ng/m3 (ambient levels at urban sites) WHO, 2003
Mallam-Site 2	1.87 - 4.03	2.95 ± 2.86	
Kaneshie First Light-Site 3	2.33 - 3.91	3.12 ± 2.09	
Graphic Road-Site 4	4.06 - 7.34	5.70 ± 3.67	

Zinc concentrations ranged between 1.79 - 2.39 ng/m^3, 1.87 – 4.03 ng/m^3, 2.33 – 3.91 ng/m^3 and 4.06 – 7.34 ng/m^3 at Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively. Graphic Road recorded the highest mean concentration (4.78 ng/m^3) whilst Mallam recorded the lowest mean concentration (1.05 ng/m^3). Concentrations of zinc recorded across the four sampling sites were all below the WHO ambient levels of 100-500 ng/m^3 at urban sites.

Table 5:
Copper (Cu) concentrations in ng/m^3 at the various sampling sites.

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija-Site 1	0.36 - 0.60	0.48 ± 0.33	54 ng/m^3 (24-hour average) MassDEP, 1990
Mallam-Site 2	0.15 - 0.22	0.19 ± 0.08	
Kaneshie First Light-Site 3	0.33 - 0.63	0.48 ± 0.39	
Graphic Road-Site 4	0.34 - 0.60	0.47 ± 0.29	

Copper concentrations ranged between 0.36 - 0.60 ng/m^3, 0.15 - 0.22 ng/m^3, 0.33 - 0.63 ng/m^3 and 0.34 - 0.60 ng/m^3 at Weija-Site 1, Mallam-

Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively. Kaneshie First Light-Site 3 and Weija-Site 1 recorded the highest mean concentrations (0.48 ng/m^3). Concentrations of copper recorded across the four sampling sites were all below the twenty-four (24) hour guideline value of 54 ng/m^3 from MassDEP.

Table 6:
Cadmium (Cd) concentrations in ng/m^3 for the various sampling sites.

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija-Site 1	0.03 - 0.06	0.05 ± 0.03	2 ng/m^3 (24-hour average) MassDEP, 1990
Mallam-Site 2	0.01 - 0.02	0.02 ± 0.01	
Kaneshie First Light-Site 3	0.06 - 0.09	0.08 ± 0.03	
Graphic Road-Site 4	0.09 - 0.19	0.15 ± 0.12	

Cadmium concentrations ranged between 0.03 - 0.06 ng/m^3, 0.01 - 0.02 ng/m^3, 0.06 - 0.09 ng/m^3 and 0.09 - 0.19 ng/m^3 at Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 respectively. Graphic Road (site 4), recorded the highest mean concentrations of 0.15 ng/m^3 whilst the lowest mean concentration of 0.02 ng/m^3 was recorded at Mallam. Concentrations of cadmium recorded across the four sampling sites were all below the twenty-four (24) hour guideline value (2 ng/m^3) from MassDEP.

Heavy Metals in PM_{10} Fraction

The pie chart below shows the percentage composition of heavy metals in the PM_{10} fraction across the four sampling sites.

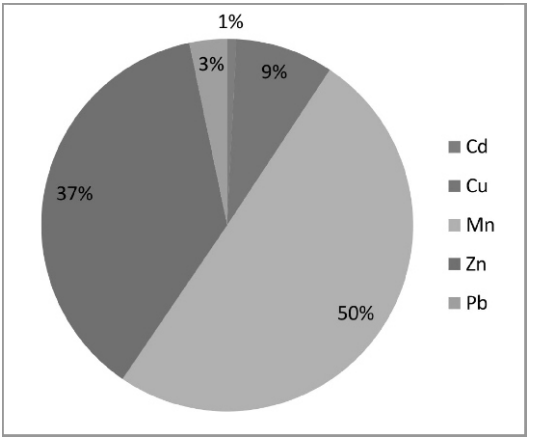

Fig 2: Percentage concentrations of heavy metals in PM_{10} fraction

From fig 2 above, it could be observed that the total PM_{10} concentrations recorded across the four sampling sites constitutes 50% Manganese, 37% zinc, 9% copper, 3% lead and 1% cadmium. The most abundant metal in PM_{10} fraction is manganese.

Discussion

Particulate Matter (PM_{10})

From fig 1, it could be deduced that Weija had the highest mean PM_{10} concentration of 227.60 $\mu g/m^3$ followed by Mallam-Site 2 (211.00 $\mu g/m^3$) and Graphic Road-Site 4 which recorded the third highest mean PM_{10} concentration of 186.25 $\mu g/m^3$. Kaneshie First Light-Site 3 had the least PM_{10} concentration (166.67 $\mu g/m^3$). PM_{10} concentrations recorded across the four sampling sites were within the range of 150.7 $\mu g/m^3$ - 236 $\mu g/m^3$.

The highest PM_{10} value recorded at Weija-Site 1 was expected because Weija-Site 1 had a lot of industrial activities aside the vehicular traffic compared to the other sampling sites. Some of these activities

included block and brick making factories, furniture/ carpentry shops, fitting shops, building and constructional activities among others. An untarred road leading to the Westfield's School close to the sampling site could also be a possible influence on PM_{10} at Weija-Site 1.

Mallam-Site 2 recorded the second highest mean PM_{10} value of 211 $\mu g/m^3$. This was because apart from the heavy vehicular traffic experienced on the Mallam road and its possible contribution to PM_{10} concentrations, there were other possible activities which contributed to particulate pollution along the road. Particle pollution along the Mallam road aside the vehicular fleet may probably come from the frequent burning of refuse and car tyres around the Mallam market. Other activities along the Mallam road which could contribute to particulate pollution include furniture making shops, fitting shops, block moulding factories amongst others.

Graphic Road-Site 4 recorded the third highest mean PM_{10} value (186.25 $\mu g/m^3$) followed by Kaneshie First Light-Site 3 which recorded the lowest PM_{10} concentrations (166.67 $\mu g/m^3$). Unlike Mallam-Site 2 and Weija-Site 1 which had a lot of industrial activities which were likely o influence PM_{10} concentrations, Graphic Road-Site 4 had just a few industrial activities which were probably not likely to contribute to high PM_{10} levels. These activities mainly comprised automobile industries, printing press, manufacturing industries such as Accra Breweries Limited amongst others. Though Kaneshie First Light-Site 3 had a lot of commercial activities, these activities were not probably likely to influence PM_{10} concentrations. The main commercial activity was at the Kaneshie market. Vehicular traffic at Kaneshie First Light-Site 3 and Graphic Road-Site 4 could probably be the most important source of Pm_{10}.

From table 1, it could be deduced that environmental factors such as rainfall and burning had an effect on PM_{10} concentrations recorded at the various sampling sites. Mallam and Weija recorded a high PM_{10} value of 1182 $\mu g/m^3$ and 708 $\mu g/m^3$ for the fourth samlple and seventh sample respectively. These high values recorded were due to the effect of waste burning close to these sampling sites**.** This resulted in increased PM_{10} concentrations at these sites. PM_{10} concentrations increased more than four times at Mallam-Site 2 and more than three

times at Weija-Site 1 compared to the previous values recorded (264 $\mu g/m^3$ and 208 $\mu g/m^3$) respectively. Results from literature revealed that biomass burning could increase PM_{10} concentrations by 10–100 times more than contemporary fuels used in rural areas, due to low thermal, combustion and heat transfer efficiencies of the biomass (Tyagi *et al*. 2012).

Sampling at Mallam for the fourth sample ended at eleven (11) hours instead of twenty-four (24) hours. The possible reason why sampling ended at eleven (11) hours instead of twenty-four (24) hours was due to the excessive accumulation of particulate matter on the quartz filter paper which caused the flow rate of the MiniVol air sampler to fall below 10% of the original flow rate (5l/min) thereby causing the sampler to shut down to avoid damage. The high particulate load was probably due to the massive burning of refuse and car tyres around the Mallam Market which was close to the sampling site. Sampling at Graphic Road for the seventh sample also ended at twelve (12) hours with a PM_{10} value of 56 $\mu g/m^3$. This anomaly was attributed to battery failure of the MiniVol Tactical Air Sampler.

All PM_{10} values recorded for the second sample were very low compared to the other sampling days. Heavy rainfall prior to the sampling day was considered the possible reason. This was consistent with other findings in literature. (Tyagi *et al.* 2012) found out that PM_{10} values in the month of February were very low in comparison to the months of January and March due to heavy rainfall in the month of February which probably washed out the particles before sampling was done. (Karar *et al.* 2006) also found out that, PM_{10} concentrations were less in June in comparison to other months due to similar reasons of particle being washout by heavy rainfall prior to sampling.

General observation shows a slight variation between the mean PM_{10} concentrations of the various sampling sites. However, results from the Analysis of Variance amongst the various sampling sites indicate a p-value of 0.118 which is greater than 0.05. This implies that the test statistic F is not significant and hence, no significant differences (variations) existed among the mean PM_{10} values of the four sampling sites.

In order to find out whether the ambient air around the sampling

sites were polluted with particulate matter or not, paired T-test was carried out on the various means and compared with standards from WHO and EPA-Ghana. Results from the paired T-test revealed that PM_{10} concentrations at the four sampling sites were far above guideline values from WHO (50 $\mu g/m^3$) and EPA-Ghana (70 $\mu g/m^3$). The p-values recorded were all less than 0.05 making the test statistics significant. Thus, based on guideline values from WHO and EPA-Ghana, the ambient air of all the four sampling sites were highly polluted with particulate matter (PM_{10}).

This finding was not different from other findings in literature. Dionisio *et al*. (2010) found out that traffic sites on average had high PM_{10} concentrations with annual means exceeding WHO air quality standards of 20 $\mu g/m^3$. (Nerquaye-Tetteh 2009) also reported high concentrations of PM_{10} along roadside with 75% and 87% of samples collected exceeding WHO and EPA Ghana standards of 50 $\mu g/m^3$ and 70 $\mu g/m^3$ respectively. A study by (Safo-Adu *et al*. 2014) also recorded high concentrations of PM_{10} along the Accra-Tema Highway with mean concentration (86.97 $\mu g/m^3$) exceeding the WHO guideline value of 50 $\mu g/m^3$. A research on the toxic metal constituents of PM_{10} carried out in Athens also showed high PM_{10} concentrations thereby revealing the presence of particulate matter pollution in the city (Manalis *et al.* 2005).

Numerous studies have shown a link between PM_{10} and adverse health effects such as cardiovascular diseases as well as respiratory diseases (Raaschou-Nielsen *et al.,* 2011; Anderson *et al.,* 2012; Du *et al.,* 2016). Due to enough evidence gathered from epidemiological studies, the International Agency for Research on Cancer (IARC) classified particulate matter under "Group 1" pollutants which makes it carcinogenic to humans.

Apart from human health effects, Particulate Matter is also responsible for effects such as changes in visibility and climate. The high concentrations of particulate matter (PM_{10}) recorded at all the four sampling sites therefore raises public health concern especially for those who live and work along these sites and also for vulnerable groups such as the elderly and children.

Heavy Metals in Particulate Matter (Pm_{10})

Metal concentrations for copper, manganese, zinc, lead and cadmium across the four sampling sites ranged between (0.15 – 0.63 ng/m^3), (0.86 - 7.22 ng/m^3), (1.79 – 7.34 ng/m^3), (0.08 - 0.70 ng/m^3) and (0.01 - 0.20 ng/m^3) respectively. Mean particulate metal concentrations recorded in the ambient air at all four sampling sites were considerably lower than those reported for other cities around the world.

(Talebi and Tavakoli-Ghinani 2008) in their study observed high concentrations of heavy metals like lead, cadmium and zinc at the south and west areas with higher traffic densities within the city of Isfahan. Heavy metal concentrations of lead cadmium and zinc ranged between 79 - 197 ng/m^3, 2.9 - 6.5 ng/m^3 and 220 – 418 ng/m^3 respectively. This range was far higher than those recorded for lead (0.08 - 0.70 ng/m^3), cadmium (0.01 - 0.20 ng/m^3) and zinc (1.79 – 7.34 ng/m^3) in this study. High levels of metals like Zn, Pb, Cu and Mn were observed in Milan in a study conducted by (Vecchi *et al*. 2007). In their study, average heavy metal concentrations observed at both daytime and night time were considerably high with Zn and Pb concentrations reaching 247 ng/m^3 and 93 ng/m^3 at night time respectively.

Concentrations of lead recorded at all the four sites of sampling were lower than the 24-hour guideline values of 1000 ng/m^3 and 140 ng/m^3 from the Central Pollution Control Board (CPCB) and the Massachusetts Department of Environmental Protection (MassDEP) respectively. This result was expected and is therefore attributable to the phase out of the use of leaded fuels in vehicles in 2004.

Similar findings were reported from the urban air monitoring programme in Accra, where there were significant reductions in roadside lead concentrations. Before the phase out of leaded fuels, lead concentrations in the ambient air ranged from 2 μg/m^3 to 188 μg/m^3 (2000-188000 ng/m^3) which was above annual EPA Ghana guideline value of 2.5 μg/m^3(2500 ng/m^3). After the phase out of lead in gasoline, lead concentrations ranged from 0 – 1.97 μg/m^3 (0 – 1970 ng/$m^{3)}$ (Nerquaye-Tetteh 2009). A study conducted by (Safo-Adu *et al*. 2014) also revealed low particulate lead levels in the ambient air along the Accra-Tema Highway. The low lead levels recorded in this study thus confirms a successful phase out of the use of leaded fuel in the Accra Metropolis.

Particulate manganese concentrations were expected to be very high due to the Methylcyclopentadienyl Manganese Tricarbonyl (MMT) additive in fuels. However, results showed significantly lower concentrations of particulate manganese in the ambient air at these sampling sites. Particulate manganese concentrations recorded ranged between 0.86 ng/m^3-7.22 ng/m^3 and were all below the twenty-four (24) hour EPA-Ghana guideline value of 1.0 µg/m^3 (1000ng/m^3). This finding was consistent with previous studies in Accra where manganese concentrations recorded were all below twenty-four (24) hour EPA-Ghana guideline value of 1000 ng/m^3. Particulate manganese concentrations ranged from 0.10 – 640 ng/m^3 (Nerqyauye-Tetteh 2009). Findings from Edmonton Central air quality monitoring station also revealed low concentrations of particulate manganese in ambient air with 24-hour averages ranging between 2.48 ng/m^3 to 225.70 ng/m^3 (WBK and Associates Inc., 2004).

Safo-Adu *et al*. (2014) also recorded low manganese levels (84 ng/m^3) compared to WHO annual mean (150 ng/m^3) in the ambient air along the Accra-Tema Highway and concluded that since the use of MMT 'as a gasoline octane enhancer in Ghana in 2004, the buildup of manganese from vehicular emissions has not yet had any significant effect on the natural background level'. The main source of particulate manganese may probably be due to emission of manganese from fuel combustion.

Zinc concentrations recorded at Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 ranged between 1.79 - 2.39 ng/m^3, 1.87 – 4.03 ng/m^3, 2.33 – 3.91 ng/m^3 and 4.06 – 7.34 ng/m^3 respectively. These ranges recorded were all below the WHO general ambient air levels of 100 – 500 ng/m^3 at urban sites. Zinc which is known to be an important nutrient for mammals occurs naturally in soil and the ambient air. However, the presence of Zinc in the ambient air across these sampling sites may be due to resuspended road dust or windblown soil. Tyagi *et al*. 2012 found concentrations of zinc to range between 3 – 4 ng/m^3 at site S_1 (roadway) in Roorkee. These values recorded were almost similar to those recorded in this study except for Graphic Road- Site 4 where zinc concentrations were slightly higher.

The presence of cadmium at all the four sampling sites may be

attributed to vehicular exhaust emission due to its presence in gasoline and as a result of corrosion of car parts as confirmed by the (European Commission 2001).

Cadmium concentrations recorded across all the four sampling sites were below the MassDEP guideline value (2 ng/m^3). Though cadmium concentrations recorded throughout the sampling sites were very low, the relatively high concentration of cadmium at Graphic Road may probably be due to the burning of cadmium containing electronic-waste close to the sampling site. Possible sources of cadmium include vehicular exhaust emissions including tyre abrasion; open burning of municipal wastes containing Ni-Cd batteries and plastics containing cadmium pigments (Awan *et al*. 2011).

Copper has been confirmed to be a good marker of traffic emissions. Literature results from (Vecchi *et al*. 2007) showed that brake wear and tear cause significant particulate matter emissions characterised by high concentrations of Cr, Cu, Zn, and other trace metals. Their study also showed that a substantial portion of particulate copper in urban places originated from the wearing out of vehicular brakes which seems to be the case in this research. Concentrations of copper across the four sampling sites ranged between 0.15– 0.63 ng/m^3. Similar outcomes were recorded by (Tyagi *et al*. 2012) who found ambient copper concentrations at roadside locations in Roorkee, Northern India to range between 0.2 - 0.4 ng/m^3. Copper concentrations recorded at all four sampling sites were below the MassDEP guideline value (54 ng/m^3).

Results from this study showed that Graphic Road- Site 4 had the highest mean heavy metal concentrations except for copper. This result was expected because of the regular burning of electronic waste close to the Agbogbloshie market aside the heavy traffic. Though the sampling site was quite far from the area where this activity took place, it might have possibly had an effect on the heavy metal's concentrations recorded at Graphic Road- Site 4.

The percentage of metal concentrations in PM_{10} fraction was 50% manganese, 37% zinc, 9% copper, 3% lead and 1% cadmium (fig 2). The use of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) as a fuel additive might possibly be the reason for the high Manganese

concentrations recorded across the four sampling sites.

ANOVA

As previously mentioned, significant variabilities between the sampling sites (Weija, Mallam, Kaneshie first light and Graphic Road) were determined using ANOVA. It was detected that variabilities between the sampling sites were not significant since p- values for all metals with the exception of Cd were greater than 0.05. The means of Cadmium concentrations among the sampling sites were significantly different from each other. Fisher's Test, a Post-hoc test for ANOVA was used to compare the means of the various sampling sites taking two at a time. Comparison of mean Cd concentrations between Graphic Road- Site 4 and Mallam-Site 2 as well as Graphic Road- Site 4 and Weija-Site 1 revealed that the means of these sites were significantly different from each other with Graphic Road- Site 4 having the highest Cd concentrations in its PM_{10} size fraction than Weija-Site 1 and Mallam-Site 2. Comparison of cadmium concentrations between two sampling sites other than Graphic Road- Site 4 and Mallam-Site 2 as well as Graphic Road- Site 4 and Weija-Site 1 were not significantly different.

Correlation Between PM_{10} and Heavy Metals

Correlation analysis carried out between PM_{10} and heavy metals showed that there was no correlation between PM_{10} and individual heavy metals at the various sampling sites. The Pearson Correlation (r) values recorded were all negative. Also, p-values recorded were all greater than 0.05 implying that there was no significant association between PM_{10} and heavy metals.

Conclusion

This study revealed that ambient air at Weija-Site 1, Mallam-Site 2, Kaneshie First Light-Site 3 and Graphic Road- Site 4 were heavily polluted with PM_{10}. The levels of PM_{10} concentrations recorded revealed the existence of the particulate pollution problem in Accra as observed by

previous researchers. However, the constituent of PM_{10} contains heavy metals at very low concentrations that are not likely to pose threat to human health and environment.

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