KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI, GHANA

COLLEGE OF SCIENCE

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN PARTICULATE MATTER (PM_{10}) IN THE AMBIENT AIR OF SELECTED ROADSIDES IN THE ACCRA METROPOLIS

A Thesis submitted to the Department of Environmental Science, Kwame Nkrumah University of Science and Technology, in partial fulfillment of the requirement of the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE

BY

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(BSc. Hons Environmental Science)

NOVEMBER, 2016

DECLARATION

I hereby declare that this submission is my own work towards this MSc. and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any degree of the University, except where due acknowledgement has been made in the text.

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ACKNOWLEDGEMENTS

I thank the Almighty God for taking me through this course successfully. Special appreciation goes to my supervisor Dr. Bernard Fei-Baffoe for the unreserved direction, guidance and tolerance throughout my writing of this thesis; God richly bless you. My appreciation also goes to our dear lecturers for their constructive criticisms during our seminars; it was indeed of great benefit to me.

I would also want to thank all staff of the Environmental Quality Department of the Environmental Protection Agency especially Dr. Sam Adu Kumi, Maxwell Sunu and all the laboratory technicians for their assistance and support during the air quality monitoring period.

Special thanks also go to Herbert Edem Kpodo and Ernest Asiamah for their assistance in researching and data analyses.

Finally, I would extend a hand of gratitude to my family members for their prayers and encouragement during tough times.

DEDICATION

This write-up is dedicated to the Almighty God and my family.

ABSTRACT

This study assessed the concentrations of heavy metals in particulate matter (PM_{10}) in the ambient air at four roadside locations (Weija, Mallam, Kaneshie First Light and Graphic Road) in the Accra Metropolis. Sampling was carried out every six days for a period of 24 hours from October to November, 2013. The Mini Vol. air sampler was used to collect the PM_{10} particles from the ambient air. PM_{10} 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 PM_{10} pollution was very high in the ambient air across the four sampling sites with mean PM_{10} concentrations exceeding guideline values from WHO and Ghana EPA. A flame atomic absorption spectrometry (FAAS) was used to investigate the presence of the following heavy metals: Cu, Mn, Zn, Pb and Cd in the particulate matter. Mean metal concentrations of copper, manganese, zinc, lead and cadmium 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. Results from ANOVA revealed that there was no significant variation between metal concentrations at the various sampling sites except for cadmium which was significantly different. Heavy metal concentrations were found to be very low compared to PM_{10} which is still a major concern.

LIST OF ACRONYMS AND ABBREVIATIONS

AED: Aerodynamic Equivalent Diameter

ATSDR: Agency for Toxic Substances and Disease Registry

CPCB: Central Pollution Control Board

DEQ: Department of Environmental Quality

EC: European Commission

EPA: Environmental Protection Agency

HAPs: Hazardous Air Pollutants

IARC: International Agency for Research on Cancer

MassDEP: Massachusetts Department of Environmental Protection

NAAQS: National Ambient Air Quality Standards

OECD: Organization for Economic Co-operation and Development

PM: Particulate Matter

PM_{10}: Particulate matter with aerodynamic diameter less than or equal to 10 microns

$PM_{2.5}$: Particulate matter with aerodynamic diameter less than or equal to 2.5 microns

$PM_{0.1}$: Particulate matter with aerodynamic diameter less than or equal to 0.1 microns

TSP: Total Suspended Particulate Matter

USEPA: Unites States Environmental Protection Agency

UNEP: United Nations Environment Programme

WHO: World Health Organization

mg/l: milligram per litre ng/m^3:

nanogram per meter cube $\mu g/m^3$:

microgram per meter cube

TABLE OF CONTENTS

LIST OF PLATES

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

In cities of most developing world, rapid economic growth together with ineffective transportation system is causing a raise 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. Although road transport has significantly affected urban lifestyle and increased economic opportunities, the increase in vehicular fleet presents a challenge to urban authorities in that air quality continues to worsen while traffic congestion increases.

Road transport has also been identified as the single largest source of air pollution with contributions from automobiles reported to fall within the range of 40 to 80% (AgyemangBonsu e*t al.*, 2010; Goyal *et al.*, 2006). According to the United Nations Environment Programme (UNEP), emissions from motor vehicles account for about 90% of air pollution in fast growing cities in most developing world (UNEP, 2013). Though there are many causes of ambient air pollution in Accra, including burning of domestic waste, biomass burning, resuspended road dust and windblown dust as well as dry harmattan winds (Nerquaye-Tetteh, 2009, Zhou *et al.*, 2013), motor vehicles contribute greatly to the air pollution problem.

Emissions from motor vehicles include a wide range of pollutants such as carbon monoxide, particulate matter, oxides of sulphur and nitrogen (Kinney *et al*., 2011).

Particulate matter is a multi-component aerosol formed by anthropogenic and natural species. Its constituents may differ depending on the prevailing weather conditions, season and place of emissions. Particulate matter is classified into different size fractions due to the different health effects associated with particles of different sizes. Of particular concern are the inhalable particles (PM_{10}) since these are the ones that can enter deep into the lungs and result in serious health effects (Kura *et al.,* 2013). The composition of inhalable particulate matter is complex and differs depending on the source and location. 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). 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 (PM_{10}), 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).

1.2 PROBLEM STATEMENT/JUSTIFICATION

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, but little information is available on the heavy metal constituents of PM_{10} (Nerquaye- Tetteh, 2009: Dionisio *et al.*, 2010).

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).

Currently, the Environmental Protection Agency of Ghana has temporal monitoring sites at roadside locations for the monitoring of PM_{10} in the Accra Meteropolis. The selected roadside locations (Weija-Westfields School, Mallam-opposite the market, Kaneshie First Light and Graphic Road-Accra Breweries Limited) used in this study are part of the temporal sites of the EPA and they fall within the main corridor for the proposed Accra Bus Rapid Transit project which extends between Kasoa along Winneba and Graphic roads to the city's Central Business District. This corridor (Winneba-Graphic Road corridor) is one of the most heavily used routes in the Accra Metropolitan Area with daily traffic volume along the entire Winneba Road and Graphic Road estimated to reach 50,000 and 40,000 respectively (Okoye

et al., 2010).

Since the occurrence of toxic heavy metals in PM_{10} 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.

1.3 OBJECTIVES OF STUDY

1.3.1 Main objective

The main objective of this study was to assess the levels of heavy metals in particulate matter at four roadside locations in the Accra Metropolis.

1.3.2 Specific objectives

The specific objectives were to:

1. Measure the levels of PM_{10} at four roadside locations (Weija, Mallam, Kaneshie first light and Graphic Road) in the Accra Metropolis.
2. Measure the levels of heavy metals (cadmium, lead, copper, zinc and manganese) at these roadside locations.

1.4 RESEARCH QUESTIONS

1. What are the levels of PM_{10} in the ambient air at these four roadside locations (Weija, Mallam, Kaneshie first light and Graphic road) in the Accra Metropolis?
2. What are the levels of heavy metals in the ambient air at these roadside locations?
3. Are there other possible activities that could contribute to particulate air pollution around these roadside locations?

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 AIR POLLUTION

Air pollution as defined by the World Health Organisation (WHO) _is the contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere (WHO, 2013)‘. Although clean air is seen as a fundamental requirement for good health, air pollution continues to cause a major threat to human health all over the world. It is estimated to cause more than 2 million premature deaths on yearly basis, with more than half of diseases caused by air pollution being borne by people in developing regions (WHO, 2006).

In the year 2008, about 1.3 million premature deaths were recorded as a result of outdoor air pollution. This represented an increase of 16% compared to the 1.15 million deaths recorded in 2004. Recent estimates also revealed that about 3.7 million premature deaths out of 7 million deaths were attributable to ambient air pollution in the year 2012. 88% of these deaths were recorded by low and middle income countries (WHO, 2014).Due to the increasing trend in air pollution as well as substantial evidence from scientific studies on the dangers of air pollution, the International Agency for Research on Cancer (IARC) classified ambient air pollution as a carcinogen. This classification according to a report by the Agency was very crucial and that there was need for the international community to take steps in order to curb the problem (IARC, 2013).

2.2 BRIEF HISTORY OF AIR POLLUTION

Air pollution did not just evolve in one day as we think but has come along as a result of the use of fossil fuels as well as other combustible materials such as wood. The growth of communities resulted in the exhaustion of wood supplies which in turn paved way for the use of coal and peat. The use of coal especially the sulfurous ones often hurled smoke into the

ambient air thereby contaminating it and settling on local structures. Although early concerns about air pollution was based on the use of coal as well as emissions from manufacturing plants, the beginning of highway systems to convey traffic from expanding towns to industrial and urban centres added a new dimension to air pollution (Stanek *et al*., 2011).

During the industrial movements, the problem of air pollution was overshadowed by the job opportunities that came. This was because the smoke emanating from industries was seen as a sign of wealth rather than a problem. In the 20th century however, people became conscious of the fact that air pollution had become a problem that must be reduced. This consciousness was the result of air pollution episodes that occurred in London, Meuse Valley in Belgium and Donora (Stanek *et al*., 2011).

In each of these events, a meteorological inversion trapped emissions from combustible materials and prevailed for many days. During this period, the levels of pollutants increased drastically above the normal levels for these polluted cities. Many people lost their lives and a lot more were hospitalized. In London alone about 4,000 excessive deaths were recorded during the London Smog episode of 1952. Sixty five (65) people were killed in the Meuse Valley episode, whereas in Donora, twenty (20) people were killed. The 1984 methyl isocyanate disaster in Bhopal, India was also another environmental catastrophe that released toxic gases into the ambient air thereby killing and injuring lots of people in Bhopal. This further intensified public awareness on the need to limit air pollution (Stanek *et al*., 2011).

2.3 AIR QUALITY GUIDELINES

Episodes of air pollution such as the methyl isocyanate disaster in Bhopal and the London smog in London brought about a great change in the history of air pollution. Public awareness on the

effects of air pollution grew and mounted pressure on governments and states to form legislations that would protect public health and environment (Stanek *et al*., 2011).

The WHO published the first air quality guidelines for the European region in 1987 to protect the health of people from dangerous air pollutants such as particulate matter. These air quality guidelines were updated in 1997 and then in 2005 as a result of new developments and findings from scientific literature. Air quality guidelines for four pollutants namely particulate matter, nitrogen dioxide (NO_2), Sulphur dioxide (SO_2) and Ozone (O_3) were updated in 2005.

The USEPA have National Ambient Air Quality Standards (NAAQS) for pollutants like lead, particulate matter, carbon monoxide, sulphur dioxide, nitrogen dioxide, and ozone. The Environmental Protection Agency in Ghana also has guideline values for pollutants such as particulate matter, nitrogen dioxide and sulphur dioxide amongst others. For particulate matter (PM_{10}), the WHO has 24-hour guideline value of 50 $\mu g/m^3$ whilst the NAAQS and the Ghana EPA has a value of 150 $\mu g/m^3$ and 70 $\mu g/m^3$ respectively. Most metals found in particulates do not have guideline values from NAAQS since most of them are considered as hazardous air pollutants. The WHO however has guideline values for some of these heavy metals (USEPA, 2013).

2.4 POLLUTANTS OF MAJOR HEALTH CONCERN

There are a wide range of air pollutants that are responsible for air pollution. The USEPA has broadly categorized air pollutants into criteria or common pollutants (particulate matter, carbon monoxide, sulphur dioxide, nitrogen dioxide, ozone and lead) and Hazardous Air Pollutants (HAPs). The HAPs are also known as toxic air pollutants and they are those pollutants that are

known to be carcinogenic to humans, cause adverse effects such as birth defects or dangerous ecological and environmental effects. With this definition of HAPs, PM could be classified as a toxic air pollutant since the IARC recently classified it as a carcinogen. Examples of HAPs include Benzene, Ethyl acrylate, Ethyl benzene, Formaldehyde, Heptachlor, Ethylene oxide, Ethylene imine and metals like nickel and cadmium (USEPA, 2013).

2.4.1 Particulate Matter (PM)

Particulate Matter is a fraction of air pollution which consists of extremely ‗small particles and liquid droplets containing acids, organic chemicals, metals, and dust particles' (Anderson *et al*., 2012). PM is categorized by size and can be described by its ‗aerodynamic equivalent diameter.' Its distribution in the ambient air can be described as trimodal, including, ultrafine, fine and coarse particles. It is worth noting that with particulate matter monitoring, sampling is often done using the size – selective method. This means that particles above, below or within a particular size range are deliberately sampled. The size that is often selected has special relevance with regards to sources, toxicity, inhalation and deposition (Pope and Dockery, 2006).

$PM_{2.5}$ which has been described as an indicator of fine particles refers to particles with an aerodynamic diameter less than or equal to 2.5μm. Sources of fine particles include burning of wood and coal, direct emissions from vehicles that use gasoline and diesels as well as industrial processes like cement plants (Pope and Dockery, 2006).

Fine particles in PM_{10} fraction often consist of combustion-derived and carbon-centered particles with associated hydrocarbons and metals (Yang *et al.,* 2013). From various toxicological and physiological considerations, human health may be affected by the presence

of $PM_{2.5}$ particles in the atmosphere. For instance, they may be more toxic because they are composed of metals, acids, sulphates and nitrate particles. They can also be inhaled into the lungs, remain suspended for longer periods of time, penetrate more readily into indoor environments, and be transported over long distances.

Coarse particles on the other hand are particles with aerodynamic diameter greater than 2.5μm cut point. Primary sources of coarse particles include dust, soil, or other crustal materials from farming, roads, mining and volcanoes (Pope and Dockery, 2006).

Particles with size less than 0.1μm are often described as ultrafine particles. Ultrafine particles are often emitted into the ambient air in industrial environments from sources related to combustion. Examples of these combustion related sources are vehicular exhausts and atmospheric photochemical reactions. These primary ultrafine particles, however, have a short life and grow through coagulation or condensation or both to form larger complex aggregates which forms part of $PM_{2.5}$. In recent times, interest in ultrafine particles has gained more attention because they serve in part as a primary source of fine particle exposure and because, poorly soluble ultrafine particles may be more likely than larger particles to translocate from the lung to the blood and other parts of the body. In studies relating to particulate matter, it is important to acknowledge that PM_{10} is made up of particles with a size fraction which is less than or equal to a 10 μm and includes fine particles and a subset of coarse particles (Pope and Dockery, 2006).

2.4.2 Health Effects of Particulate Matter

Particulate matter continues to be the portion of air pollution that is mostly related to diseases in humans. According to the WHO, about 800,000 premature deaths recorded on yearly basis could be attributable to PM pollution. This makes it the 13th primary cause of death worldwide. It is believed to be responsible for many cerebrovascular as well as cardiovascular diseases through the processes of direct and indirect coagulation activation and systemic inflammation (Anderson *et al*., 2012). Many studies have however proved that the relationship between particulate matter and mortality is more complex than formerly thought. For instance the IARC confirmed that ambient air pollution was carcinogenic to humans with the PM portion of it being related to high incidence of cancer, especially lung cancer (IARC, 2013).

2.5 HEALTH EFFECTS OF SELECTED HEAVY METALS IN PM_{10} FRACTION

Heavy metals have been categorized amongst the most hazardous groups of man-made pollutants in the environment. This is due to their toxic and persistence nature in the environment. Although they occur naturally in the environment, their levels may be highly elevated as a result of anthropogenic undertakings such as mining, combustion of fossil fuels, metal smelting amongst others. Certain metals like lead, cadmium and copper are known to be hazardous contaminants which are capable of accumulating in the human body for relatively long periods of time (Leili *et al*., 2008).

The existence of particulate metals in the ambient air at elevated levels may have adverse health effects on humans. Lead, for example at elevated levels may induce neurological and haematological effects. It may also interfere with metabolism and bio-accumulate in living tissues (Razos and Christides, 2010).

2.5.1 Effects of Manganese in the Ambient Air

Manganese is a vital element required for growth and development. Most people get ample amount of manganese via the consumption of either water or food. However, a major source and adverse effects of manganese exposure to the public is from inhaling air that is contaminated with manganese rather than ingestion (DEQ, 2012).

Inhalation of manganese dust may lead to an inflammatory response in the lungs of mammals. This may in turn lead to high occurrence of cough and bronchitis and may result in lung injury especially the tissues. At elevated levels however, exposure to manganese could lead to the disease condition known as manganism which is the disabling of neurological effects in humans. Subclinical neurological effects such as decreased performance on neurobehavioral tests and lower levels of cognitive flexibility have also been seen in employees exposed to manganese dusts at lower levels. Concentrations of manganese in air that produces these effects range from 0.07 to 0.97 mg manganese/m^3 (ATSDR, 2012).

According to studies performed on laboratory mammals, inhalable particles of manganese may be deposited in the nasal cavity which may be transported to the brain through the olfactory nerve. Though the importance of this process to humans is not clear, it raises concerns with regards to the total particulate manganese exposure rather than the $PM_{2.5}$ or PM_{10} exposure to manganese (DEQ, 2012). Manganese is classified under the HAP's list by the USEPA. This is because it is seen as a toxic air pollutant rather than a criteria pollutant.

The Ghana-EPA and WHO however have a guideline value of 1 μg/m^3 and 0.15 μg/m^3 for a 24 hour and annual averaging time respectively (Nerquaye-Tetteh, 2009; WHO, 2000).

2.5.2 Effects of Zinc

Zinc is an essential element for living tissues since it is involved in biochemical processes which are required for physiological functions like sexual function and normal immune function. Traditionally, zinc has been considered as a non- toxic element but current studies reveal that free ionic zinc could eradicate neurons, gill and other types of cell.

High dose and short term exposures are usually the cause of acute zinc effects. This however depends on the point of contact. At a lower level of zinc exposure coupled with a prolonged period of time, chronic somatic effects may arise. Also, intense inhalation of industrial fumes containing zinc oxide in humans can induce a disease condition known as metal fume fever.

Symptoms of this metal fume fever include chills, fever, chest pains and cough (Nriagu, 2007).

2.5.3 Effects of lead

Lead is a bluish grey metal which is found in the earth‘s crust. It occurs naturally in the form of leaded compounds rather than a metal, making it a less common metal compared to oxygen and silicon which are the two most abundant metals in the earth‘s crust (ATSDR, 2007). Lead can enter the atmosphere through burning of oil, coal or waste as well as emissions from factories that use lead or leaded compounds. In the atmosphere, its concentrations vary greatly, with the highest concentrations observed near stationary sources like lead smelters. Concentrations of lead in outdoor air may range from about 7.6×10^{-5} μg/

m^3 in distant places to >10 μg/m^3 around point sources (ATSDR, 2007).

The USEPA has a guideline value of 0.15 μg/m^3 (for 3 months rolling average) whilst the Central Pollution Control Board (CPCB) has a 24 hour guideline value of 1 μg/m^3. Its (lead) widespread in the environment is as a result of its former use as an additive in fuel as well as its use in paints (ATSDR, 2007).

Lead remains a major public health issue in countries of most developing world due to the differences in the sources as well as pathways of exposure. At high exposure levels, most organs and systems such as the kidneys and central nervous systems are injured. However, at lower levels, ‗haeme synthesis and other biochemical processes are affected, psychological and neurobehavioural functions are also impaired' (Tong *et al*., 2000).

2.5.4 Effects of Copper

At low concentrations, copper, a reddish metal may be found in the soil, water, rocks, sediments and air. Its concentrations in the ambient air ranges from a few nanograms to about 200 ng/m^3. Copper may find its way into the environment via emissions such as mining of copper, burning of fossil fuels and from natural sources like windblown dust (ATSDR, 2004).

Populations are often exposed to copper through inhalation of air containing copper dust, eating or drinking substances contaminated with copper or by skin contact with soil or other copper containing substances. Copper is an essential element for living organisms including humans at low levels of intake. It is necessary for the development and functioning of the central nervous system and the brain. Deficiencies in copper may affect the development of the brain as well as abnormalities in brain function (Opazo *et al*., 2014).

At much higher levels, toxic effects such as headaches, dizziness, and irritation of the nose, mouth, and eyes may occur. Copper intakes at extremely high doses may also result in kidney and liver injury, and eventually lead to premature death (ATSDR, 2004).

2.5.5 Effects of Cadmium

Cadmium is often found in the earth‘s crust in association with other metal ores like lead and zinc. In the atmosphere, it exists in the form of particulates and sometimes vapour (ATSDR, 2012).

The health effects of cadmium are well documented. The IARC and the USEPA both classify it as being carcinogenic to humans. Prolonged exposure to cadmium may cause renal dysfunction which may in turn lead to devastating bone disease in people with risk factors like poor nutrition. Populations that live in places polluted with cadmium often suffer from diseases like osteoporosis and increase risk of fractures. However, a link between exposure to cadmium and bone effects has also been noticed in people exposed to high concentrations of cadmium but not living in cadmium polluted areas (ATSDR, 2012).

2.6 PM_{10} STUDIES CARRIED OUT IN DIFFERENT REGIONS OF THE WORLD

Due to the harmful health effects of particulate matter (PM_{10}) and its associated heavy metal components, numerous studies have been carried out in various regions of the world (Aryal *et al*., 2013).

2.6.1 India

In India, PM_{10} and heavy metal concentrations were investigated in Roorkee in three suburban and three rural sites. The study revealed high PM_{10} concentrations at all the sites with concentrations exceeding the CPCB Standards. However in the month of February, due to particle washout by rain, concentrations did not exceed the CPCB standards. Metal concentrations were however below the WHO and USEPA standards. Road construction, wood

burning, industrial emissions amongst others were some of the sources of particulate matter and heavy metal pollution identified in the study (Tyagi *et al*., 2012).

2.6.2 Iran

In the city of Isfahan, in Iran, PM_{10} concentrations and the concentrations of heavy metals in the atmosphere were very high. The South and West parts of the city with higher traffic densities recorded high levels of PM_{10} and heavy metal concentrations compared with the North and East parts. PM_{10} concentrations ranged between 149 -183μg/m^3 across all the sites. Metal concentrations for cadmium, lead and zinc ranged between 2.9-6.5 ng/m^3, 79-197 ng/m^3 and 220-418 ng/m^3 respectively (Talebi and Tavakoli-Ghinani, 2008).

2.6.3 Ghana

In Ghana, studies carried out by researchers (Nerquaye-Tetteh, 2009 and Dionisio *et al*., 2010), revealed high concentrations of PM_{10} in the city of Accra especially at roadside locations. PM_{10} concentrations recorded exceeded guideline values from WHO and EPAGhana. Work done by Safo-Adu *et al*. (2014) on heavy metal and black carbon assessment of PM_{10} along the Accra-Tema Highway also revealed high concentrations of PM_{10} with annual mean average (86.97 μg/m^3) exceeding WHO standards. Concentrations of Heavy metals such as lead and manganese were also low compared with WHO standards. However levels of cadmium (0.007 μg/m^3), nickel (0.218 μg/m^3) and arsenic (0.059 μg/m^3) were higher than the mean concentrations threshold limit set by the European Commission (EC).

2.7 INSTRUMENTS FOR MONITORING OF PARTICULATE MATTER IN AMBIENT AIR

Several instruments such as optical analysers, Beta attenuation analysers, tapered element oscillating microbalance analysers and filter based gravimetric samplers can be used for the measurement of particulate matter in the ambient air. These instruments may either measure

directly or indirectly. Direct reading instruments often provide continuous measurement whilst the indirect reading instruments such as the gravimetric samplers often collect particles on filter papers such as quartz filter papers which are often weighed in the laboratory to determine particle mass.

2.7.1 Filter-based Gravimetric Samplers

Filter-based gravimetric samplers are often made up of a size selective inlet (PM_{10}/$PM_{2.5}$), a flow rate monitor and a filter substrate. Particulate matter is often collected on a filter paper for a particular period of time and then taken to the laboratory for gravimetric determination. That is weighing of field exposed filters and pre field filter papers in laboratory before calculation of PM_{10} concentration. An example of the filter based gravimetric sampler is the mini volume tactical air sampler (AQEG, 2005).

2.8 THE MINIVOL PORTABLE AIR SAMPLER

The Minivol Portable Air Sampler is a type of filter based gravimetric sampler that can be used for the sampling of both particulate matter and non-reactive gases in the open air. In an effort to address the need for portable air sampling technology, the MiniVol air sampler was manufactured jointly by the Lane Regional Air Protection Agency and the USEPA (Airmetrics, 2002).

Unlike the High Volume Sampler, the MiniVol sampler has been extensively used for ambient air sampling due to its ability to be powered from either an Alternative Current (rechargeable battery) or Direct Current (DC) power source as well as its portability which makes it easy to be deployed to the field (Airmetrics, 2002).

Plate 2.1: The MiniVol Air Sampler

2.8.1 Principle of Operation of the MiniVol Sampler

Air passes through a sample air inlet and then through a filter medium which traps particles onto its surface. The type of inlet selected determines the particle size that will be sampled. For instance an inlet with a size of 10 micro meter (PM_{10}) or a 2.5 micro meter ($PM_{2.5}$) when selected will sample particles with a size less than or equal to 10 micro meter or 2.5 micro meter respectively. On the other hand if the sampler is operated without an impactor, Total Suspended Particulates (TSP) would be collected.

After air has been drawn into the preferred sample inlet, the air passes through a pump where it is forced through a flow meter. Once sampling has been completed, the pump is automatically turned off by a programmable timer. However, sampling may be brought to an abrupt end even

though the programmable timer is on. This may happen in case of low flow rate or low battery fault which causes the sampler‘s pump to shut down in order to prevent the machine from damage.

Air flow through the pump may also fall below 10% of the original flow rate (5 litres per minute) as a result of too much accumulation of particulate load, resulting in the sampler shutting down. The operator will however be alerted of this problem when the flow rate indicator lights up. A low battery fault however occurs when the battery fails to provide enough power (above 10.3 volts) to the pump. The low battery circuit shuts down the sampler to protect the battery from damage. The operator is once again alerted of this problem when the low battery indicator lights up (Airmetrics, 2002).

CHAPTER THREE

3.0 METHODOLOGY

3.1 STUDY AREA

The Accra Metropolis is situated in the Greater Accra Region and its capital, Accra, is also the regional as well as the national capital. Accra is located on latitude 05°35'N and longitude 00°06'W with a population of 2.27 million people (CIA, 2016). The metropolis occupies an area of 173 square kilometres and shares boundaries with the Gulf of Guinea to the South, the La-Dadekotopon Municipal Assembly to the East, the Ga South and Central Municipal Assemblies to the West and the Ga West and La-Nkwatanang Municipal Assembly to the North (Fig 3.1). The metropolis which lies in the savannah zone has two rainy seasons. The first starts in May and ends in mid-July whilst the second starts in August and ends in October. The average annual rainfall is about 730mm.

The mean monthly temperature ranges from 24.7°C in August to 28°C in March with annual average of 26.8°C. Relative humidity is generally high varying from 65% in the midafternoon to 95% at night. Wind speeds normally range between 8 to 16 km/hr (www.ghanadistricts.com). The monitoring sites (Fig 3.1) fall along the Winneba-Graphic Road corridor which experiences heavy vehicular traffic most often. The road is a three lane road leading to the city‘s Central Business District.

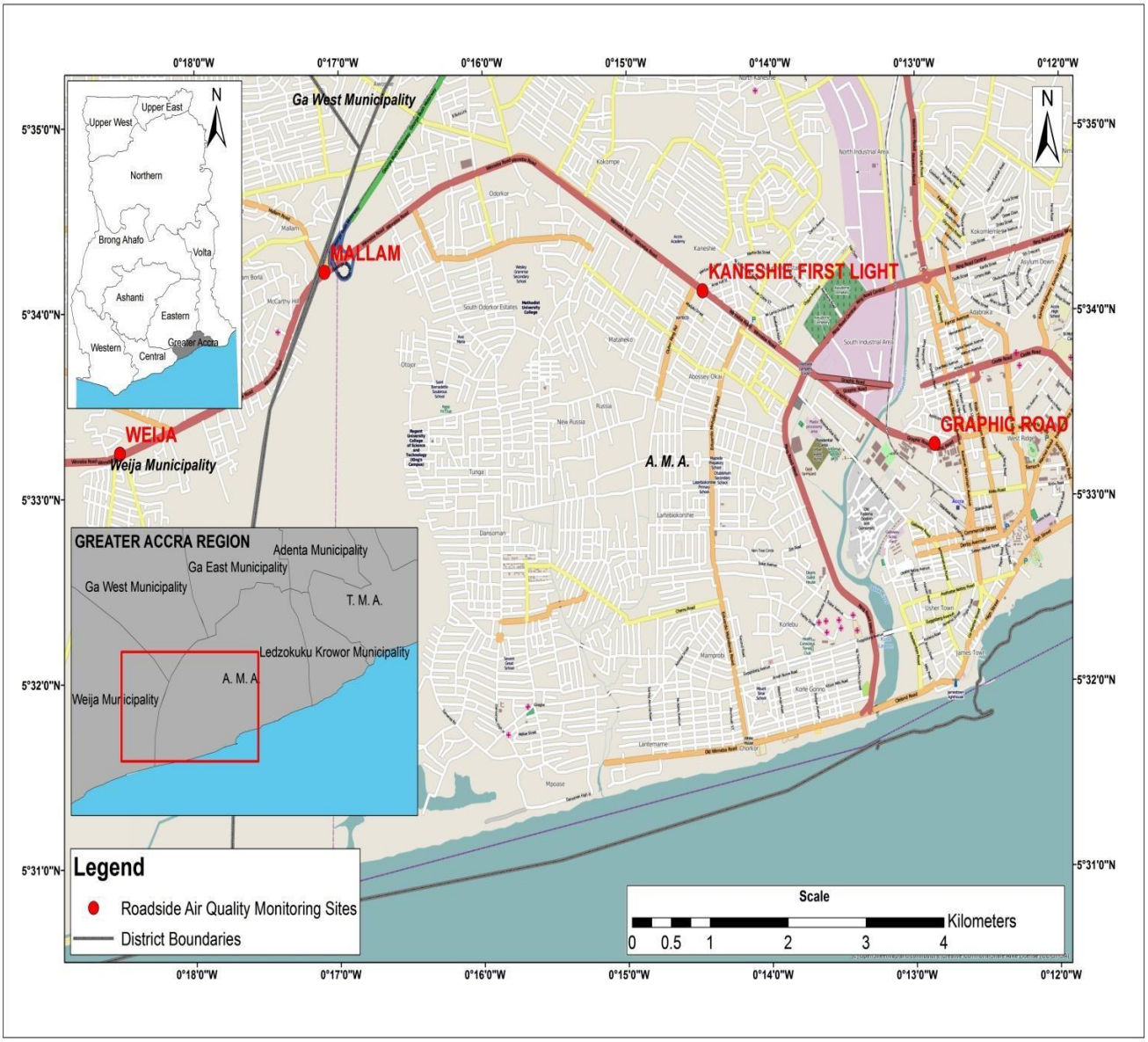

Figure 3.1 Map showing roadside air quality monitoring sites

3.2 MEASUREMENT OF PM_{10}

Air was sampled at four roadsides (Weija, Mallam, Kaneshie First Light and Graphic Road) for particulate matter (PM_{10}) using MiniVol Tactical Air Samplers (Plate 2.1). 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 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 µg/m3 using the USEPA method for calculating PM_{10} (USEPA, 1999).

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

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 µg/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 2013 (Plate 3.1). A total of twenty seven (27) samples were collected for determination of PM_{10} concentrations during the sampling period. Sample identifications were given to each sampling site in order to identify samples collected from each site. The first letter bearing the name of each sampling site followed by date of sampling (in subscript) was used to create the sample identifications. For instance $W_{24/10/13}$ identifies a sample collected at Weija on the 24th October, 2013.

Analyses for heavy metals were carried out at the Metal Laboratory of the Water Research Institute in Accra.

Plate 3.1: Mounting the Mini Vol.air samples at Weija.

3.3 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 (Plate 3.2). 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 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 µg/m^3 using the following equation:

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

Where:

C_1 = metal concentration in solution of sample (mg/l)

C_2 = 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 cubic meter (m^3).

Plate 3.2: Extraction of PM10 loaded filter paper in the laboratory

3.4 DATA ANALYSIS

Analysis Of Variance (ANOVA) was used to compare the Mean PM_{10} 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 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.

CHAPTER FOUR

4.0 RESULTS

This chapter presents the results that were recorded after the air quality monitoring period carried out from October to November, 2013.

4.1 PM_{10} CONCENTRATIONS

The Fig 4.1 below shows the mean PM_{10} concentrations at the various sampling sites compared with guideline values from WHO and EPA-Ghana.

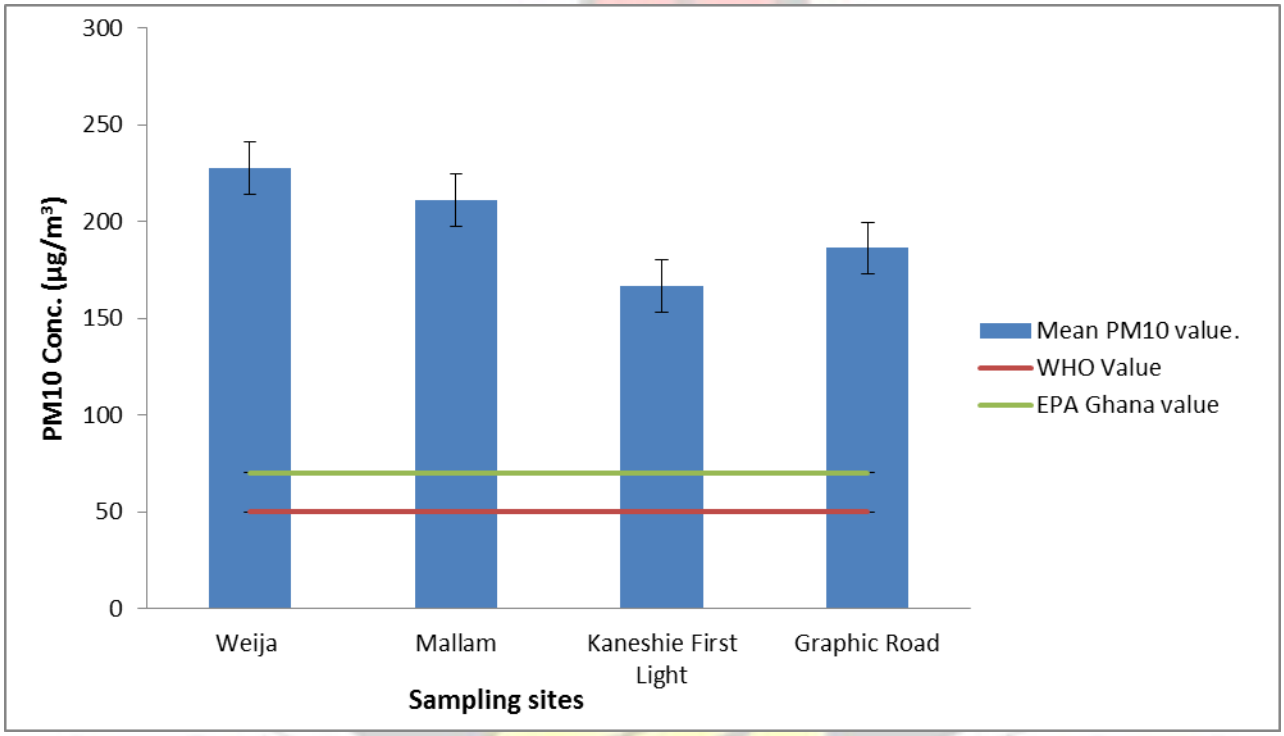

Figure 4.1: Mean PM_{10} Concentrations at the Sampling Sites

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 µg/m^3) followed by Mallam (211.00 µg/m^3), Graphic Road (186.25 µg/m^3) and Kaneshie First Light (166.67 µg/m^3).

4.2 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 4.1: Daily PM_{10} concentrations at the sampling sites

SAMPLING DATE	SAMPLING SITE			
	WEIJA	MALLAM	KANESHIE FIRST LIGHT	GRAPHIC ROAD
24/10/2013	250	236	153	236
30/10/2013	97*	56*	56*	69*
5/11/2013	208	264	222	217
11/11/2013	236	1182*	153	-
17/11/2013	236	139	139	111
23/11/2013	208	222	208	181
29/11/2013	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 on the second day (30/10/2013) of sampling were lower than those recorded on other days except for the last sampling day 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 on the fourth (11/11/2013) and seventh sampling day (29/11/2013) respectively were far higher than those recorded on the other days.

Without the influence of these environmental factors (rainfall and burning), PM_{10} concentrations ranged between 219.20–236.00 µg/m^3, 189.80-232.20 µg/m^3, 150.70-182.70 µg/m^3, 158.70-213.90 µg/m^3 for Weija, Mallam, Kaneshie First Light and Graphic Road respectively.

4.3 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 4.2: Lead (Pb) concentrations in ng/m^3 at the various sampling sites

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

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 Weija, Mallam, Kaneshie First light and Graphic Road respectively. The highest mean concentration of lead was recorded at Graphic Road (0.47ng/m^3) and the lowest mean at Mallam (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 (Mass DEP) guideline value of 1000 ng/m^3 and 140 ng/m^3 respectively.

Table 4.3: Manganese (Mn) concentrations in ng/m^3 at the various sampling sites

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija	2.09 - 3.55	2.82 ± 1.93	1000 ng/m^3 (24 hour average) EPA Ghana
Mallam	0.86 - 1.23	1.05 ± 0.42	
Kaneshie First light	1.66 - 2.94	2.30 ± 1.69	
Graphic Road	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, Mallam, Kaneshie First light and Graphic Road 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). Manganese values recorded at the four sampling sites were all below the EPA Ghana guideline value of 1000 ng/m^3.

Table 4.4: Zinc (Zn) concentrations in ng/m^3 at the various sampling sites

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

Zinc concentrations ranged between 1.79 - 2.39 ng/m3, 1.87 – 4.03 ng/m3, 2.33 – 3.91 ng/m3 and 4.06 – 7.34 ng/m3 at Weija, Mallam, Kaneshie First Light and Graphic Road respectively. Graphic Road recorded the highest mean concentration (4.78 ng/m3) whilst

Mallam recorded the lowest mean concentration (1.05 ng/m3). Concentrations of zinc recorded across the four sampling sites were all below the WHO ambient levels of 100-500 ng/m3 at urban sites.

Table 4.5 Copper (Cu) concentrations in ng/m^3 at the various sampling sites.

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija	0.36 - 0.60	0.48 ± 0.33	54 ng/m^3 (24 hour average) MassDEP, 1990
Mallam	0.15 - 0.22	0.19 ± 0.08	
Kaneshie First light	0.33 - 0.63	0.48 ± 0.39	
Graphic Road	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, Mallam, Kaneshie First light and Graphic Road respectively. Kaneshie First Light and Weija recorded the highest mean concentrations (0.48 ng/m^3). Concentrations of copper recorded across the four sampling sites were all below the 24 hour guideline value of 54 ng/m^3 from MassDEP.

Table 4.6 Cadmium (Cd) concentrations in ng/m^3 for the various sampling sites.

Sampling Site	Range	Mean ± SD	Reference/guideline values
Weija	0.03 - 0.06	0.05 ± 0.03	2 ng/m^3 (24 hour average) MassDEP, 1990
Mallam	0.01 - 0.02	0.02 ± 0.01	
Kaneshie First light	0.06 - 0.09	0.08 ± 0.03	
Graphic Road	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, Mallam, Kaneshie First light and Graphic Road respectively. Graphic Road 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 24 hour guideline value (2 ng/m^3) from MassDEP.

4.4 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.

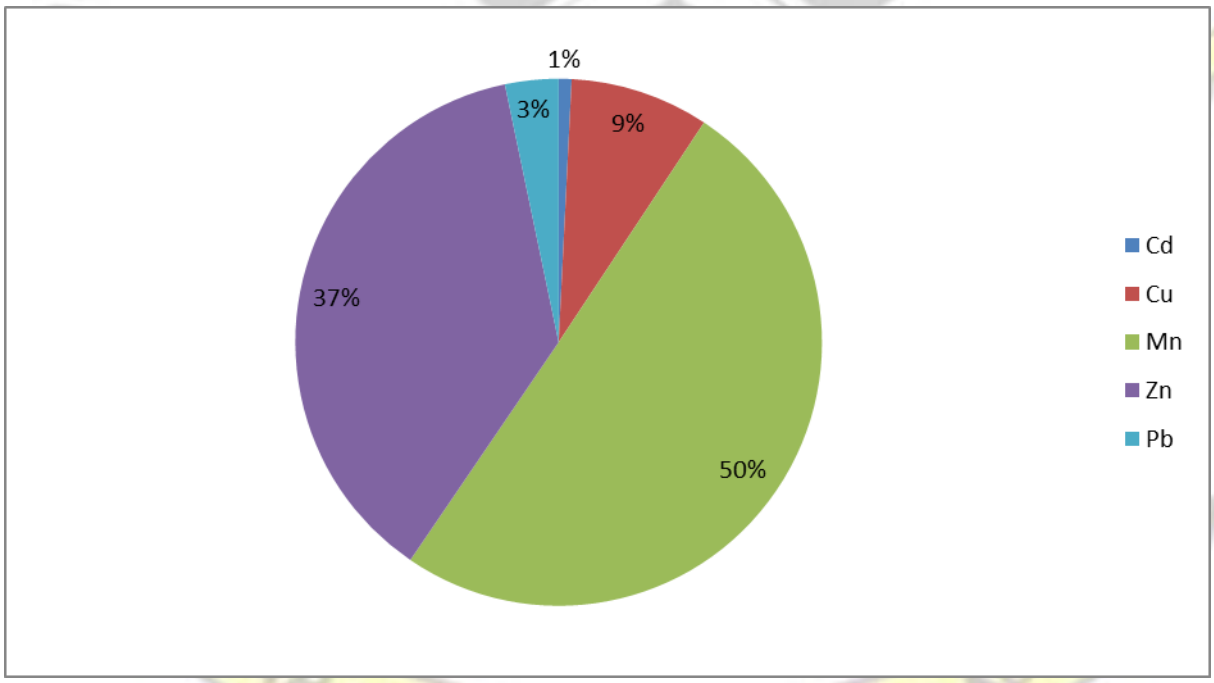

Figure: 4.2 Percentage concentrations of heavy metals in PM_{10} fraction

From fig 4.2 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.

CHAPTER FIVE

5.0 DISCUSSION

5.1 PARTICULATE MATTER (PM_{10})

From fig 4.1, it could be deduced that Weija had the highest mean PM_{10} concentration of 227.60 $\mu g/m^3$ followed by Mallam (211.00 $\mu g/m^3$) and Graphic Road which recorded the third highest mean PM_{10} concentration of 186.25 $\mu g/m^3$. Kaneshie First Light 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 was expected because Weija 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/carpentary shops, fitting shops, building and constructional activities and others. An untarred road leading to the Westfields School close to the sampling site could also be a possible influence on PM_{10} at Weija.

Mallam 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 recorded the third highest mean PM_{10} value (186.25 µg/m^3) followed by Kaneshie first light which recorded the lowest PM_{10} concentrations (166.67 µg/m^3). Unlike Mallam and Weija which had a lot of industrial activities which were likely to influence PM_{10} concentrations, Graphic road 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 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 and Graphic Road could probably be the most important source of PM_{10}.

From table 4.1, 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 µg/m^3 and 708 µg/m^3 on the fourth (11/11/2013) and last sampling day (29/11/2013) 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 and more than three times at Weija compared to the previous values recorded (264 µg/m^3 and 208 µg/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 on the fourth day ended at 11hours instead of 24 hours. The possible reason why sampling ended at 11 hours instead of 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 on the last sampling day (29/11/2013) also ended at 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 on the second day (30/10/2013) of sampling 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 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 recent 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.

5.2 HEAVY METALS IN PARTICULATE MATER (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 was 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 (2000188000 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 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 the 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, Mallam, Kaneshie First Light and Graphic Road 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 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 causes 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 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 metals concentrations recorded at Graphic road.

The percentage of metal concentrations in PM_{10} fraction was 50% manganese, 37% zinc, 9% copper, 3% lead and 1% cadmium (fig 4.2). 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.

5.2.1 ANOVA

As previously mentioned, significant variability‘s 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 and Mallam as well as Graphic Road and Weija revealed that the means of these sites were significantly different from each other with Graphic Road having the highest Cd concentrations in its PM_{10} size fraction than Weija and Mallam. Comparison of cadmium concentrations between two sampling sites other than Graphic Road and Mallam as well as

Graphic Road and Weija were not significantly different.

5.3 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.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMENDATIONS

6.1 CONCLUSION

This study revealed that ambient air at Weija, Mallam, Kaneshie first light and Graphic Road 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.

6.2 RECOMMENDATIONS

Though PM_{10} concentrations recorded in this study were very high, the metal constituents were very low. There is therefore need for further research to be carried out to determine what these high concentrations of PM_{10} is composed of. (e.g. the organic and ionic constituents could be determined).

Efforts should be made to reduce the levels of PM_{10} around these sites and in Accra as a whole in order to safeguard the health of people who live and work around these areas. To this end, long term studies should be carried out to determine the effects of PM_{10} on public health.

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APPENDICES

Appendix I: PM_{10} measurements carried out on the first sampling day (24/10/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{24/10/13}$	1224.3-1248.3	24	9.4139	9.4157	0.0018	250
$M_{24/10/13}$	1729.0-1753.0	24	9.2662	9.2679	0.0017	236
$K_{24/10/13}$	1227.4-1251.4	24	9.9405	9.9416	0.0011	153
$G_{24/10/13}$	4904.0-4928.0	24	9.5258	9.5275	0.0017	236

Appendix II: PM_{10} measurements carried out on the second sampling day (30/10/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{30/10/13}$	1248.3 - 1272.3	24	9.4224	9.4231	0.0007	97
$M_{30/10/13}$	1753.0 – 17770	24	9.2577	9.2581	0.0004	56
$K_{30/10/13}$	1251.4 – 1275.4	24	9.9560	9.9556	0.0004	56
$G_{30/10/13}$	4928.0 – 4952.0	24	9.5312	9.5317	0.0005	69

Appendix III: PM_{10} measurements carried out on the third sampling day (5/11/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{5/11/13}$	1272.3 – 1296.3	24	9.2512	9.2527	0.0015	208
$M_{5/11/13}$	1777.1 – 1801.1	24	9.2600	9.2619	0.0019	264
$K_{5/11/13}$	1271.4 - 1295.4	24	9.5167	9.5183	0.0016	222
$G_{5/11/13}$	4952.0 – 4975.0	23	9.5279	9.5294	0.0015	217

Appendix IV: PM_{10} measurements carried out on the fourth sampling day (11/11/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{11/11/13}$	1296.3 – 1320.3	24	9.2564	9.2581	0.0017	236
$M_{11/11/13}$	1801.1 – 1812.5	11	9.2484	9.2523	0.0039	1182
$K_{11/11/13}$	1281.4 – 1305.4	24	9.9483	9.9494	0.0011	153
$G_{11/11/13}$	4975.0 – 4975.0	0	9.5234	-	-	0

No sampling at graphic road battery fault

Appendix V: PM_{10} measurements carried out on the fifth sampling day (17/11/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{17/11/13}$	1368.3 – 1392.3	24	9.2496	9.2513	0.0017	236

$M_{17/11/13}$	1854.3 – 1878.3	24	9.5398	9.5408	0.001	139
$K_{17/11/13}$	1389.5 – 1413.5	24	9.5303	9.5313	0.001	139
$G_{17/11/13}$	5011.0 – 5035.0	24	9.5123	9.5131	0.0008	111

Appendix VI: PM10 measurements carried out on the sixth sampling day (23/11/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{23/11/13}$	1320.3 – 1344.3	24	9.2593	9.2608	0.0015	208
$M_{23/11/13}$	1812.5 – 1836.5	24	9.5501	9.5517	0.0016	222
$K_{23/11/13}$	1305.4 – 1329.4	24	9.9538	9.9553	0.0015	208
$G_{23/11/13}$	4975.0 – 4999.0	24	9.5380	9.5393	0.0013	181

Appendix VII: PM_{10} measurements carried out on the seventh sampling day (29/11/2013).

Sample ID	Elapsed time	Sampling period (hrs)	Initial weight of filter paper (W_1), g	Final weight of filter paper (W_2), g	PM_{10} Weight (W_2-W_1), g	PM10 Conc. (ug/m^3)
$W_{29/11/13}$	1344.3 – 1368.3	24	9.2396	9.2447	0.0051	708

$M_{29/11/13}$	1830.3 – 1854.3	24	9.5367	9.5381	0.0014	194
$K_{29/11/13}$	1353.4-1377.4	24	9.5192	9.5201	0.0009	125
$G_{29/11/13}$	4999.0 – 5011.0	12	9.5191	9.5193	0.0002	56

Appendix VIII: Metal concentrations in (ng/m^3) at Weija.

Weija					
Sample ID	**Cd (ng/m^3)**	**Cu (ng/m^3)**	**Mn (ng/m^3)**	**Zn (ng/m^3)**	**Pb (ng/m^3)**
$W_{24/10/2013}$	0.08	0.95	0.58	1.40	0.33
$W_{30/10/2013}$	*	0.91	4.40	3.40	*
$W_{5/11/2013}$	0.03	0.45	3.80	2.00	0.19
$W_{11/11/2013}$	0.04	0.21	5.90	2.00	0.09
$W_{17/11/2013}$	0.02	0.18	2.30	1.50	0.09
$W_{23/11/2013}$	0.08	0.24	1.48	2.94	0.30
$W_{23/11/2013}$	0.02	0.42	1.30	1.40	0.11

*= metal below limit of detection by the Atomic Absorption Spectrophotometer (AAS)

Appendix IX: Metal concentrations in (ng/m^3) at Mallam.

Mallam					
Sample ID	**Cd (ng/m^3)**	**Cu (ng/m^3)**	**Mn (ng/m^3)**	**Zn (ng/m^3)**	**Pb (ng/m^3)**
$M_{24/10/2013}$		0.18	1.40	1.80	0.09
$M_{30/10/2013}$	*	*	*	7.70	*
$M_{5/11/2013}$	0.02	0.16	0.76	1.40	0.08
$M_{11/11/2013}$	0.01	0.08	1.32	0.15	0.04
$M_{17/11/2013}$	0.01	0.30	0.44	0.84	0.15
$M_{23/11/2013}$	0.02	*	*	6.15	0.09

M29/11/2013	0.02	0.21	1.30	2.60	0.11

*= metal below limit of detection by the Atomic Absorption Spectrophotometer (AAS)

Appendix X: Metal concentrations in (ng/m^3) at Kaneshie First Light.

Kaneshie First Light					
Sample ID	**Cd (ng/m^3)**	**Cu (ng/m^3)**	**Mn (ng/m^3)**	**Zn (ng/m^3)**	**Pb (ng/m^3)**
K24/10/2013	0.11	1.20	0.33	2.70	*
K30/10/2013	*	0.75	4.90	6.90	*
K5/11/2013	0.05	0.19	3.80	1.70	0.09
K11/11/2013	0.11	0.57	1.10	0.27	0.14
K17/11/2013	0.03	0.30	3.00	3.70	0.15
K23/11/2013	0.10	0.02	0.74	2.54	0.46
K29/11/2013	0.07	0.33	2.23	4.03	0.60

*= metal below limit of detection by the Atomic Absorption Spectrophotometer (AAS)

Appendix XI: Metal concentrations in (ng/m^3) at Graphic Road.

Graphic Road					
Sample ID	**Cd (ng/m^3)**	**Cu (ng/m^3)**	**Mn (ng/m^3)**	**Zn (ng/m^3)**	**Pb (ng/m^3)**
G24/10/2013	0.08	0.95	0.58	1.40	0.33
G30/10/2013	*	0.91	4.40	3.40	*
G5/11/2013	0.03	0.45	3.80	2.00	0.19
G17/11/2013	0.02	0.18	2.30	1.50	0.09
G23/11/2013	0.08	0.24	1.48	2.94	0.30
G23/11/2013	0.02	0.42	1.30	1.40	0.11

No sampling at Graphic Road on the 11/11/2013 due to battery failure of air sampler.
*= metal below limit of detection by the Atomic Absorption Spectrophotometer (AAS)

Appendix XII: Mean concentrations of metals (ng/m^3) at the sampling sites.

Sampling site	Cd	Cu	Mn	Zn	Pb
Weija	0.05	0.48	2.83	2.09	0.18
Mallam	0.02	0.19	1.05	2.95	0.09
Kaneshie First Light	0.08	0.48	2.30	3.12	0.29
Graphic Road	0.15	0.47	4.78	5.70	0.47

Appendix XIII: ANOVA results of mean metal concentrations.

Metal	F-value	p-value
Cadmium	4.33	0.018 *
Copper	1.16	0.35
Manganese	1.53	0.24
Zinc	2.22	0.11
Lead	1.53	0.24

Appendix XIV: Descriptive statistics for cadmium at the four sampling sites.

Variable	Total Count	Mean	SE Mean	St Dev	Minimum	Maximum
WCd (ng/m^3)	6	0.05	0.01	0.03	0.02	0.08
MCd (ng/m^3)	5	0.02	0.00	0.01	0.01	0.02
KCd (ng/m^3)	6	0.08	0.01	0.03	0.03	0.11
GCd (ng/m^3)	5	0.15	0.05	0.12	0.05	0.30

One-Way ANOVA:

Source	DF	SS	MS	F	P
Factor	3	0.04843	0.01614	4.33	0.018
Error	18	0.06709	0.00373		
Total	21	0.11552			

S = 0.06105 R-Sq = 41.92% R-Sq(adj) = 32.24%

Appendix XV: Descriptive statistics for copper at the four sampling sites.

Variable	Total Count	Mean	SE Mean	St Dev	Minimum	Maximum
WCu (ng/m^3)	7	0.48	0.12	0.33	0.18	0.95
MCu (ng/m^3)	5	0.19	0.04	0.08	0.08	0.30
KCu (ng/m^3)	7	0.48	0.15	0.39	0.02	1.20 GCu
(ng/m^3)	5	0.47	0.13	0.29	0.18	0.96

One-way ANOVA:

Source	DF	SS	MS	F	P
Factor	3	0.3399	0.1133	1.16	0.350
Error	20	1.9560	0.0978		
Total	23	2.2959			

S = 0.3127 R-Sq = 14.80% R-Sq (adj) = 2.02%

Appendix XVI: Descriptive statistics for manganese at the four sampling sites.

Variable	Total Count	Mean	SE Mean	St Dev	Minimum	Maximum
WMn (ng/m^3)	7	2.82	0.73	1.93	0.58	5.90

MMn (ng/m^3)	5	1.05	0.19	0.42	0.44	1.40
KMn (ng/m^3)	7	2.30	0.64	1.69	0.33	4.90
GMn (ng/m^3)	5	4.78	2.44	5.45	0.30	14.00

One-way ANOVA:

Source	DF	SS	MS	F	P
Factor	3	36.51	12.17	1.53	0.237
Error	20	158.98	7.95		
Total	23	195.49			

S = 2.819 R-Sq = 18.68% R-Sq(adj) = 6.48%

Appendix XVII: Descriptive statistics for zinc at the four sampling sites.

Variable	Total Count	Mean	SE Mean	St Dev	Minimum	Maximum
WZn (ng/m3)	7	2.09	0.29	0.79	1.40	3.40
MZn (ng/m3)	7	2.95	1.08	2.86	0.15	7.70
KZn (ng/m3)	7	3.12	0.79	2.09	0.27	6.90
GZn (ng/m3)	5	5.70	1.64	3.67	1.80	11.00

One-way ANOVA:

Source	DF	SS	MS	F	P
Factor	3	40.12	13.37	2.22	0.114
Error	22	132.55	6.03		
Total	25	172.67			

S = 2.455 R-Sq = 23.23% R-Sq(adj) = 12.76%

Appendix XVIII: Descriptive statistics for lead at the four sampling sites.

Variable	Total Count	Mean	SE Mean	St Dev	Minimum	Maximum
WPb (ng/m3)	6	0.18	0.04	0.12	0.09	0.33
MPb (ng/m3)	6	0.09	0.02	0.04	0.04	0.15
KPb (ng/m3)	5	0.29	0.10	0.23	0.09	0.60
GPb (ng/m3)	6	0.47	0.23	0.57	0.05	1.50

One-way ANOVA:

Source	DF	SS	MS	F	P
Factor	3	0.4581	0.1527	1.53	0.238
Error	19	1.8904	0.0995		
Total	22	2.3485			

S = 0.3154 R-Sq = 19.51% R-Sq(adj) = 6.80%

Appendix XIX: Pearson correlation analysis between PM_{10} concentrations and metal concentrations at Weija.

Metal	Pearson correlation (r)	p-value
Cadmium	-0.43	0.39
Copper	-0.19	0.68
Manganese	-0.42	0.35
Zinc	-0.58	0.17
Lead	-0.35	0.50

Appendix XX: Pearson correlation analysis between PM_{10} concentrations and metal concentrations at Mallam.

Metal	Pearson correlation (r)	p-value

Cadmium	-0.54	0.35
Copper	-0.81	0.09
Manganese	0.41	0.49
Zinc	-0.51	0.24
Lead	-0.79	0.06

Appendix XXI: Pearson correlation analysis between PM_{10} concentrations and metal concentrations at Kaneshie First Light.

Metal	Pearson correlation (r)	p-value
Cadmium	-0.05	0.92
Copper	-0.21	0.66
Manganese	-0.25	0.58
Zinc	-0.76	0.05
Lead	-0.78	0.12

Appendix XXII: Pearson correlation analysis between PM_{10} concentrations and metal concentrations at Graphic Road.

Metal	Pearson correlation (r)	p-value
Cadmium	-0.23	0.77
Copper	0.04	0.95
Manganese	-0.46	0.44
Zinc	-0.91	0.03
Lead	-0.05	0.95

Plate 1: Atomic Absorption Spectrophotometer (model AA-200 Series; Agilent Technologies)

Plate 2: loaded quartz filter papers being conditioned in a desiccator.

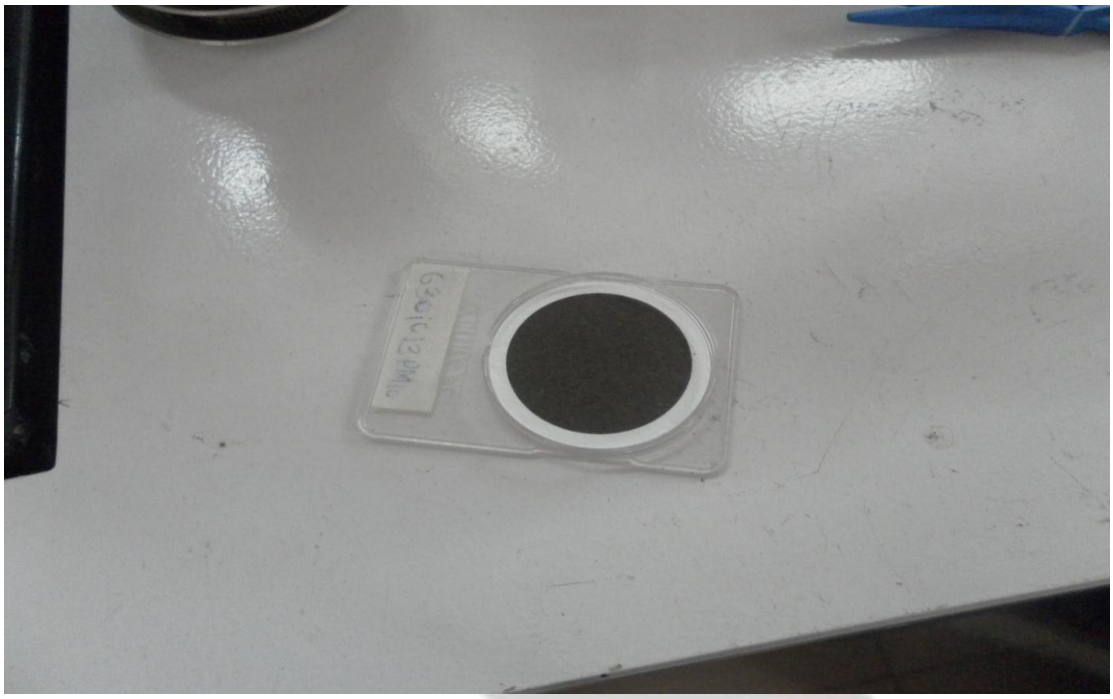

Plate 3: quartz filter paper loaded with particles in a sample cassette with identification.

Plate 4: Unmounting the Mini Vol. Air Sampler at Kaneshie First Light

Plate 5: Vehicular traffic, a major source of air pollution in Accra

Plate 6: Air pollution from vehicular exhaust

Plate 7: Biomass burning; a source of particulate matter emission into the Atmosphere

Plate 8: Air pollution around Graphic Road in Accra due to waste burning