DESIGN AND FABRICATION OF AIR SAMPLER IN AIR QUALITY ASSESSMENT FOR SELECTED HEAVY METALS IN KADUNA METROPOLIS

By

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P13EGWR8010

DEPARTMENT OF WATER RESOURCES AND ENVIRONMENTAL

ENGINEERING FACULTY OF ENGINEERING

AHMADU BELLO UNIVERSITY ZARIA

NIGERIA

MAY, 2017

COVER PAGE

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A DISSERTATION SUBMITTED TO THE DEPARTMENT OF WATER RESOURCES AND ENVIRONMENTAL ENGINEERING AHMADU BELLO UNIVERSITY, ZARIA NIGERIA

DEPARTMENT OF WATER RESOURCES AND ENVIRONMENTAL ENGINEERING FACULTY OF ENGINEERING AHMADU BELLO UNIVERSITY ZARIA NIGERIA

MAY, 2017

DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled "DESIGN AND FABRICATION OF AIR SAMPLER IN AIR QUALITY ASSESSMENT FOR SELECTED HEAVY METALS IN KADUNA **METROPOLIS**"has been carried out by me in the Department of Water Resources and Environmental Engineering.is in the fulfillment of the requirement of the award of the degree of Master of Science in Water Resources and Environmental Engineering, The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any Institution.

_____ _____

GUJBAWU Halima Habib. **Date**
P13EGWR8010

CERTIFICATION

This dissertation entitled"DESIGN AND FABRICATION OF AIR SAMPLER IN AIR QUALITY ASSESSMENT FOR SELECTED HEAVY METALS IN KADUNA **METROPOLIS**", submitted by GUJBAWU HALIMA HABIBmeets the regulations governing the award of the degree Master of Science inWater Resources and Environmental Engineering of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicate this work to my husband Engr Muhammed Habib, All members of Gujbawu family for their love and to all the staff of the Department of Water Resources and Environmental Engineering, Ahmadu Bello University for their tireless and selfless efforts they have spared in making me who I am today.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to Dr. E .M. Shaibu-lmodagbe for his guidance and assistance in this project. I will always be indebted to him for all the knowledge he shared with me. His prompt responses and availability despite his constantly busy schedule were truly appreciated. The reality is that he was much more than a supervisor to me. His encouragement and efforts led this project to successful completion. I would also like to thank Dr. A .Giwa for his insightful suggestions, which have been greatly helpful for the advancement of my research and further study.

I would also like to thank Prof. C.A Okuofu for being an excellent advisor and mentor. He was always open minded, helpful and provided me with strong broad ideas of knowledge.

I would also like to thank Prof. A. Ismail, my head of department for providing a good research environment. I feel privileged to have passed through the distinguished lecturers of the Department of Water Resources and Environmental Engineering and as well, a million thanks to Mr. P.C Alika, Mallam Yahaya Yakubu, Mr. Sani, Hajiya Dr F .B.Ibrahim. In addition, I would like to express my heartfelt gratitude to my wonderful course mates for their sacrifices especially Juliana Iji, Haruna Yusuf,Shamsu Jamilu,Rabiyu Musa,Aliyu,Abdulmajid, Mayaki Daniel for their constant encouragement and help throughout my whole study, just to mention, but a few cannot go unmentioned.

My deepest appreciation goes to my loving parents, my brothers and sisters for their unfailing love, unconditional sacrifices and tutelage which gave me a solid foundation by instilling in me the spirit of discipline, hard work and the principle of success. Finally, I'm most grateful to the Almighty God for His good hands of wisdom, grace, mercies, faithfulness and favors upon me. ALLAMDULILAH.

ABSTRACT

Investigations were carried out for heavy metals composition of ambient air using a special instrument designed for this purpose. The lack of portable air sampler is a major obstacle to air pollution studies in Nigeria of recent. As a remedy to this, a simplified air sampler was designed and fabricated at the Water Resources and Environmental Engineering Department. Varied designs of this sampler were constructed and deployed for assessing the air quality of some selected heavy metals in some commercial areas in Kaduna metropolis such as Chechenia Market, Ahmadu Bello Way, Old and New Panteka. The instrument was mounted in strategic locations free from interference by humans and other natural factors. In accordance with standard methods, the trapped samples were washed in de-ionized water, diluted and digested and analyzed by Atomic Absorption Spectrometer (AAS) for the heavy metals zinc (Zn) lead (Pb) and iron (Fe). From the results Chechenia Market recorded mean values of Zn=1.55, Pb=0.00 and Fe=1.65 mg/l, Old Panteka recorded mean values of Zn= 0.13, Pb=0.00, Fe=4.29 mg/l and New Panteka recorded mean values of Zn=3.05, Pb=0.02, Fe=2.37 mg/l. These results were compared with national and international standards of National Environmental Standards and Regulations Enforcement Agency (NESREA) (2009) and the World Health Organization (WHO) (2011).Pb showed low mean values in the rainy season while the mean values obtained in the dry season were high. Zn and Fe maintained a fairly constant mean value though the values for Fe were high above recommended values of NESREA (2009)/WHO (2011).The results showed that Zn and Fe were above the permissible limits while Pb was within the permissible limit.The presence of these heavy metals in these areas maybe from numerous on-going human activities such as smelting of metals, vehicle exhaust, wearing of brake pads, tire abrasion, road dust and burning of refuse, among others. This investigation has highlighted that these heavy metals fractions exist in the air around these parts of Kaduna metropolis and they could be detrimental to human health. Further studies are recommended to determine the risks posed by these fractions and develop technological and management options for their reduction. Phasing out any remaining use of heavy metal additives should be encouraged.

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LIST OF ABBREVIATIONS

PM	Particulate matter
WHO	World Health Organization
LPG	Liquid Petroleum Gas
TSP	Total Suspended Particulate
SPM	Suspended Particulate Matter
GEMS	Global Environment Monitoring System
AMIS	AirManagement Information System
APEG	Airborne Particulates Expert Group
USEPA	United State Environmental Protection Agency
PAH	Polyaromatic Hydrocarbons
AAS	Atomic Absorption Spectrometry (AAS).
GFAAS	Graphite furnace atomic absorption spectrophotometry
ASV	Anode stripping voltametry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ETV-ICP-MS	Electrothermal Inductively Coupled Plasma Mass Spectrometry
XRFS	X-ray fluorescence spectroscopy
NAA	Neutron Activation Analysis
IDMS	Isotope Dilution Mass Spectrometry
FAAS	Flame Atomic Absorption Spectroscopy
ETAAS	Electrothermal Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
STGFAA	Temperature Graphite Furnace Atomic Absorption

ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
FID	Flame-Ionization Detection
ECD	Electron Capture Detection
INAA	Instrumental Neutron Activation Analysis
PHD	Pulmonary Heart Disease
FVC	Forced Vital Capacity
FEV	Forced Expiratory Volume
ANOVA	Analysis of Variance
SPSS	Statistical Package for Social Sciences
NESREA	National Environmental Standards Regulation and Enforcement Agency
SRM	Standard Reference Material
HDV	Heavy Duty Vehicles
LDV	Light Duty Vehicles
MMT	Methylcyclopentadienyl Manganese Tricarbonyl

CHAPTER ONE

INTRODUCTION

Pollutants can be in the form of solid particles, liquid droplets, or gases, in addition, they may be natural or man-made (Anderson, 2005). It can be air, water or land and can result from mining, automobile exhaust, agricultural and industrial activities among others. Heavy metals were since classified among major causes (Galadima *et al.,* 2011). Of the important pollutants, heavy metals cause serious harmful effects on the environment. Standard limits andinternational guidelines specify maximum level for various pollutants in air samples; however no restrictions have yet been set in Nigerian towns and cities. Major towns and cities have often suffered from smoke emanating from residential building, refused dumps and bio-mass incineration. Residual oil combustion and automobile exhaust which are all as a result of human activities results in release of toxic materials (e.g. heavy metals) into the atmosphere (Okou and Nchiokwere, 2005).

Suspended particulate matter is one of the most important constituents of atmospheric pollution. Consequently, exposure to airborne particles is a common event. Suspended particulate matter is a complex mixture of elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements and water droplet. Among all air pollutants, particulate matter (PM) especially respirable PM which can be inhaled into the human respiratory system (Wallenborn *et al*., 2009) is related to the most serious health effects including pulmonary and cardiovascular illnesses (Harrison, 1999). The chemical characteristics of atmospheric particulate are important for both particle toxicity and its role in climate change (Hueglin *et al*, 2005, IPCC, 2001; Salve *et al*, 2007).

Suspended particulate matter is a mixture of organic and inorganic substances characterized by their physical attributes, which influence their transport and deposition, and their chemical composition which influences their effect on health. Heavy metals are chemical elements with a

specific gravity which is at least 5 times the specific gravity of water (which is 1 at $4^{\circ C}$ (39°F). Known toxic metallic elements with a specific gravity that is 5 or more times that of water are Arsenic – 5.7, - Cadmium – 8.65 Iron – 7.9, Lead - 11.34 and Mercury 13.546, (WBG, 1998). This classification also includes some heavy metals in group III to V in the periodic table. Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed (Galadima and Garba, 2012). Although these elements are lacking in abundance they are not lacking in significance (Chen and Chen, 2001). Mercury and lead for example are commonly used in technology but are so toxic that minute quantities can destroy life. In Nigeria numerous studies indicated that industrial activities releaseheavy metals either as solids, gas or liquids in the form of waste water allowed to drain into water bodies and water ways.

1.1 HEAVY METALS IN NIGERIAN ENVIRONMENT

Heavy metals are generally introduced into the environment through water, air and soil (Ayodele and Abubakar, 2001, Ibeto and Okoye, 2010). However the degrees of concentration depend on the type of heavy metals and activities taken place in a particular area. Nowadays in Nigeria several ways have been identified through which specific heavy metal can be transmitted into living species.

Heavy metals are released from various sources such as municipal wastewater sludge, urban composts, road traffics, atmospheric deposits and agrochemicals such as fertilizers, pesticides, fungicides and so on. Within the terrestrial ecosystem, soil plays a major role in element cycling and accumulates heavy metals in concentration orders of magnitude higher than in water and air (Udensi, 2010). The impact of heavy metals on the environment is a concern to the government

regulatory agencies and the public. Deposition of air pollutants is captured by the plant canopy and accumulated in or on the leaves. As the accumulation is roughly a function of the deposited amount of pollutants, the exposure time and the effects of climatic factors are of prime importance.

Metals that are from airborne sources are usually discharged as particulates consist on the gas stream. Some metals like cadmium (Cd), Arsenic (As) and lead (Pb) can similarly volatilize by high temperature activities. These metals will change to oxides because of smaller suspended particulate matter until the pollution levels are high (Smith *et al*. 1995). Emissions from chimney may be circulated over an extensive area by natural air flow still dry and wet precipitation actions thereby eliminate them from the gas tributary and into the environment.

Heavy metal is a general term which applies to the group of metals and metalloids with an atomic density greaterthan 4g/cm3 (Ademoriti, 1996). Most of the heavy metals accumulate in the biological environment in different ways, via the nutrient chain. Increasing heavy metal accumulation at critical levels in living organisms, some contaminated environment may have morbidity and mortality effects. Commercial and industrial garbage may contain toxic materials such as lead, mercury, cadmium, manganese from batteries, insect sprays, nails, polish cleaners, plastics or polyvinyl chlorides, bottles and other assorted product which have unknown physiological effect when ingested (Dosumu *et al*, 2003). The major effect of lead may include anemia, effects on the nervous system, reproductive system, cardiovascular, and hepatic, renal endocrinal and gastrointestinal systems. Lead is toxic even at low concentration and has no function in biochemical process (Sobolv *et al*, 2008). Once liberated into the environment through the air, drinking water, food, or countless varieties of man-made chemicals and products,

heavy metals are taken into the body via inhalation, ingestion and skin absorption. If heavy metals enter and accumulate in body tissues faster than the body's detoxification pathways can dispose of, then a gradual build-up of these toxins occurs. High concentration exposure is not a necessity to produce a state of toxicity in the body, as heavy metal accumulation occurs in body tissues gradually and, over time, can reach toxic concentration levels, much beyond the permissible limits (Suruchi *et al*, 2012). Lead and cadmium are among the most abundant heavy metals and are particularly toxic. The excessive amount of these metals in food is associated with etiology of a number of diseases, especially with cardiovascular, kidney, nervous as well as bone diseases (Sanchez-Castillo *et al*., 1998; Steenland and Boffetta, 2000). Lead is well known for its toxicity and adverse effects on human health. Absorption of ingested lead may constitute a serious risk to public health. Some chronic effects of lead poisoning are colic, constipation and anemia (Bolger *et al*. 2000).

1.2 SCOPE OF THE STUDY

The scope of the study was developing a model that was used to collect heavy metals in suspended particulate matter in Ahmadu Bello Way, Old Panteka and New Panteka.

1.3 LIMITATION OF THE STUDY

Limitations of the study include:

1. Difficulties in situating the model
2. Sampling with the model was also difficult because of placing the sampler; people were also scared due to the security challenge in the country.

3. There was also the problem of power due to difficulty in changing the battery because the sampler discharges its battery often.

1.4 STATEMENT OF RESEARCH PROBLEM

Like in most developing nations the issues of maintaining good atmosphere are much and these importance include; lack of equipment and tools, inadequate expertise, lack of infrastructure and weak policy frame work. This and many other factors has been the obstacle to achieving the much desired goals towards preserving the quality of the air and safeguarding the health of the public in the region. Hence the need to provide a local air sampler in order to achieve one of this goals.

1.5 JUSTIFICATION.

The fabrication of a local air sampler will help in address some of the factors that will help in achieving air quality and environmental health in developing nations, cause assessing pollutants in different components of the ecosystem has become an important task in preventing risk to wildlife and public health.

1.6 AIM OF THE STUDY

The aim of this work is to design an air sampler for air quality and assess the heavy metal concentration of ambient air of some selected commercial Areas in Kaduna Metropolis.

1.7 OBJECTIVES

i. To design and construct a Model Air sampler.

ii. To determine the atmospheric levels of heavy metals in the selected areas.

iii. To clarify the status of the area's air quality.

iv. To determine the probable sources of the pollution.

CHAPTER TWO

LITERATURE REVIEW

2.0 URBAN VERSUS RURAL EMISSION SOURCES

In addition to problems of local versus regional sources, urban and rural areas in developing countries also merit a closer examination as they exhibit unique characteristics with respect to particulate matter(PM) sources and concentrations and each other. Rural areas contain approximately two thirds of the developing world population, although this is slowly changing with urbanization. Urbanization is a process that has characterized much of the developing world in the latter part of the twentieth century. The majority of the megacities in the world are located in the developing world. Most of those cities are ill equipped to absorb such a fast growing population. The lack of infrastructure has brought on severe problems such as waste management, lack of clean water and sanitation and high levels of air pollution (PAHO 1998). Caught in a period of economic transition, urban centers of the developing world have a curious mix of rural air pollution problems of the developing world and urban air pollution problems of the developed world. A survey conducted by the WHO in 1994 looked at air pollution levels in 12 megacities, 10 of which were located in developing countries. Megacities located in developing countries have a wider range of air pollution sources compared to cities located in developed countries. The range of sources, however, is closely linked with key factors such as level of motorization, and the level, density, and type of industry present (WHO 1994). Sources of air pollution within megacities include motor traffic, power generation and industry, domestic coal and biomass fuel use; open burning of refuse, natural windblown particles. Motor traffic is the most important source of particulate matter (PM) in cities with a high motor vehicle density, e.g., in Lagos in Nigeria. The majority of the cars in some developing countries are diesel

powered, which generate on the order of ten times more irrespirable particles than gasoline engines per kilometer driven (Rallis 1988, Krupnick 1991). Cars found in developing countries also tend to be older and thus more polluting. Vehicles play a much less significant role in pollution where there is either a lower level of motorization, e.g., in Africa, or particulate matter(PM) sources are dominated by domestic coal or biomass fuel combustion, e.g., in temperate regions such as China and parts of Eastern Europe. In addition to the sources of air pollution within the developing countries, topography will also influence the fate of air pollution. The WHO has divided the megacities under examination into one of three categories: Cities not influenced by a body of water, under which fall cities such as Beijing, Cairo, Delhi, and Moscow; Cities influenced by a body of water with a relatively level topography, which include Bangkok, Bombay, Buenos Aires, Calcutta, Jakarta, Karachi, London, Manila, and Shanghai; And cities whose meteorology is influenced by surrounding mountains with a variable topography, which include Mexico City, Santiago, Rio de Janeiro, and São Paulo.

These topographical features as well as certain seasonal features can either exacerbate or lessen the problems related to the severity of air pollution. In cities located in regions with temperate and cold climates fuel consumption due to heating is higher than in areas with moderate and warm climates. Meteorological phenomena such as thermal inversions are more frequent. Thermal inversions reduce the dilution and dispersion capability of the atmosphere and trap air pollutants (including particulate matter{ PM}) close to the emission source (Terblanche, 1993). Similar effects are seen in areas that are surrounded by mountains, where mountains act as a barrier and trap air pollution close to the city (WHO, 1994).

Sources of particulate matter(PM) in rural areas of developing countries can differ quite significantly from those that were observed in the megacities of the world. They are dominated by domestic sources, namely stoves used for cooking, and in the colder climates, for space heating as well. In 1988, about half of the world's households used unprocessed biofuels such as wood, dung, and crop residues for daily cooking purposes (Smith, 1988). Most unprocessed biofuels and fuels such as coal are high emitters of particulate matter, and a multitude of other pollutants such as sulfur oxides, nitrogen oxides, hydrocarbons, and carbon monoxide (Smith 1988). Type of biofuel used, and thus emissions, varies from region to region. In China, coal is burned in unvented stoves, whereas in most of South Asia, kerosene is used in inexpensive stoves giving off high levels of particulate emissions. Africa's fuel consumption drives the use of such biofuels as wood, which has led to problems of deforestation in some sub-Saharan African regions. Wood fulfills the fuel consumption needs of some 90% of the urban households in Africa for cooking, and is probably as high if not higher in rural areas (Krupnick 1991). In general, biofuels are used in developing countries because of their availability and affordability. The use of poor quality biofuels decreases with development, thus the least developed areas are most likely to experience the highest levels of air pollution (Smith 1993). Cook stove efficiencies, according to fuel, are 20%, 30%, 50%, and 70% for wood, charcoal, kerosene, and Liquid Petroleum Gas (LPG) stoves respectively. Unfortunately fuel efficiency seems to be inversely correlated with the amount of health damaging pollutants it emits per joule of energy (Smith 1994). Biofuels such as wood, charcoal and kerosene emit known carcinogens such as 1,3butadiene, benzene and benzo[A]pyrene. For these reasons, Smith observes that air pollution tends to be worse in rural indoor environments than urban outdoor environments (Smith, 1988).

2.2 CONCENTRATIONS OF SUSPENDED PARTICULATE MATTER (PM).

Particulate matter(PM) in the air is a complex mixture of particles from primary sources (direct emissions to the atmosphere) and secondary sources (chemical transformation in the atmosphere). Particulate matter measured at different locations may differ considerably in sizes as well as in chemical and physical properties. In developed countries, the difference between the mass concentration of Total suspended particulates (TSP) and particulate matter(PM) between PM_{10} and $PM_{2.5}$ is usually larger in urban and industrial areas than in rural areas. This is due to the larger fraction of relatively small secondary particles in rural areas, originating mainly from long-range transport of air pollutants (Tarrasón and Tsyro 1998). Sedimentation and deposition of large particles takes place close to the emission sources. Thus, the proportion of $PM_{2.5}$ relative to TSP and PM_{10} is usually higher in rural areas. Typical contributions of sulfate, nitrate and ammonium particulates to the total $PM_{2.5}$ mass are about 40% in urban areas and 50% in rural regions (e.g., Seinfelt and Pandis 1998). Elemental and organic carbon is the second significant component contributing to $PM_{2.5}$ mass. However, in developing countries primary PM emissions from local sources such as stoves (heating and cooking) may influence ambient PM concentrations in urban and rural areas to a bigger extent than in developed countries. Peters *et al*. (1997) looked at both size and mass concentrations of fine PM, i.e., $PM_{2.5}$ in Erfurt, a city in Eastern Germany. Ambient air samples were taken during winter months in 1991 and 1992. Since Erfurt is located in a valley (Thüringer Wald), frequent inversions trap air in the city in winter. Peters *et al*. (1997) found that ultrafine particles accounted for 73% of the particles counted per cm^3 air even though their total contribution to the mass concentration of all fine particles was approximately 1%. And as size of the particles increased, their contribution to the total number concentration decreased, while their contribution to the overall mass concentration

increased (Peters *et al.* 1997). Most monitoring stations in developed and developing countries are located in urban areas. Thus, information on ambient PM concentrations in rural areas is generally sparse. PM measurement results depend also on the sampler type used. A wide variety of particulate sampling instrumentation is available, e.g., impactor samplers, filter pack or denuder systems. The samplers usually collect selected parts of the Suspended particulate matter(SPM), e.g., containing teflon filters with a 2-µm pore size collecting fine $PM_{2.5}$ and coarse $PM_{2.5}$ to PM_{10}. Additionally, there are different techniques to analyze the samples, e.g., gravimetric methods to measure mass concentrations or X-ray analyses and ion chromatography to detect selected chemical elements. Few studies on comparing different sampling and analytical methods have been conducted so far, emphasizing that there is a need to introduce reference methods within monitoring programs (e.g., in Canada; Nejedlý *et al.* 1998).

2.2.1 PM Concentrations in Developing Countries

The particulate matter concentrations that have been observed in developing countries have traditionally been high, much higher than those seen in developed countries. The literature gives a wide array of measurements, making it difficult to directly compare the results. Measurements are given as outdoor ambient concentrations of PM, indoor concentrations of PM and personal exposures measurements. Most of the measurements are taken for the duration of the study period. Thus long-term PM measurements are not available. One of the only programs to actually measure long term concentrations is the Global Environment Monitoring System (GEMS) air monitoring program established by the World Health Organization (WHO) in 1973. Many of the studies cited in this literature review use data from the GEMS air monitoring program. GEMS is set up to monitor for pollutants such as sulfur dioxide (SO_2) and SPM, and measurements are made at two or three designated sites per city (Bennett *et al.* 1985).

Krzyzanowski and Schwela (1999) looked at trends of air pollution using WHO's Air Management Information System (AMIS), a part of the GEMS air monitoring program, as the main source of measurements. The 1990s data show both increasing and decreasing trends in a similar number of cities, with no systematic and/or significant change in TSP levels. Both Bangkok and Mexico City exhibited decreases in Total Suspended particulate (TSP) levels, although Mexico City more consistently than Bangkok. Certain Chinese cities, on the other hand, have experienced increases in TSP levels, with the fastest rising levels occurring in 1990-1992to more in recent years. PM_{10} levels were also measured for some cities. The highest concentrations were found in Calcutta and New Delhi with levels exceeding 200. The majority of the PM_{10} concentrations observed fell within the range of 50. Already high PM_{10} levels were observed to increase over the last decade in most towns, even while TSP levels were falling (Krzyzanowski and Schwela, 1999). Some Southern American cities experienced the reverse trend, and had falling PM_{10} levels. In Mexico City, however, the relative decrease in PM_{10} was greater than that of TSP.

A report entitled "Air Pollution in Megacities" was put out in 1994 by the WHO to compare air pollution problems in 20 megacities, the majority of which located in developing countries. Given that the WHO air pollution guidelines at this time for TSP for 24-hour for PM_{10} 24-hour average concentration, the WHO found that the majority of the megacities were out of compliance. Of the 20 megacities that the WHO looked at in their Air Pollution in Megacities report, 17 of them had suspended particulate matter levels exceeding WHO guidelines by up to or more than a factor of two. SPM is a critical problem in megacities, but even more so in cities with simultaneously high concentrations of SO_2. Peak concentrations can be as (WHO, 1994).In the urban and industrial areas of São Paulo state, measurements of TSP (Sato *et al.* 1995).

Studies conducted in Mexico City looked at TSP levels for 1990 through 1992 and where measurements were recorded every sixth day as a 24-hour integrated (Borja-Aburto *et al*. 1997) PM_{10} levels were also for 24 hours (Romieu *et al.* 1996). A study conducted in Lucknow, India had measurements of SPM, for 1993 to 1994, (Awasthi *et al.* 1996a). Cropper and colleagues' measurements for TSP between the years 1991 and 1994 (Delhi) found and reached a maximum concentration of 1714 $\mu g/m^3$. TSP levels in Delhi exceeded the WHO's 1987 24 hour standard on 97% of all days on which readings were taken (Cropper *et al.* 1997).

Although measurements of PM are taken as TSP and to a lesser extent PM_{10}, the more health relevant particles are PM_{10} or smaller. Thus available data on PM_{10} and TSP has allowed ratios of PM_{10}/TSP to be calculated. In developing countries where this information is accessible, the range is approximately from 0.4-0.8 (Krzyzanowski and Schwela 1999). A PM_{10}/TSP ratio of 0.5 was found for Mexico City (Borja-Aburto *et al.* 1997). In a Bangkok study, ratios of $PM_{2.5}$ to PM_{10} were looked at for indoor and outdoor environments and found to be ranging from 0.45 to 0.88 indoors, and 0.48 to 0.86 outdoors (Chestnut *et al*. 1998).

Since most of the measurement data in developing countries is only for TSP and PM_{10},

Wilson and Suh (1997) used available data from Philadelphia, to more closely examine the relationship between the health relevant PM fractions.

Both the mass and the number of particles in the PM_{10} category are comprised of $PM_{2.5}$ (< 2.5 μm) and $PM_{10\text{-}2.5\mu m}$, but the question is to what degree. $PM_{2.5}$ dominates both the PM_{10} mass and number concentrations, and as such actually is the primary cause of the day-to-day variability in PM_{10}. $PM_{2.5}$ contributes approximately 2.75 times more variability to PM_{10} than $PM_{10\text{-}2.5}$ (Wilson and Suh 1997). In addition, PM_{10} and $PM_{2.5}$ levels exhibited a high degree of correlation whereas the lowest level of correlation existed between $PM_{10\text{-}2.5}$ and $PM_{2.5}$. The conclusion reached seems

to be that in cities with fine particulates exceeding levels of coarse PM, the variation in PM_{10} arises mostly from the fine particulates (Wilson and Suh, 1997). If this conclusion can be generalized for all areas with higher levels of fine PM than coarse particulates, then it may be reasonable to use PM_{10} as a proxy for exposure to $PM_{2.5}$. This finding seems to be fairly important as more and more research finds that human health risks are increasingly associated with the finer fraction of PM.

2.3 TYPES OF PARTICULATE MATTER

2.2.2 Atmospheric Particulate Matter

Atmospheric PM displays a wide range of physical and chemical properties. It is a complex mixture oforganic and inorganic substances, in solid or liquid form, which undergo modification or transformationwithin the atmosphere. Airborne particles range in size from less than 10μm to around 100μm. Particles largerthan 100μm tend to fall out of the atmosphere rather quickly, and are generally termed 'dustfall' (Warner *et al*., 2000).

. Particle sources are termed either ‘primary’, where particles are emitted directly into theatmosphere or ‘secondary’ where they are formed by reactions between gas-phase components. The non-exhaustprocesses discussed in this Report are primary, and mainly anthropogenic, particle sources. However,natural particle sources also need to be taken into account when considering resuspended road dust.

Nucleation mode and accumulation mode particles primarily originate from combustion sources, such as roadvehicle exhaust, waste incineration, and industrial and domestic burning Warner, *etal.,* 2000. Coarse particles, on the other hand are usually generated by mechanical processes such as erosion, construction, quarrying, and tyre wear. Themain constituents of primary particles are crustal elements (*e.g*. silicon, aluminum, calcium, iron), elementalcarbon, and

various organic compounds. Secondary particles are mainly composed of inorganic compounds,including sulphates, ammonium and nitrates.

A number of metrics are used to define atmospheric particle samples. Prior to 1990, total suspendedparticulate (TSP) was commonly sampled. However, according to the UK Airborne Particulates Expert Group(APEG, 1999), such data are of limited use since TSP is an old specification for airborne particles, and it is not necessarily relevant to those particles that can enter the human respiratory system. The parametercommonly used now is the mass concentration of the PM_{10} fraction. PM_{10} describes the particles which pass asampler entry with 50% efficiency at 10μm. To a reasonable approximation, PM_{10} describes PM smallerthan 10μm aerodynamic diameter. These particles can penetrate the larynx and enter the thoracic region of their respiratory system. Other metrics that are in common use are the mass concentrations of the $PM_{2.5}$, PM_1, and$PM_{0.1}$ particle fractions.

2.2.3 Tyre Wear Particles

In 1999 more than 54 million passenger car tyres were used in the UK, equating to a total weight of more than430,000 tones (Used Tyre Working Group, 2000). A new tyre on an average European passenger car weighsaround 8kg, and loses roughly 1-1.5kg in weight during its service lifetime, which is typically around 3 yearsor 50-60,000 km. Thus, between around 10% and 20% of the rubber which goes into a tyre will disappearbefore the tyre is ready to scrap (Environment Agency, 1998). Similarly, Ahlbom and Duus (1994) arrived atan average rubber loss figure for Swedish roads of 17%. Based on the upper estimate for rubber loss of 20%,around 90,000 tonnes of tyre material was lost to the UK environment from passenger cars alone during 1999,mainly as a result of in-service wear. The potential environmental impact of this loss of

rubber, in terms ofemissions of PM to the atmosphere, could be relatively high (Environment Agency, 1998).

2.3. BRAKE WEAR PARTICLES

During forced deceleration, vehicle brake linings are subject to large frictional heat generation and associatedwear. This mechanically-induced wear generates brake lining particles which are subsequently released to theenvironment. A Swedish study found that around 934 tonnes of brake linings were used in 1993 (MalmoEnvironmental Health Administration, 1998). Westerlund (2001) calculated that, in Stockholm, passengercars, goods vehicles and buses released around 45 tonnes, 7.6 tonnes, and 3.3 tonnes of brake lining material to the environment each year, respectively. The UK National Atmospheric Emissions Inventory (Goodwi*etal.*, 2002) indicates that in 2000 brake wear was responsible for 4,200 tonnes of PM_{10} emissions in the UK.

2.3.1 Particle emission factors

The PART5 model developed by the USEPA includes particle emission factors due to brake wear. However,the brake wear PM_{10} emission factor for light-duty petrol vehicles of 7.8 mg/vkm given in PART5 is based onwork conducted during the early 1980s, and using asbestos-based brakes (Cha *et al.*, 1983). Since then, theasbestos in brakes has been replaced by various other materials, and these emission factors may not beapplicable to modern vehicles. Little work has been performed on emissions from brakes using non-asbestosmaterials, although Garg *et al.* (2000b) obtained a PM emission factor for light-duty vehicles of 3.2-8.8mg/vkm. For the pads tested, emission rates for PM_{10} and $PM_{2.5}$ were calculated to be 2.9-7.5 mg/vkm and2.2-5.5 mg/vkm respectively. In fact, the upper limit of the range for PM_{10} emissions is very close to the oldervalue used by the USEPA. Westerlund (2001) determined a similar emission factor for

brake wear PM_{10} fromcars (6.9 mg/vkm), and an emission rate for HDVs of 41.2 mg/vkm. Lower values were obtained byRauterberg-Wulff (1999): 1 mg/vkm for cars, and 24.5 mg/vkm for HGVs. Lukewille *et al*. (2001) citeresearch by Carbotech which indicated PM_{10} emission factors for LDVs of 1.8-4.9 mg/vkm, and an emissionfactor for HDVs of 3.5 mg/vkm. Based on PM_{10} measurements at a range of roadside locations, Abu-Aballan*et al*. (2003) found that LDV emission factors varied between 0 and 79 mg/vkm, and HDV emission factorsvaried between 0 and 610 mg/vkm. Emissions from brake wear were highest near motorway exits.

Malmqvist (1983) estimated that, of the particles emitted by brake systems, 1.5 mg/vkm are deposited on theroad surface.

Although gaseous emissions do occur as a result of the mechanical abrasion of brake linings, they do notappear to be significant. During the tests conducted by Garg *et al.* (2000b), increases in the concentrations ofCO, CO_2 and hydrocarbons above the background levels in the test chamber could not be detected.

2.3.2 Particle composition

The chemical composition of dust samples taken from inside car brake mechanisms was investigated byHildemann *et al.* (1991) who reported the inorganic content (Appendix A), and Rogge *et al.* (1993) whoreported the solvent-soluble organic content (Appendix B). However, it was found that only a small fractionof the organic fraction of brake dust could be extracted. Because brake linings have to withstand excessivemechanical and heat stress and must be resistant to possible leaking brake fluid, organic fibers and binders areused that show high boiling points and resistance to solvents. Hence it is not surprising that only a smallfraction of the brake lining dust can be examined using conventional laboratory techniques. Nevertheless,potential trace compounds could still be identified in the solvent-extractable

fraction.Hildemann *et al.* (1991) found that the fine fraction of the brake dust sample consisted mainly of iron andsilicon compounds, organics, magnesium, and barium. Brake abrasion dust has also been found to containlarge amounts of iron in other studies (Muschack, 1990; Filip *et al.*, 1997; Garg *et al.*, 2000b). About 13% ofthe fine particle mass consisted of organic compounds. Hildemann *et al.* (1991) reported that brake wear mayaccount for up to 2.3% for the total atmospheric organic carbon in air in an urban area. The identifiableportion of the brake particle organics consisted mainly of *n*-alkanoic acids (34.3%) and polyalkylene glycolethers (56.9%), the latter being a typical component of brake fluid. By mass, the most abundant solventsolubleorganic compounds were found to be triethylene glycol monomethyl ether (2-[2-(2-methoxyethoxy)-ethoxy]ethanol) and triethylene glycol monoethyl ether (2-[2-(2-ethoxyethoxy)-ethoxy]ethanol). Again, asboth compounds are used mainly in hydraulic fluids the findings suggest that the presence of thesecompounds is indicative of mechanical failure, and they cannot therefore be considered as reliable tracers(Rogge *et al.*, 1993).

The study by Garg *et al.* (2000b) revealed that 18% of the airborne PM was carbonaceous material. Elementalanalysis indicated that metallic species, together with Si, P, S, and Cl accounted for most of the remainingmass. The analysis showed the presence of a variety of elements that could provide a unique source profile for use in receptor models.

2.4 CLUTCH WEAR PARTICLES

The friction materials used in clutch linings are similar to those used in brake linings (*i.e.* a combination ofmineral fibers, including asbestos in older vehicles, and binders). However, although some studies of the wearof asbestos-based clutches were conducted in the 1970s (Jacko *et al.*, 1973), there appears to be no recentinformation relating to the amount of material lost to the environment, or emissions of particulate matter,from this source.

2.5 CORROSION PARTICLES

The corrosion of vehicle components, crash barriers, and street furniture can contribute to the dust depositedon the road surface, and hence to resuspension. Corrosion may also be a source of airborne particles, but thereis little information relating to its significance.

Compositional analysis of used car body parts and fresh primer paint by Brewer (1997) revealed that anumber of heavy metals are found in a range of concentrations in different vehicle body parts. Exhaust components also contain high concentrations of Pb, Zn, and Cu, Pb probably originates from the use of leaded fuel. Car paint, and other coatings, were found to contain high levels of Ba, Al, Fe, Cr, Zn, and Pb.Legret and Pagotto (1999a) conducted a study of the corrosion of galvanised steel safety barrier on the northbypass motorway of Nantes by means of an experimental set-up consisting of a 150m long barrier equippedwith a gutter. Rain water was collected and the heavy metal content was determined over a one year period.The amount of zinc removed was approximately 950 g/km/year. The corresponding fluxes for Cd, Cu and Pb were 0.16, 0.23, and 2.1 g/km/year respectively.

2.6 ROAD SURFACE WEAR PARTICLES

Bitumen is a viscous hydrocarbon material containing many chemical components, and with a meanmolecular weight of around 800 (Jennings *et al.*, 1992). Its complexity makes it very difficult to characterize (Lindgren, 1996), and few workers have attempted to identify bitumen particles in the environment. Theprecise composition of bitumen varies according to the source of the crude oil from which it originates, andany subsequent modification (Whiteoak, 1990). Bitumen has been described as a colloidal dispersion of solidparticles, known as maltenes (which are soluble in *n*-heptane) and asphaltenes (which are not), in a medium ofsaturated hydrocarbons with a molecular weight range of 200-600 (oils) and polyaromatic hydrocarbons (PAHs) witha

higher molecular weight (resins). The asphaltenes have a molecular weight of up to 1000 (C80) (Hagen *etal.,* 1989). It has been suggested by Fauser (1999) that asphaltenes and maltenes from bitumen, which areamongst the largest molecules present in the atmosphere, can be used as tracers for road surface wear. Fauserfound that airborne bitumen particles mainly ranged in size between 0.35μm and 2.8μm, with a mean of around 1μm. Elvebakken (1991) attempted to use PAHs as bitumen tracers, and noted that more than 300different PAHs are present in bitumen. However, each compound could only be found at a concentration ofless than 0.1% by mass, and there is no PAH that is unique to bitumen. This lack of specificity probablyrenders PAHs unsuitable as tracer species for bitumen. He *et al*. (1993) and Rosenmejer (1993) used the polararomatic and aliphatic fractions as bitumen tracers, but did not reveal a usable fingerprint profile for bitumen.Lindgren (1996) determined the metal composition of bitumen (B180) and two rock minerals used in asphalt,a gabbro and porphyry. For the bitumen, chromium, copper, and zinc were below their detection limits. A sample of stone used in the asphalt of the French A11 motorway was analysed for heavy metal content by Legret and Pagotto (1999b). A study reported by Van Heystraeten (1996) showed that old rubber tyre material can be used in modifiedasphalt mixes. The amount of crumb rubber used influences the amount of bitumen added to the mix, andhence the mineral content of the material. This road surface technology was developed in Sweden with thepurpose of using the rubber properties to control snow and ice. Van Heystraeten (1996) noted that severalstudies have been performed in Sweden to assess the resistance to abrasion and rutting of asphalt surfacescontaining rubber. These tests were evaluated against asphalt surfaces containing other materials, such asconventional asphalt concrete mixes, various surface dressings and stone mastic asphalt.

Asphalt wear has been estimated by Muschack (1990) to be 3.8 mg/vkm. CBS (1998) – cited in Lukewille *etal*. (2001) – reported wear rates for LDVs and HDVs of 7.9 and 38 mg/vkm respectively, although thesevalues also included tyre and brake wear. However, in areas where there is extensive use of studded tyresduring the winter, the wear of the road surface is considerably higher. In Sweden, road surface wear due to theuse of studded tyres amounts to 100,000 tonnes per year Gustafsson (2001) and an average of 24 g/vkm ofasphalt is worn off during winter (Lindgren, 1996), although it was estimated by Carlsson *et al.* (1995) thatthe introduction of softer studs and more durable asphalt would have reduced this to 11 g/vkm by 2000. InNorway, the use of studded tyres is thought to be responsible for the wear of around 250,000 tonnes of asphaltper year (NILU, 1996).

The dust burden due to road wear and the use of studded tyres varies greatly by time and place. On cold, drywinter days near major arterial roads, the concentrations measured by NILU (1996) were often higher than therecommended air quality guideline by a factor of three to four. The highest concentrations measured were more than 600μg/m^3 as a daily mean. By comparison, the recommended Norwegian air quality guideline is 70 μg/m3. In these situations, an estimated 80% of the PM_{10} originates from resuspended road dust. On anannual basis calculations of annual mean concentrations of PM_{10} in the centre of the largest cities in Norway show that 20%-30% of the airborne dust comes from studded tyre wear. During wet road conditions outside the studded tyre season, the contribution from road wear is insignificant compared with the contribution from exhaust emissions (NILU, 1996).

2.7 RESUSPENDED DUST

The term resuspension is commonly used to include both suspension of newly generatedparticles and re-entrainment of previously deposited particles into the atmosphere (Nicholson1988).

Resuspension is a complex process that can be initiated by mechanical disturbancessuch wind, traffic-induced turbulence and tyre stress, and construction activities. The windblowndust is often called 'natural dust' because of its origin from mostly non-urban areas thatare subject to suspension by the wind (Chow *et al*. 1999). In non-arid urban environments,particulate matter can be made available for resuspension in a variety of ways, includingapplication of traction sands or de-icing salts, track-out from construction sites and otherunpaved areas, vehicle exhaust, tyre and brake wear, oil leaks and spills from vehicles,wearing and maintenance of streets, and atmospheric deposition of anthropogenic PMemissions (Claiborn *et al.* 1995).

Road dust is an agglomeration of contributions from several anthropogenic and biogenicsources of particulate matter (Rogge *et al*. 1993). In all road environments, the dust fromvarious sources accumulates on road shoulders, near the curbs and along center dividers(Etyemezian *et al*. 2003). Resuspension, deposition, washout of materials on and off the road,and generation of new particles constitute a dynamic source and sink relationship in the trafficenvironment (Rogge *et al*. 1993, Kuhns *et al.* 2003). Paved and unpaved roads are among thelargest emitters of particulate matter in many urban areas, and numerous studies have shownthat traffic-induced resuspension is the predominant source of coarse particles and manyelements at traffic-influenced sites (Pakkanen *et al*. 2001b, Ruellan and Cachier 2001, Manoli*et al.* 2002, Sternbeck *et al*. 2002).

Kupiainen *et al.* (2003 and 2005) have studied the effects of road sanding on the compositionand concentrations of urban suspended road dust. They found that concentrations ofsuspended PM_{10} increased subsequent to application of traction sand. The observed increase was larger when studded tyres were used and when the sand contained more small particlesize fractions. One interesting finding was that the wear of the pavement was greatlyincreased by the grinding

impact of sand under the tyres. This finding was corroborated by asubsequent field study showing that only about 10% of the number of all inorganic $PM_{1.5-10}$ particles and 17% of the number of all $PM_{1.5-10}$ mineral particles were directly associated withroad sanding material (Kupiainen and Tervahattu 2004). Laschober *et al*. (2004) found thatless than 5% of vehicular particulate matter emissions (no particle size segregation insampling) were due to resuspension and road abrasion during a traffic tunnel study in Vienna,Austria. On the other hand, a Swedish traffic tunnel study revealed that as much as 50% offine PM (0.6-2.5 μm) could be attributed to traffic-induced turbulence at vehicle speeds >75km/h (Kristensson *et al*. 2004).

2.8 SOURCES OF HEAVY METAL POLLUTION OF THE ENVIRONMENT

Lead is a common industrial metal that has become widespread in air, water, soil and food. It is a naturally occurring metal that has been used in many industrial activities and therefore many occupations may involve exposure to it such as auto-mechanic, painting, printing, welding putting the workers at risk of potential high exposure. In the atmosphere, lead exists primarily in the form of $PbSO_4$ and $PbCO_3$. Lead in paints and automobile exhausts are still recognized for its toxicity (Hughes, 1996). Episodes of poisoning from occasional causes such as imperfectly glazed ceramics (Matte *et al*., 1994), the use of medicines which may contain as much as 60% lead available from Asian healers and cosmetic preparations, may affect any age group and cases may present as acute emergencies (Bayly *et al*., 1995). The main source of adult exposure is food, air inhalation accounts for 30% and water of 10% (John *et al*., 1991). Special population at risk of high exposure to tetra ethyl lead produced by reacting chloroethane with a sodium–lead alloy includes workers at hazardous sites and those involved in the manufacturing and dispensing of tetraethyl lead (Gerbeding, 2005a). Individuals living near sites where lead was produced or

sites where lead was disposed and also hazardous waste sites where lead has been detected in some environmental media also may be at risk for exposure (Hazdat, 2005).

2.8.1 Cadmium

The principal form of cadmium in air is cadmium oxide, although some cadmium salts, such as cadmium chloride, can enter the air, especially during incineration. Environmental discharge of cadmium due to the use of petroleum products, combustion of fossil fuels (petroleum and coal) and municipal refuge contribute to airborne cadmium pollution (De Rosa *et al.,* 2003) and possibly introduce high concentrations of this potential reproductive toxicant into the environment. This may be particularly true for Nigeria where refuse are burnt without control. In addition, humans may be unwittingly exposed to cadmium via contaminated food or paper (Wu *et al*., 1995) cosmetics and herbal folk remedies (Lockitch, 1993). All these factors put Nigerian population at high risk of cadmium toxicity (Okoye, 1994).

2.8.2 Nickel

A person may be exposed to nickel by breathing air, drinking water, or smoking tobacco containing nickel. Skin contact with soil, bath or shower water, or metals containing nickel, as well as metals plated with nickel can also result in exposure. Coins contain nickel. Some jewellery are plated with nickel or made from nickel alloys (Gerbeding, 2005b). Exposure of an unborn child to nickel is through the transfer of nickel from the mother's blood to fetal blood. Likewise, nursing infants are exposed to nickel through the mother to breast milk.

However, the concentration of nickel in breast milk is either similar or less than the concentration of nickel in infant formulas and cow's milk. Children may also be exposed to nickel by eating soil. Normally, the exact form of nickel one is exposed to is not known. It could

be in form of nickel sulphate, nickel oxide, nickel silicate, iron-nickel oxides, nickelsubsulfide or metallic nickel (Gerbeding, 2005b).

2.8.3 Manganese

Populations living in the vicinity of ferromanganese or iron and steel manufacturing facilities, coal-fired power plants, or hazardous waste sites are exposed to elevated manganese particulate matter in air or water, although this exposure is likely to be much lower than in the workplace (Koplan, 2000a). Manganese is eliminated from the body primarily through the bile. Interruption of the manufacture or flow of bile can impair the body's ability to clear manganese. Several studies have shown that adults and children as well as experimental animals with cholestatic liver disorders have increased manganese levels in their blood and brain and are at risk from potentially increased exposure to manganese due to their decreased homeostatic control of the compound (Devenyi *et al*., 1994). In addition to oral diets, people on partial and total parenteral nutrition may be exposed to increased amounts of manganese. People who ingest fruits and vegetables that have been treated with these pesticides and that contain higher-than-usual residues of the compounds (due to incomplete washing or over-application) may be exposed to increased concentrations of the pesticides. It is possible that medical workers may be exposed to higher concentrations of mangafodipir than the general population, although exposure routes other than intravenous are not expected to pose a significant risk (Koplan, 2000a). Manganese in the environment is in the form of their oxides or carbonates e.g MnO_2, $MnCO_3$.

2.8.4 Chromium

Blue prints, primer paints, household chemicals and cleaners, cements, diesel engines utilizing anti-corrosive agents, upholstery dyes, leather tanning processes, welding fumes, battery, rubber, dye, candles, printers and matches are occupational and environmental sources of chromium

(Koplan, 2000b). In addition to individuals who are occupationally exposed to chromium, there are several groups within the general population that have Persons using contaminated water for showering and bathing activities may also be exposed via inhalation to potentially high levels of chromium(VI) in airborne aerosols. Elevated levels of chromium in blood, serum, urine, and other tissues and organs have also been observed in patients with cobalt-chromium knee and hip arthroplasts (Koplan, 2000b).

Chromium in the environment can exist in many forms e.g chromium trioxide, potassium dichromate, sodium dichromate, potassium chromate, Sodium chromate or ammonium dichromate.

2.9 SOME SPECTROSCOPIC METHODS FOR HEAVY METALS DETERMINATION

The most common methods employed are flame atomic absorption spectrometry (AAS). Graphite furnace atomic absorption spectrophotometry (GFAAS) and Anode stripping voltametry (ASV) are the methods of choice for the analysis of lead. In order to produce reliable results, background correction, such as Zeeman background correction that minimizes the impact of the absorbance of molecular species, must be applied. Limits of detection for lead using AAS are on the order of μg/mL (ppm) for flameAAS measurements, while flameless AAS measurements can detect blood lead levels at about 1ng/mL (Flegal & Smith, 1995). Inductively coupled plasma mass spectrometry (ICP-MS) is also a very powerful tool for trace analysis of lead and other heavy metals. ICP/MS not only can detect very low concentrations of lead but can also identify and quantify the lead isotopes present. Other specialized methods for lead analysis are X-ray fluorescence spectroscopy(XRFS), neutron activation analysis (NAA), differential pulse anode stripping voltametry, and isotope dilution mass spectrometry (IDMS). The most reliable method for the determination of lead at low concentrations is IDMS but due to the

technical expertise required and high cost of the equipment, this method is not commonly used (Gerbeding, 2005a).

2.9.1 Cadmium

The most common analytical procedures for measuring cadmium concentrations in samples is through methods of atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES). Methods of AAS commonly used for cadmium measurement are flame atomic absorption spectroscopy (FAAS) and graphite furnace (or electrothermal) atomic absorption spectroscopy (GFAAS or ETAAS). A method for the direct determination of cadmium in solid biological matrices by slurry sampling ETAAS has been described (Taylor *et al*., 2000).

Analysis for cadmium in environmental samples is usually accomplished by AAS or AES techniques, with samples prepared by digestion with nitric acid. Since cadmium in air is usually associated with particulate matter, standard methods involve collection of air samples on glass fiber or membrane filters, acid extraction of the filters, and analysis by AAS. Electrothermal inductively coupled plasma mass spectrometry (ETV-ICP-MS) has also been used to analyze size classified atmospheric particles for cadmium. The accuracy of the analysis of cadmium in acid digested atmospheric samples, measured by ACSV, was evaluated and compared with graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) (Koplan, 1999).. The AAS techniques appear to be most sensitive, with cadmium recoveries ranging from 94 to 109%(Koplan, 1999).

2.9.2 Nickel

Analytical methods used in the determination of nickel in samples are the same as those used for environmental samples. Atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), with or without preconcentration or separation steps,

are the most common methods. These methods have been adopted in standard procedures by EPA and the International Union of Pure and Applied Chemistry. Direct aspiration into a flame and atomization in an electrically heated graphite furnace or carbon rod are the two variants of atomic absorption. The latter is sometimes referred to as electrothermal AAS (ETAAS). Typical detection limits for ETAAS are <0.4 μg/L, while the limit for flame AAS and ICP-AES is 3.0 μg/L (Todorovska *et al*., 2002). Good precision was obtained with flame AAS after pre-concentration and separation, electrothermal AAS, and ICP-AES. Inductively coupled plasma mass spectrometry (ICP-MS) techniques have been used to quantify nickel in urine with detection sensitivities down to approximately 1 μg/L.

Voltammetric techniques are becoming increasingly important for nickel determinations since such techniques have extraordinary sensitivity as well as good precision and accuracy.

Direct measurement of nickel in urine in the presence of other trace metals (e.g., cadmium, cobalt, and lead) was demonstrated using adsorption differential pulse cathodic stripping voltammetry at a detection limit of 0.027 μg/L (Gerbeding, 2005b).

The most common methods used to detect nickel in environmental samples are AAS, either flame or graphite furnace, ICP-AES, or ICP-MS. Nickel can also be analyzed in ambient and marine water using stabilized temperature graphite furnace atomic absorption (STGFAA) detection techniques as described in EPA methods 1639 and 200.12 respectively, which give limits of detection for nickel concentrations ranging between 0.65 and 1.8 μg/L and recoveries of >92%. Two other EPA standard test methods, 200.10 and 200.13, also use pre-concentration techniques in conjunction with ICP-MS or graphite furnace AAS detection techniques, respectively, for analysis of nickel in marine water. One method uses activated charcoal to pre-concentrate nickel in natural waters, followed by elution with 20% nitric acid and analysis by

inductively coupled plasma-optical emission spectrometry (ICP-OES). This method achieved a detection limit of 82 ng/L (Gerbeding, 2005b).

2.9.3 Manganese

Flame atomic absorption analysis is the most straightforward and widely used method for determining manganese. In this method, a solution containing manganese is introduced into a flame, and the concentration of manganese is determined from the intensity of the colour at 279.5 nm. Furnace atomic absorption analysis is often used for very low analyte levels and inductively coupled plasma atomic emission analysis is frequently employed formultianalyte analyses that include manganese. Simple methods for the direct determination of Mn in whole blood by ETAAS have been described. Methods for measuring manganese therefore include spectrophotometry, mass spectrometry, neutron activation analysis and X-ray fluorimetry (Koplan, 2000a). A number of analytical methods for quantifying MMT in gasoline have been described including simple determination of total elemental manganese by atomic absorption and gas chromatography followed by flame-ionization detection (FID). In a certain method, in which MMT is detected in gasoline by gas chromatography coupled with flame photometric detection (FPD); the chemiluminescence of manganese is measured to determine MMT levels in a method that uses simple, inexpensive, and commercially available instrumentation (Koplan, 2000a).

2.9.4 Chromium

The use of GC-MS and ETAAS to determine total Cr inbiological fluids in order to investigate the distribution of Cr in lactating women following oral administration of a stable 53Cr tracer have been reported. The authors detected 53Cr in blood within 2 h of administration. They noted, however, that blood Cr changes in response to oral administration were variable and they considered that blood Cr was not tightly regulated. Similarly, the reported serum and plasma

chromium concentrations of normal subjects have varied more than 5,000-fold since the early 1950s (Taylor *et al*., 2000).

The four most frequently used methods for determining low levels of chromium in biological samples are neutron activation analysis (NAA), mass spectrometry (MS), graphite spark atomic emission spectrometry (AES), and graphite furnace atomic absorption spectrometry (GFAAS). Of these four methods, only the GFAAS is readily available in conventional laboratories, and this method is capable of determining chromium levels in biological samples when an appropriate background correction method is used. The three commonly used methods that have the best sensitivity for chromium detection in air are GFAAS, instrumental neutron activation analysis (INAA), and graphite spark atomic emission spectrometry. Measurements of low levels of chromium concentrations in water have been made by specialized methods, such as inductively coupled plasma mass spectrometry (ICP-MS), capillary column gas chromatography of chelated chromium with electron capture detection (ECD), and electrothermal vaporization inductively coupled plasma mass spectrometry (Koplan, 2000b).

2.10 HEALTH EFFECTS ASSOCIATED WITH SUSPENDED PARTICULATE MATTER

Biological plausibility is reinforced by the observation of a coherent cascade of cardiopulmonary effects as well as the fact that non-cardiopulmonary effectsare not typically associated with particulate matter pollution (Pope and Dockery 1999).

Once an association and biological plausibility has been established, animal toxicology studies and/or human clinical trial studies are usually undertaken to define thatbiological mechanism. Within these studies it is especially difficult to accuratelyreproducing the relevant “particulate matter” mixture. PM is a complicated blend ofchemicals that is dependent upon the primary

source from which it originates, but alsoupon meteorological factors which could influence to what extent certain compoundswill undergo secondary chemical transformations.

Epidemiological studies are categorized as either acute or chronic studies. Acuteepidemiological studies typically use short-term changes in air pollution over time asthe source of exposure variability, and relate those changes to changes in certain healthendpoints related to particulate pollution. Chronic studies use longer-term pollutiondata, usually on the order of one year or more and tend to be cross-sectional by nature.

Numerous studies have been done that have looked at and established quite firmly arelationship between certain health endpoints, such as premature mortality, andparticulate pollution. The problem lies in the ability to compare results of these studies(in detail). With the number of studies being significantly less in developing comparedto developed countries, the difference in the health endpoints examined, themeasurement of PM, be it TSP, PM_{10} or $PM_{2.5}$, and type of study either acute or chronic study, it is even more difficult to directly compare results.

2.11 ACUTE HEALTH EFFECTS

Respiratory related mortality and total mortality was significantly related to PM levels in all studies but one.COPD related mortality was also significantly related to PM as opposed to PulmonaryHeart Disease (PHD) which was not. In developed countries, associations between PM increase in PM_{10}, with an average increase of 1.0 percent (Ostro 1996). All mean TSP levels reported in these studies are relatively elevated. On the other hand, neither children's respiratory related mortality nor intrauterine mortality were found to be significantly associated with PM alone (Pareira *et al*. 1998, Saldiva *et al.* 1994). In spite of the fact that no relationship was noted between children's respiratory related mortality and PM, the results of Saldiva *et al*. (1994) point to the possibility of NO_2 increasing thesusceptibility to respiratory infection and thus respiratory related mortality in theexposed population. Although intrauterine mortality was not significantly

correlatedwith PM measurements alone, the authors found a significant association when lookingat all the pollutants together (PM_{10}, NO_2, SO_2 and CO).

2.11.1 Morbidity

The significant association between acute mortality and particulate pollution provokedfurther interest in other possible health effects caused by air pollution. Studies in China,looking at morbidity related health endpoints found associations between high levels ofparticulate pollution and increased daily hospital admissions, non-surgery visits, wherethe association increased 1.5 to 2.0 fold for specific departmental visits, e.g. pediatricand internal medicine visits (Xu *et al* 1995c). The association between daily hospitaladmissions, hospital admissions from respiratory and cardiovascular symptoms, and PMwas confirmed by a Bangkok study (Chestnut *et al.* 1998). Birth outcomes such as lowbirth weight and preterm delivery were also found to be significantly associated withhigh PM values. As has already been stated above, respiratory related symptoms weresignificantly correlated with PM pollution, measured by forced vital capacity (FVC) andforced expiratory volume (FEV), which decreased with increasing pollution levels.

2.11.2 Long-Term Health Effects

Repeated exposure to particulate matter, with its obvious dire effects on acute mortality, is postulated to have longer-term health effects as well. There have been relatively fewstudies conducted that measure the health effects from chronic exposure to PM, andnone that have been conducted in developing countries. Overall, the studies found arobust association between mortality and particulate matter, as well as higher levels ofmortality in cities with higher average levels of particulate matter (Dockery *et al.* 1993;Pope*et al.* 1995; Lipfert 1994).

2.11.3 Cancer

In developing countries, the primary chronic health endpoints that researchers have hypothesized to be associated with PM, primarily through coal combustion, are cancer, primarily lung cancer.

The incidence of lung cancer in some cities of China, where there is heavy use of coal for cooking and heating, is almost as high or is as high in women as in men. This is rather a remarkable figure considering the fact that prevalence of smoking in men, at the time of the study, was about 40% and less than 0.1% in women (Mumford *et al.* 1987). Therefore the similarity in lung cancer prevalence was hypothesized to be due to presence of a cook stove and type of coal used in the cook stove. A study conducted in Fuzhou, China looked at possible risk factors associated with lung cancer, and using presence of a cook stove as a proxy for indoor air pollution. They found indoor air pollution to be a significant risk factor for lung cancer (Luo *et al*. 1996). In terms of the type of coal used, they found that mortality from lung cancer was higher in households or regions that used primarily smoky coal as opposed to smokeless coal (Mumford *et al.* 1987). In addition to lung cancer, use of biomass cooking fuels has been established to be a possible risk factor for nasopharyngeal cancer (Zhang and Smith 1996, Smith 1993). Emissions have been found to contain carcinogenic compounds. Smith examined certain fuel/cookstove combinations in Manila and found some sixty hydrocarbons to be emitted from those stoves. A further study by Zhang and Smith (1996) examined emissions concentrations of specific known carcinogens, namely benzene, 1, 3-butadiene, styrene, and xylene. The cancer risks, which also depends on amount of emissions and type of fuel/cookstove combination used, were highest for 1,3 butadiene and then benzene,for wood, charcoal and then kerosene/wick stoves (Zhang and Smith 1996).

CHAPTER THREE

MATERIALS AND METHODS

3.1 STUDY AREA AND SAMPLING STATIONS

The study was carried out in Kaduna Metropolis.

Kaduna State is classified as belonging to the North-West zone of the Six Geo-political zones in Nigeria, with a population of about 50-63 different ethnic groups. It is located between the coordinates 10° 20¹N, 70°45¹E to the Greenwich meridian. It has a total area of 46,053 Km^2 and a total population 6,066,562 (census 2006). Kaduna metropolis is underlain by basement complex rock of Precambrian origin which consists of undifferentiated igneous and metamorphic rock. The natural vegetation is that of the Sudan Savannah. The climate of the state is the tropical wet and dry type with rainy season lasting for 5months between May and September (Olofin and Tanko, 2002).

Kaduna State is a metropolitan as well as cosmopolitan industrialized state with 80 commercial and manufacturing industries. Goods ranging from textiles, bicycles assembly, toiletries and cigarettes, not to mention the agricultural activities which add significantly to the economy of the state.

The selection of the sampling site was based on several factors including ease of access, safety, minimizing potential for sample contamination, and representativeness. Based on the above criteria, the site chosen are Chechenia market along Ahmadu Bello Way Kaduna, Old Panteka in Tudun Wada, Kaduna and New Panteka along Eastern By-pass Kaduna. All sites are located on Latitude 10°31.194¹N and Longitude 007°25.847¹E, Latitude 10°31.242¹N and Longitude 007°25.376¹E and Latitude 10°34.188¹N and Longitude 007°25.100¹E respectively. The map of the study area is shown in Fig. 1.

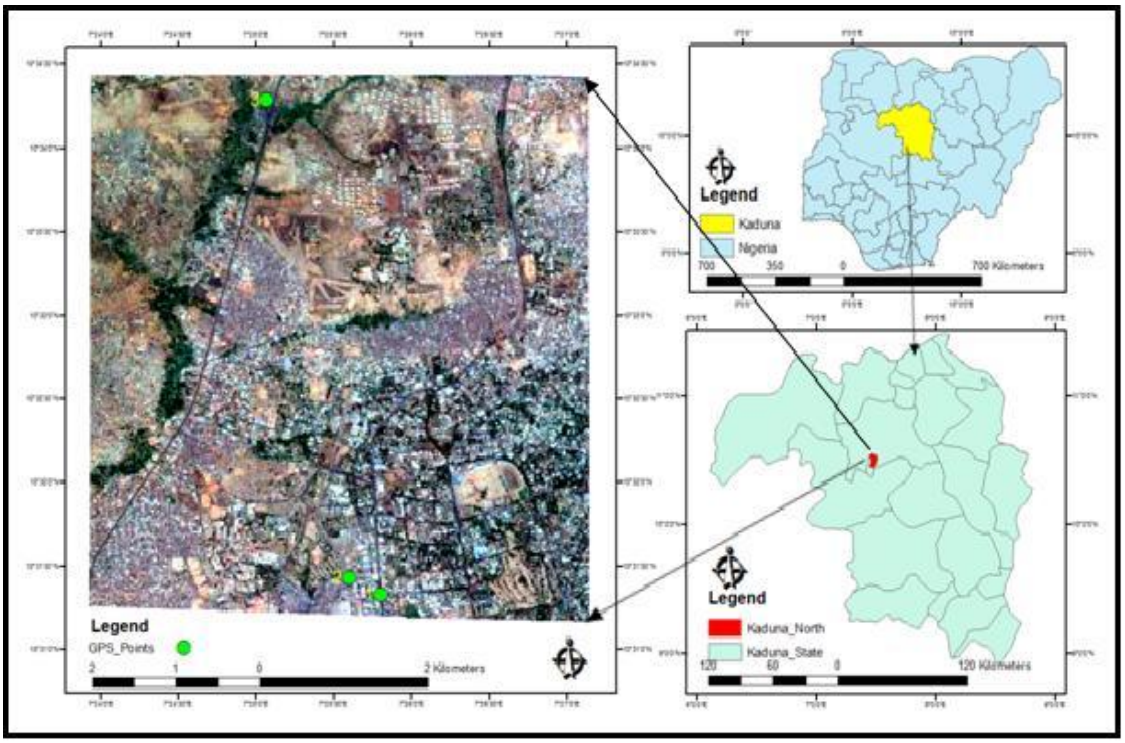


Figure 1: Administrative Map of Kaduna State showing Kaduna North Local

Chechenia market is located in Ahmadu Bello Way Kaduna which densely populated and most of the activities there is commercial.

3.1.1 New Panteka, Old Panteka and Ahmadu Bello Way

The above mentioned areas are very popular places. New Panteka and Old Panteka are areas where everything metal can be fabricated; it is even believed that what is brought to Panteka can hardly be recognized by the owner after being worked on. It is because it can be converted into any form or many forms and put to special use. For the simple fact that the artesian working, they are talented and gifted with the act of being able to convert anything metal to different object and instruments for unique use and special purpose. The activities of these areas includes blacksmithing, fabrication of metals of any type, mechanic workshops, selling of motor spare parts, building metal works materials, dismantling of old cars. Ahmadu Bello Way has a lot of vehicular movements where automobile and human activities take place. With all the happening

in these areas there is need to study the environment and possible effect it may have on the habitants especially humans living and working there.

3.2 SAMPLE COLLECTION AND PREPARATION

Sampling was done bi-weekly between the months of August-October, 2015 (Wet Season) November, 2015 and January, 2016, for(dry season) so as to cover two seasons, and it was placed at the locations simultaneously.

3.2.1 Standardization of the Instrument

The newly constructed local air sampler was compared to the existing one. The two instruments were placed in Old Panteka which has a relatively high commercial activity and high refuse of scrap metal disposal rate and it is situated in the centre of the city. Samples were collected on the 27/08/2015 at an interval of 8hrs each during peak hours.

3.2.2 REAGENTS AND STANDARD SOLUTION

Analytical reagent-grade chemicals will be used for all procedures, unless stated otherwise. According to international standard procedures.

Table 3.1 Material Selection and Specification

S/N	Item	Description	Specification	Quantity	Cost
1	Main frame	Rectangular box	Plywood 15mm thick	box = 8	5,000
2	Main box	Square	180 x 180mm	**8**	
3	Suction pipe	Circular	3inch Ø	1 yard each x 8	1,500
4	Battery	Rectangular	12 volts	**8**	2,500
5	Fan	Plastic	12 volts	**8**	1,500
6	Switch	Plastic		8	100
7	Battery case	Rectangular	100 x 21mm	8	
8	Saucer Pad lock			8	50
9	Flat bottom flask	Conical	250ml	8	500
10	Hinges	Metal	1 pair	8	50

3.3 AIR SAMPLER

The air sampler was fabricated using locally available materials, due to the high cost of purchasing the foreign standard air sampler. It has a casing of 180mm by 180mm square box with a 3inch diameter suction hole at the top the size of the hole was as a result of the suction fan that was attached to the hole. A suction pipe was also connected to the fan in order to suck the air into a flat bottom flask that is placed in the box. The fan is being powered by a 12 volts battery which can also be recharge in case the battery runs down, but the battery can run for 20hours if fully charged. (See Fig. 2a) A switch was attached to the box for the control of the fan. This set-up was placed in another constructed mainframe rectangular wooden box. The conical flask in the air sampler contains distilled water. This flask are removed from the box every 8hours and taken to the laboratory for analysis.



Fig.2a. Isometric projection of the air sample for the collection of Suspended Particulate Matter.

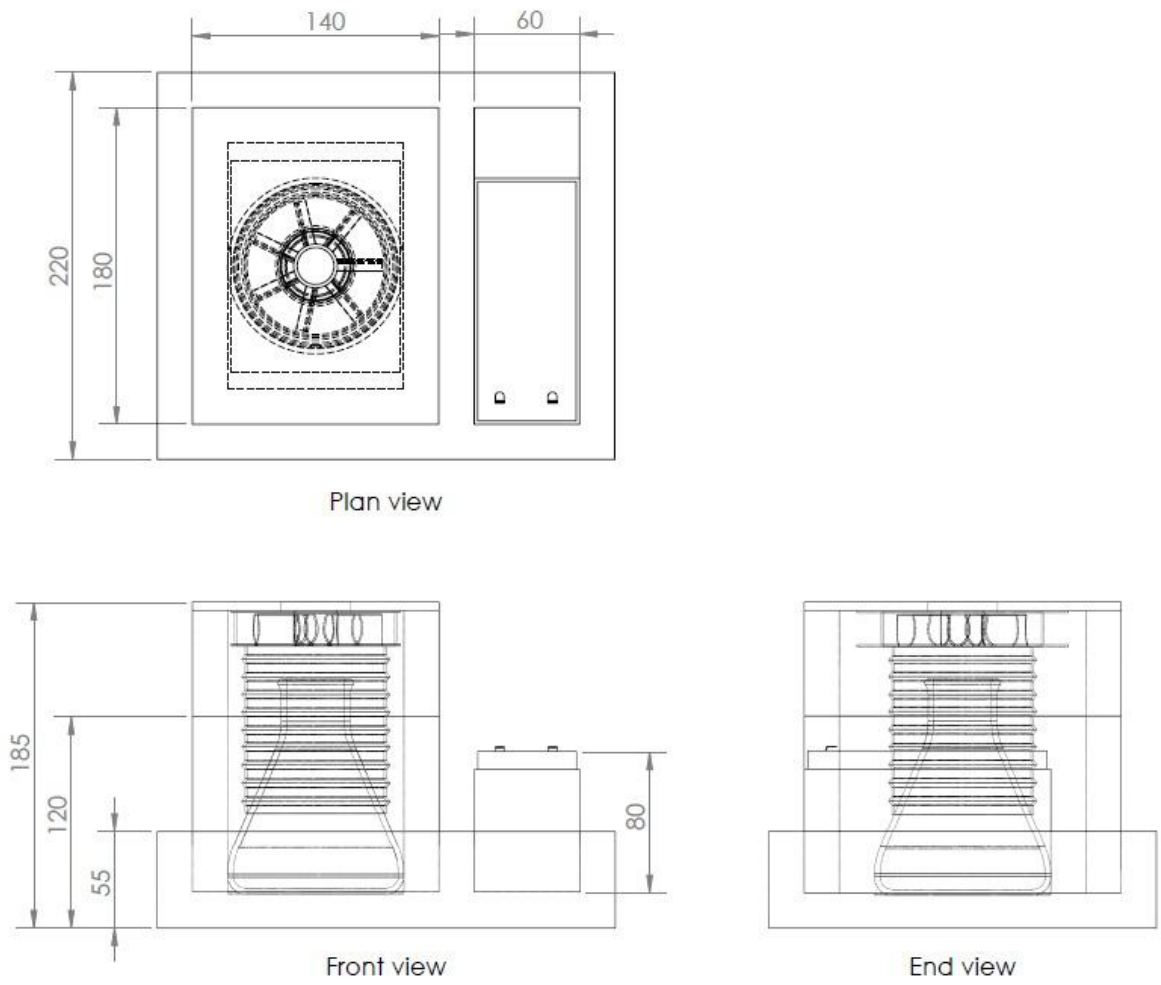
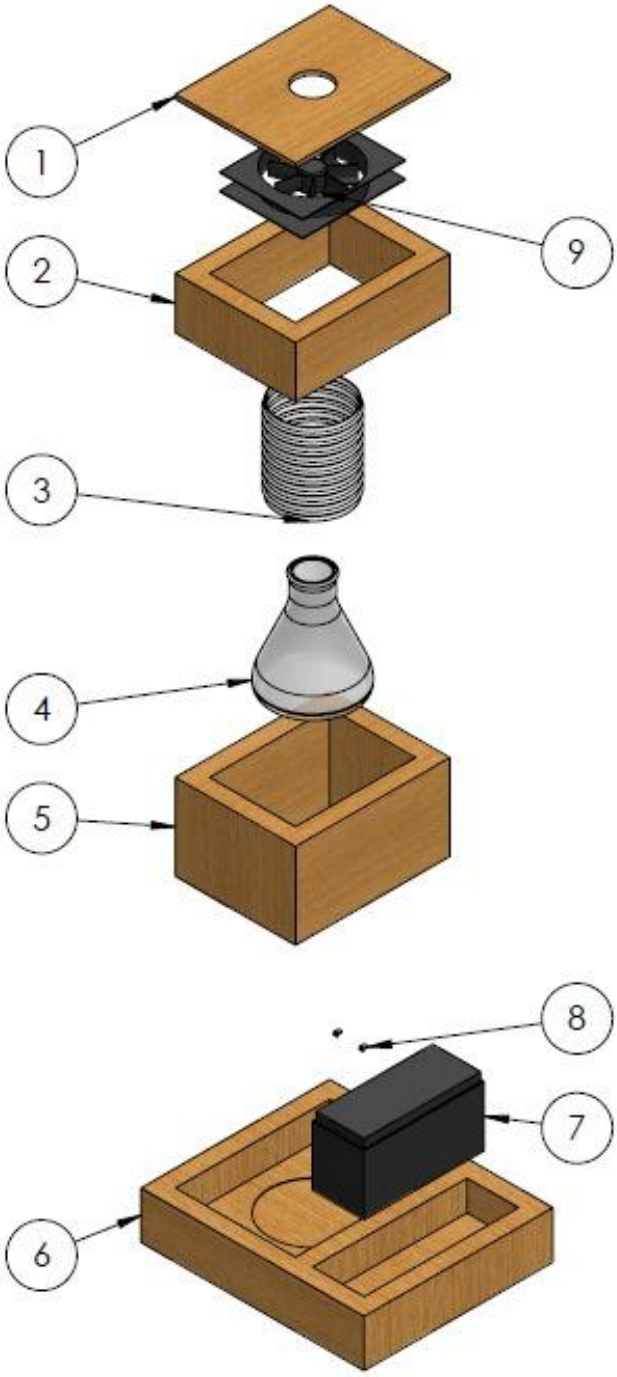


Fig.2b. Orthographic projection of the air sample for the collection of Suspended Particulate Matter. (dimensions in mm)



1. **Wooden Cover with circular opening**
2. **Upper Casing**
3. **Suction Pipe**
4. **Flat bottom flask (250ml)**
5. **Lower Upper**
6. **Wooden tray.**
7. **12 volts battery.**
8. **Switch.**
9. **Suction fan.**

Fig. 2c: Explosive diagram of the Air Sampler

3.3.1 DESIGN CALCULATIONS

FAN SPECIFICATIONS

Fan size:	60x60x15mm.
Bearing type:	Ball bearing.
Rated Voltage:	12V DC.
Start Voltage:	7V DC.
Operating Voltage:	10.8-13.2V DC.
Rated Current:	0.17±10%A.
Input Power:	2.04W.
Fan speed:	2000±10% RPM.

Maximum Air Flow Volume:	12 – 32 cfm (cubic feet per minute)
Max. Fan Speed:	2500 rpm (rotation per minute)

CALCULATED DATA

Actual Fan Speed: 1541 rpm (Tacho meter reading)

If 2000 rpm = 32 cfm

1541 RPM = x (Actual vol. of Air)

$x = \frac{1541\ x\ 32}{2000}$ = 24 cfm

therefore,

Air Flow rate = 679.68 l/min*(Conversion from cfm to l/min)*

Sample time = 8 hours = 8 x 60 = 480 minutes

Volume of air = 679.68 (l/min) x 480 (minutes) =326246.4litres

Volume of air = 326246.4 / 1000 = 326.2 m^3 (cubic metres)

3.4 SAMPLE COLLECTION AND PRETREATMENT

All the samples were collected the same for the three different locations and stored in a cylindrical plastic containers. Ambient air samples collected on glass fiber filters was wrapped with aluminum foil and sealed in a zip-lock bag immediately after collection and stored at 4°C until the samples will be subjected to aqua regia digestion.

3.5 AQUA REGIA DIGESTION

The heavy metal content in the air samples was extracted using aqua regia digestion, following the procedure recommended by International Organization for Standardization, ISO 11466 (Melaku *et al*., 2005).

3.6 ELEMENTAL ANALYSIS

Metal composition and concentration in air that was collected was determined using Atomic Absorption Spectrophotometer (AAS), model AA240FS.According to international Standards.The heavy metals of interest are Iron, Lead and Zinc. The analysis will be done at the Multi-User Science Research Laboratory of the Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

3.6.1 Calibration

The data for calibration curve plot for individual metals was obtained by injecting 20 ml of five standard solutions containing 0 - 15 mg/l of iron, zinc, and lead, into the graphite tube and measuring the corresponding absorbance at the four respective wavelengths.

This was followed by the determination of the individual heavy metal content in the standard reference material. To work in the linear range of AAS, the aqua regia digested SRM sample will be diluted 100-fold with 1% nitric acid.

3.7 CONTROL

For the purpose of this research, my control area was Afaka Area, located along Kaduna Airport Road, Mando. The instrument was also placed in that area in order to obtain the sample. The reason for selecting afaka is the presence of dense tress in the area.

3.8 EQUIPMENT

1. Atomic Absorption Spectrometer (AAS)
2. Filter paper (125mm Ø")
3. Conical flask
4. Thermometer
5. Beaker
6. Hand glove
7. Pipette
8. Hot plate
9. Masking tape
10. 12 volt battery
11. Switches
12. Suction fans
13. Flat bottom flask
14. Air sampler.

3.7.1Material

1. Water sample
2. De-ionized water
3. Hydrochloric acid (HCl)

4. Nitric acid

3.9 STATISTICAL ANALYSIS

Data that was obtained from the concentration of heavy metals from was subjected to different specific statistical analysis such as:

Microsoft Excel for Windows 2007 was used to compute for mean values in different site. Analysis of Variance (ANOVA) was computed using Statistical Package for Social Sciences (SPSS) version 15 to test for level of significance between the heavy metals studied. The level of significance was set at $P \leq 0.01$.

CHAPTER FOUR
RESULTS

4.1 DATA PRESENTATION

At this stage the researcher present the data obtained from the sampling locations to analyze and discuss findings. Mean Concentration Of Heavy Metal Content In Particulate Matter From Ahmadu Bello Way In The Months Of August – October, 2015. The result of heavy metals is presented in Tables 4.1- 4.3, these results represent the months of August-October in the rainy season.

Table 4.1 Mean Values of Elements for Ahmadu Bello Way in the Month of August, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.450	0.393	0.951	0.681	0.20	-
Pb	0.038	0.026	0.000	0.000	0.05	0.01
Fe	1.882	0.939	2.753	1.084	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.2 Mean Values of Elements for Ahmadu Bello Way in the Month of September, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.431	0.413	1.639	0.385	0.20	-
Pb	0.042	0.030	0.000	0.000	0.05	0.01
Fe	1.897	0.722	1.999	0.658	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.3 Mean Values of Elements for Ahmadu Bello Way in the Month of October, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.622	0.404	0.655	0.22	0.20	-
Pb	0.048	0.026	0.036	0.031	0.05	0.01
Fe	1.772	0.802	1.067	0.937	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

The Table 4.1 above show the results of mean values for the various elements under study of Ahmadu Bello Way in the month of August from this table 4.1 it can be seen that Zinc (Zn) with mean value of 0.951 in acid and 0.681 in base has a higher value than the acceptable units in both the acid and base. It was also notice to be above in the control area also which was Afaka, which recorded 0.450 in acid and 0.393 in base. This may be as a result of the exhaust components of the heavy vehicle along these areas as they contain high concentration of Pb, Zn, Cu. Brewer (1997) revealed that a number of heavy metals are found in a range of concentration in different vehicle body parts.

Lead was not detected in this results in both the acid and base solutions, this absence could be explained as a result of the complicated blend of chemical in the particulate matter is mostly dependent upon the primary source from which it originates, and also upon the metrological factors which could influence to what extend certain compounds will undergo secondary chemical transformation, which may be what happen to the lead. As for the presence of lead in the control area, it may be as a result of the vehicles plying the road or from the pesticides being use by farmers around the area as a result of the mechanized farming encourage in the location.

The highest value of heavy metal understudy was that of Iron which had values of 2.753 and 1.084 in both acid and base, and also 1.882 and 0.939 in acid and base solution for the control area.

Comparing their values with Nesrea (2009)/WHO (2011), it showed that Iron (Fe) which had the highest value of acceptable unit pose environmental threat to man and other organism.

The table of the element concentration in Ahmade Bello Way for the month of August show high values of Iron(Fe) followed by zinc(Zn) with absence of lead(pb) in the study area only to be obtained in the control which may be as a result from the byproducts of petroleum being used

for the vehicles plying the area, since diesel is also a by product and may not have been purified of impurities.

The result in Table 4.2 is the result from Ahmadu Bello Way for the month of September, where the level of Zinc (Zn) in Acid was 1.639mg/l and 0.385mg/l in base, and also values of 0.431mg/l and 0.413mg/l in our control area. These values are reasonably high in comparing it with the standard limits. Also observing the high value of Zinc in the acid is a better medium to determine the pollution level of this element in a given environment.

Lead (Pb) was not detected in the study area but was in the control area with values of 0.042 and 0.030 in acid and base respectively. Which may also be as a result of the activities of the area.

Iron (Fe) had the highest value of 1.999mg/l and 0.658mg/l in the area considered which was Ahmadu Bello Way and also values of 1.897mg/l and 0.722mg/l in acid and base respectively in the controlled area. This values are high in accordance to the standard units of Nesrea (2009)/WHO (2011) thus poisoning serious environmental pollution problems in the area.

This Table 4.3 shows the values of the elements in Ahmade Bello Way recorded in the month of October. From this table it shows a value of 0.655mg/l in acid which is above the accepted limit and 0.22mg/l for base which is slightly above the accepted unit in zinc(zn) . While for the control values of 0.622mg/l and 0.404mg/l in acid and base was observed.

Iron (Fe) had values of 1.067mg/l and 0.937mg/l in acid and base indicating the highest value of the element in the area for the month, and also values of 1.772 and 0.802 for the control area showing that the level of (Fe) in the environment is reasonably very high.

4.2 Mean Concentration of Heavy Metal Content in Particulate Matter from Old Panteka in the Months of August – October, 2015

The result of heavy metals is presented in Tables 4.4- 4.6, these results represent the rainy season results from Old Panteka for the months of August-October, 2015.

Table 4.4 Mean Values of Elements for Old Panteka in the Month of August, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.450	0.393	0.877	1.602	0.20	-
Pb	0.038	0.026	0.000	0.000	0.05	0.01
Fe	1.882	0.939	2.488	1.336	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.5 Mean Values of Elements for Old Panteka in the Month of September, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.431	0.413	1.519	0.279	0.20	-
Pb	0.042	0.030	0.000	0.000	0.05	0.01
Fe	1.897	0.722	1.519	0.742	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.6 Mean Values of Elements for Old Panteka in the Month of October, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.622	0.404	0.781	0.448	0.20	-
Pb	0.048	0.026	0.056	0.061	0.05	0.01
Fe	1.772	0.802	1.645	1.380	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

The Table 4.4 above shows values of Zinc (Zn) to be 0.877mg/l and 1.602mg/l in acid and base and also observed 0.450mg/l and 0.393mg/l in acid and base respectively for the study area and its control. This indicates that the values are high against the accepted units provided internationally.

Lead (Pb) was not detected in the suspected study area but only in the control area of Afaka with values of 0.038mg/l in acid and 0.026mg/l in base, showing that it is slightly above the limit

Iron (Fe) for this month also recorded the highest values in the location with 2.488mg/l in acid and 1.336mg/l in base and also 1.882mg/l in acid and 0.939mg/l in base for the control. This high values indicated a serious threat to the environment.

The 4.5 Table shows values of the element Zinc (Zn) being 1.519mg/l and 0.279mg/l in acid and base and 0.431mg/l and 0.431mg/l in acid and base for the control which clearly shows that it is above the standard international and national limits.

Lead (Pb) was also not observed in the study area for the month of September, although traces of 0.042mg/l in acid and 0.030mg/l in base was observed in the control area.

Also in the month of September Iron (Fe) was recorded as the highest element observed in Old Panteka with values of 1.519mg/l in acid and 0.742mg/l in base and for the control it was observed to be 1.897mg/l and 0.722mg/l in acid and base respectively, which clearly indicates that it is above the acceptable limit.

Table 4.6 is result obtained from Old Panteka of the elements under study with Iron (Fe) recorded the highest value of 1.645mg/l in acid and 0.802mg/l in base for the control area in

Afaka Forest. This element is followed by Zinc (Zn) level which was 0.781mg/l in acid and 0.448mg/l in base for the location of Old Panteka and 0.622mg/l in acid and 0.404mg/l in base for the control.

Lead (Pb) was also detected in the month of October for the first time with the area of study. Although in low values.

4.2 Mean Concentration of Heavy Metal Content in Particulate Matter from Old Panteka in the Months of August – October, 2015

The result of heavy metals is presented in Tables 4.7- 4.9, these results represent the rainy season results from New Panteka for the months of August-October, 2015.

Table 4.7 Mean Values of Elements for New Panteka in the Month of August, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.622	0.404	2.902	0.315	0.20	-
Pb	0.048	0.026	0.000	0.000	0.05	0.01
Fe	1.772	0.802	2.193	1.219	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.8 Mean Values of Elements for New Panteka in the Month of September, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.622	0.404	4.056	0.508	0.20	-
Pb	0.048	0.026	0.001	0.011	0.05	0.01
Fe	1.772	0.802	2.59	1.014	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.9 Mean Values of Elements for New Panteka in the Month of October, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.622	0.404	1.349	3.201	0.20	-
Pb	0.048	0.026	0.135	0.025	0.05	0.01
Fe	1.772	0.802	1.597	0.491	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

For Table 4.7 it shows high values of Zinc at 2.902 mg/l in acid and 0.315mg/l in base as against 0.622mg/l in acid to 0.404mg/l in base for the control. Followed by mean values of Iron (Fe) at 2.193 at 2.193mg/l in acid and 1.219mg/l in base for New Panteka and Afaka (Control) recorded 1.772mg/l in acid to 0.802mg/l in base. There was no presence of lead detected in the area but for the control site which was of low value. Comparing values with the National and International permissible limits it was indicated that both Zinc (Zn) and Iron (Fe) where above the permissible limits and these pose a threat to the environment.

The result in Table 4.8 is the result from New Panteka in the month of September. The highest value was recorded in Zn which had values of 4.056 in the acid and 0.508mg/l in base. Iron had mean value 2.59mg/l in acid and 1.014mg/l in base, in this month of September, lead was also detected but in low values of 0.001mg/l. it can be clearly seen that the values of Zinc and Iron are very high in the month of September in New Panteka and it is as a results of the various activities taking place in the area. Keeping in mind that the typical determination process for Iron and Zinc process of oxidation which begins an exposure to air and moisture and will continue until the metal is gone, and the probability of this determination mainly depends on

i. Degree of protein and Degree of moisture present in the area in which case both are present in the location. This pose a serious environmental threat to the habitants of the area.

Table 4.9 shows that mean values of heavy metals recorded for the month of October in New Panteka with the highest value in Zinc of 1.349mg/l in acid and 3.201mg/l in base. This may be as a result of Zinc having naturally slow reaction to kinetics, is the metal of choose for the coating process. Since the corrosion will happen at an acceptably slow rate. Iron (Fe) was next in

values with 1.597mg/l in acid and 0.491mg/l in base showing that it is also above the permissible unit of the standards.

Lead was also present in mean values of 0.135mg/l in acid and 0.025mg/l in base. The mean value of lead in this location is above both the local and international standards. Indicating that all the heavy metals under consideration are above the acceptable units, which show it is very detrimental to man and all living organism in the area.

4.3 Mean Concentration Of Heavy Metal Content In Particulate Matter From Ahmadu Bello Way In The Months Of November, December, 2015 – January, 2016

The result of heavy metals is presented in Tables 4.10- 4.12, these results represent the dry season results from Ahmadu Bello Way for the months of November, December, 2015-January, 2016.

Table 4.10 Mean Values of Elements for Ahmadu Bello Way in the Month of November, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.086	0.033	0.213	0.139	0.20	-
Pb	1.068	1.085	1.546	1.428	0.05	0.01
Fe	0.327	2.208	1.431	1.336	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.11 Mean Values of Elements for Ahmadu Bello Way in the Month of December, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.077	0.021	0.109	0.136	0.20	-
Pb	1.128	1.056	1.640	1.712	0.05	0.01
Fe	0.223	2.110	4.159	4.698	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.12 Mean Values of Elements for Ahmadu Bello Way in the Month of January, 2016

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.920	0.101	0.141	0.247	0.20	-
Pb	1.277	1.092	1.860	1.911	0.05	0.01
Fe	0.290	2.310	0.952	0.560	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.10 is the value of heavy metals recorded in the month of November, which tool a different dimension with lead (Pb) having the highest value of 1.546mg/l in acid and 1.431mg/l in base, followed by Iron (Fe) which had 1.431mg/l in acid and 1.336mg/l in base, while the least value was recorded for Zinc (Zn) at 0.213 in acid and 0.139mg/l in base. Showing that the concentration of lead has increase in the dry season as of that of the raining season. Comparing these values with Nesrea (2009)/WHO (2011) shows that there are presents of environmental pollution.

The result in Table 4.11 shows the concentration of Iron (Fe) increasing again with values of 4.159mg/l in acid and 4.698mg/l in base, which was followed by lead (Pb) with values of 1.640mg/l in acid and 1.712mg/l in base, with zinc (Zn) having the least values of 0.109mg/l in acid and base respectively.

Table 4.12 is the result obtained from Ahmadu Bello Way. The highest value was recorded in lead(Pb) which had values of 1.860mg/l in acid and 1.911mg/l in base. Then followed by zinc with 1.141mg/l in acid and 0.247mg/l in base. In this month Iron (Fe) recorded the lowest value of 0.952mg/l and 0.560mg/l. This indicates that all the metals are high in value which show the indication of the area being heavy polluted.

4.4 Mean Concentration of Heavy Metal Content in Particulate Matter from Old Panteka in the Months of November, December, 2015 – January, 2016

The result of heavy metals is presented in Tables 4.13- 4.15, these results represent the dry season results from Old Panteka for the months of November, December, 2015-January, 2016.

Table 4.13 Mean Values of Elements for Old Panteka in the Month of November, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.086	0.033	0.334	0.161	0.20	-
Pb	1.068	1.085	1.973	1.959	0.05	0.01
Fe	0.327	2.208	2.589	6.893	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.14 Mean Values of Elements for Old Panteka in the Month of December, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.077	0.021	0.119	0.246	0.20	-
Pb	1.128	1.056	2.077	2.093	0.05	0.01
Fe	0.223	2.110	4.409	17.009	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.15 Mean Values of Elements for Old Panteka in the Month of January, 2016

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.920	0.101	0.322	0.139	0.20	-
Pb	1.277	1.092	2.063	2.070	0.05	0.01
Fe	0.290	2.310	3.291	0.766	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

From Table 4.13, it could be observed that Iron (Fe) had the highest concentration of 2.589mg/l in acid and 6.893mg/l in base in Old Panteka. Then the concentration of lead (Pb) 1.973mg/l in acid and 1.959mg/l in base while Zinc (Zn) has the least value of 0.334 in acid and 0.161mg/l in base, although even with the low concentration it is still in fact all the heavy metals present are above the permissible limits.

The result in Table 4.14 is the result from Old Panteka in the month of December, 2015 the highest value of concentration was recorded was that of Iron (Fe) 4.409mg/l in acid and 17.009mg/l in base followed by lead (Pb) is 2.077mg/l in acid and 2.093mg/l in base. The least value was recorded in Zinc (Zn) with 0.119mg/l in acid and 0.246mg/l in base. This is still an indication that the metals are present in values that are above the acceptable limits of the standards.

From the Table 4.15 the result obtained show high value of Irom (Fe) 3.291mg/l in acid and 0.766mg/l in base. With lead (Pb) being followed with concentration values of 2.063mg/l in acid and 0.322mg/l in acid which is above the limits but also recorded 0.139mg/l in base which in this case the concentration within the base is acceptable.

4.5 Mean Concentration of Heavy Metal Content in Particulate Matter from New Panteka in the Months Of November, December, 2015 – January, 2016

The result of heavy metals is presented in Tables 4.16- 4.18, these results represent the dry season results from New Panteka for the months of November, December, 2015-January, 2016.

Table 4.16 Mean Values of Elements for New Panteka in the Month of November, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.086	0.033	0.213	0.172	0.20	-
Pb	1.068	1.085	2.064	2.069	0.05	0.01
Fe	0.327	2.208	1.364	1.523	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.17 Mean Values of Elements for New Panteka in the Month of December, 2015

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.077	0.021	0.108	0.162	0.20	-
Pb	1.128	1.056	2.085	2.107	0.05	0.01
Fe	0.223	2.110	0.359	1.076	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.18 Mean Values of Elements for New Panteka in the Month of January, 2016

Element	Control		Mean		NESREA-2009	WHO -2011
	Acid	Base	Acid	Base		
Zn	0.920	0.101	0.141	0.131	0.20	-
Pb	1.277	1.092	2.149	2.093	0.05	0.01
Fe	0.290	2.310	0.824	0.875	0.10	0.30

Source: NESREA- National Environmental Standards Regulation and Enforcement Agency, 2009, World Health Organization (WHO), 2011.

Table 4.16 showed lead (Pb) with a high value of 2.064mg/l in acid and 2.069mg/l in base. Iron (Fe) was next with values of 1.364mg/l in acid and 1.523mg/l in base; in this case also Zinc (Zn) recorded the lowest value of 0.213mg/l in acid and 0.172mg/l in base. This result also shows the area of study is highly polluted as all the value of the metals is above the acceptable limits.

Table 4.17 showed the result of the month of December in New Panteka, lead (Pb) recorded the highest result of 2.085mg/l in acid and 2.107mg/l in base, followed by Iron (Fe) with values of 0.359mg/l in acid and 1.076mg/l in base. The least value was recorded in Zinc (Zn) as 0.108mg/l in acid and 0.162mg/l in base which could pose serious threat to the environmental and organism within the environment.

Table 4.18 is the result obtained from New Panteka in the month of January 2016 which showed values of lead (Pb) as 2.149mg/l in acid and 2.093mg/l in base as the highest, followed by Iron (Fe) with 0.824mg/l in acid and 0.875mg/l in base and zinc having the least of 0.141mg/l in acid and 0.131mg/l in base.

4.6 Seasonal Variation of Heavy Metals in Areas Studied in both the Wet and Dry Season during the Study Period

Table 4.19 shows statistical analysis of seasonal variation of heavy metals from Ahmadu Bello Way, Old Panteka and New Panteka during the period of study. The F-Value obtained for the Zinc tests in comparison of wet and dry seasons showed the quantity of Zinc that is being discharged into the atmosphere not to be significantly differentat $p < 0.01$. This shows that seasons have no significant impact on presence of Zinc molecules in the atmosphere.

The F-Value for Lead tests in comparison of wet and dry seasons showed the quantity of Lead being released into the atmosphere to be significantly differentat $p < 0.01$, thus indicating the effect of seasons on discharge of Lead into the atmosphere. The F-Value obtained for the Iron tests in comparison of wet and dry seasons showed the quantity of Iron that is being discharged into the atmosphere not to be significantly differentat $p < 0.01$. This shows that seasons have no significant impact on presence of Iron molecules in the atmosphere**.**

Although the data provided strong evidence that the rainfall have impacts on the heavy metal concentration, statistically it showed no significant difference at $p < 0.01$ between the two seasons being considered with all correlation coefficient being less than 0.01. The high values of the metals concentration in dry season could be as a result of combination of elevated energy consumption while the concentration of heavy metals in wet season has been observed in various climatic regions to be related to the amount of precipitation.

Table 4.19 Seasonal Variation of Heavy Metals from the three locations during the period of Study.

Heavy Metals	Interactions	Sum of Squares	Df	Mean Square	F	Sig.
Zn	Between Groups	4.145	1	4.145	3.768	.061
	Within Groups	37.408	34	1.100		
	Total	41.553	35			
Pb	Between Groups	33.308	1	33.308	1275.261	.000
	Within Groups	.888	34	.026		
	Total	34.196	35			
Fe	Between Groups	74.394	1	74.394	3.926	.056
	Within Groups	644.261	34	18.949		
	Total	718.655	35			

Level of significant was set at $p < 0.01$

4.7 Variation in Acid and Base of Heavy Metals Studied in both the Wet and Dry Season during the Study Period

Table 4.20 represents results for wet season. From the results obtained, the F-value for the Analysis of variance for the two methods considered i.e. acid and base methods, gave the same result for Zinc and Lead tests for all the locations and same in Fe test in Ahmadu Bello Way and Old Panteka. The results obtained for the two methods for the tests were not significantly different at $p < 0.01$for Zinc and Lead as well as Fe in ABW and OP. However, the F-value obtained for Iron in NP showed that the two methods i.e. acid and base methods gave different results.

Tables 4.21 represent result for dry season. The F-value obtained for the Analysis of variance for the two methods considered i.e. acid and base methods, gave thesame result. The results obtained for the two methods for the tests were not significantly different at $p < 0.01$ for all the locations in consideration.

The level of significance difference was high at $p < 0.01$ in the dry season when compared with the wet season.

Table 4.20 Variation in Acid and Base of Heavy Metals from the three locations during the wet season

Heavy metals	Interactions	Sum of Squares	Df	Mean Square	F	Sig.
Zn ABW	Between Groups	.309	1	.309	2.016	.186
	Within Groups	1.535	10	.153		
	Total	1.844	11			
Zn OP	Between Groups	.239	1	.239	.333	.576
	Within Groups	7.181	10	.718		
	Total	**7.421**	**11**			
Zn NW	Between Groups	6.095	1	6.095	.947	.353
	Within Groups	64.336	10	6.434		
	Total	**70.431**	**11**			
Pb ABW	Between Groups	.000	1	.000	.018	.896
	Within Groups	.006	10	.001		
	Total	**.006**	**11**			
Pb OP	Between Groups	.000	1	.000	.007	.937
	Within Groups	.010	10	.001		
	Total	**.010**	**11**			
Pb NP	Between Groups	.003	1	.003	.891	.367
	Within Groups	.038	10	.004		
	Total	**.041**	**11**			
Fe ABW	Between Groups	3.289	1	3.289	8.192	.017
	Within Groups	4.015	10	.401		
	Total	**7.303**	**11**			
Fe OP	Between Groups	1.605	1	1.605	5.694	.038
	Within Groups	2.818	10	.282		
	Total	**4.423**	**11**			
Fe NW	Between Groups	4.455	1	4.455	14.737	.003
	Within Groups	3.023	10	.302		
	Total	**7.479**	**11**			

Level of significant was set at $p < 0.01$

Table 4.21 Variation in Acid and Base of Heavy Metals from the three locations during the dryseason

Heavy metals	Interactions	Sum of Squares	Df	Mean Square	F	Sig.
Zn ABW	Between Groups	.001	1	.001	.050	.827
	Within Groups	.236	10	.024		
	Total	**.237**	**11**			
Zn OP	Between Groups	.018	1	.018	1.216	.296
	Within Groups	.144	10	.014		
	Total	**.162**	**11**			
Zn NW	Between Groups	.000	1	.000	.001	.972
	Within Groups	.077	10	.008		
	Total	**.077**	**11**			
Pb ABW	Between Groups	.000	1	.000	.000	.997
	Within Groups	.380	10	.038		
	Total	**.380**	**11**			
Pb OP	Between Groups	.000	1	.000	.006	.939
	Within Groups	.049	10	.005		
	Total	**.049**	**11**			
Pb NP	Between Groups	.000	1	.000	.118	.738
	Within Groups	.024	10	.002		
	Total	**.025**	**11**			
Fe ABW	Between Groups	.001	1	.001	.000	.991
	Within Groups	69.832	10	6.983		
	Total	**69.833**	**11**			
Fe OP	Between Groups	68.914	1	68.914	1.522	.245
	Within Groups	452.708	10	45.271		
	Total	**521.622**	**11**			
Fe NP	Between Groups	.287	1	.287	.390	.546
	Within Groups	7.349	10	.735		
	Total	**7.636**	**11**			

Level of significant was set at $p < 0.01$

4.8 Variation in Acid and Base of Heavy Metals in Locations Studied in both the Wet and Dry Season during the Study Period

Table 4.22 represents results for wet season, the zinc tests for all the locations were not significantly different at $p < 0.01$, thus indicating that the same quantity of zinc is being released into the atmosphere. The Lead tests for all the locations were not significantly different at $p < 0.01$, thus indicating that the same quantity of Lead is being released into the atmosphere. The Iron tests for all the locations were not significantly different at $p < 0.01$, thus indicating that the same quantity of Iron is being released into the atmosphere.

Table 4.23 represents result for dry season. The zinc tests for all the locations were not significantly different at $p < 0.01$, thus indicating that the same quantity of zinc is being released into the atmosphere. The Lead tests for all the locations were significantly different at $p < 0.01$, thus indicating that the quantity of Lead in all these is significantly different at $p < 0.01$. However, the Duncan test showed two of the locations to have nearly the same quantity of Lead in the atmosphere while the quantity of Lead in the other location were not the same as the other two locations. The Iron tests for all the locations were not significantly different at $p < 0.01$, thus indicating that the same quantity of Iron is being released into the atmosphere.

Table 4.22 Mean Values of Heavy Metals with respect to locations in the wet season.

Heavy metals	Interactions	Sum of Squares	Df	Mean Square	F	Sig.
Zn	Between Groups	2.565	2	1.283	.556	.585
	Within Groups	34.588	15	2.306		
	Total	**37.153**	**17**			
Pb	Between Groups	.000	2	.000	.277	.762
	Within Groups	.009	15	.001		
	Total	**.010**	**17**			
Fe	Between Groups	.256	2	.128	.806	.465
	Within Groups	2.381	15	.159		
	Total	**2.637**	**17**			

Level of significant was set at $p < 0.01$

Table 4.23 Mean Values of Heavy Metals with respect to locations in the wet season.

Heavy metals	Interactions	Sum of Squares	df	Mean Square	F	Sig.
Zn	Between Groups	.002	2	.001	.069	.934
	Within Groups	.252	15	.017		
	Total	**.254**	**17**			
Pb	Between Groups	.589	2	.294	15.231	.000
	Within Groups	.290	15	.019		
	Total	**.878**	**17**			
Fe	Between Groups	174.591	2	87.295	2.804	.092
	Within Groups	467.034	15	31.136		
	Total	**641.625**	**17**			

Level of significant was set at $p < 0.01$

CHAPTER FIVE

CONCLUTION AND RECOMMENDATION

Metal levels studied in this research included Lead (Pb), Zinc (Zn) and Iron (Fe), in the wet season (August, September and October 2015)and the dry season (November, December, 2015 and January, 2016) the result showed that the values were lower than those in the dry season, these metals analysed are major sources of air pollution within the area of study because there are commercial and local industrial around these areas which agrees with reports by Quiterio *et al*. (2004) who assessed concentrations of total suspended particles and airborneparticulate trace metals in the industrial district of Santa Cruz, Rio de Janeiro, Brazil, where the main source of pollution was from the local industries.

The mean metal concentrations in Ahmadu Bello Way Kaduna showed that Pb had the lowest value followed by Zn while Fe had the highest value throughout the study period. The mean metal values obtained in this study compared with the safe limits proposed by NESREA (2009)/WHO (2011) showed that Pb was within the acceptable limit while Zn and Fe were above the safe standard. The results obtained from New and Old Panteka followed the same trend as that of Ahmadu Bello Way and this result agreed with values reported inprevious studies by Espinosa *et al.*, 2001; Karanasiou *et al*., 2007, of their total concentrations in PM10, respectively. The results for the Dry season in the months of November, December, 2015 and January of 2016 showed higher concentration as compared with that the wet season. These months of dry season showed that Pb had a higher value followed by Fe while Zn had the least value, comparing this with the safe limits proposed by NESREA (2009)/WHO (2011) all the metals had values above the acceptable limits by NESREA (2009)/WHO (2011). These three months November, December, 2015 and January, 2016 were characterized by low wind speed and serenity as compared to the other months. High concentration of heavy metals may be

because of poor dispersing condition due to low wind speed and surrounding conditions in these months, this agreed with reports made by Gupta and Karar, 2006, that higher mean metal concentration may be due to poor mixing condition during the dry season, various studies made too by Aneja *et al.*, 2012; Roy *et al*., 2012 reported higher concentration exceeding the prescribed standards. Similar patterns were also found in previous studies, such as of Mongolia (Nishikawa *et al.,* 2011), and Beijing (Sun *et al*., 2004) between the warm and cold seasons.Meanwhile, it is believed that traffic emissions are now the main source in urban areas due to the rapidly increasing number of motor vehicles in cities (Zhao *et al*., 2013).

ZINC (Zn)

Zn occurs naturally in ambient air particulate matter and so it was detected in this study.

The concentration of Zn in the first three months of study which cover months of the wet season (August, September and October, 2015) showed that the mean concentration of Zn was above recommended standards of NESREA (2009)/WHO (2011). The highest mean value of Zn throughout the period of study in the wet season was in the months of August, September and October, 2015 and it was recorded in New Panteka, which may be due to the types of commercial activities taking place in that area like iron smelting and fixing of vehicular parts which agreed with the report made by Nriagu and Davidson (1980) that Zn containing particles might have been released by metallurgical plants and brass/zinc production facilities to the environment. The high presence of Zn in these areas might be due to wind-blown soil and road dust, the concentrations of mean metals determined in present study has same order of magnitude as was reported in a study conducted in Islamabad by Shaheen *et al*., 2005. Major sources of Zn are Tire wear, Motor oil, Grease, Brake emissions, Corrosion of galvanized parts as it was observed in the results obtained in Ahmadu Bello Way which is a commercial area with higher

vehicular traffic that might be the cause of higher concentration of Zn. Another factor which might have lead to the presence of Zn in these areas of study could be due to road temperature which was always very high which leads to high amount of tire wear of vehicles passing from the highway this suggest several scientific reports which revealed that particulate matter of lesser particles size were emitted from the automobile emission depending on the speed of vehicles and type of fuel used (Morawska *et al*., 2002; Sharma *et al*., 2006). The usage of Zn for protective coating on iron, steel etc. by the industries in Old and New Panteka could be the major reason for the higher concentration of this heavy metal in this area. Values obtained during the dry season showed a low concentration of mean value for Zn. In the month of November, all the mean values were below the recommended limits of NESREA (2009)/WHO (2011) except in New Panteka which showed value above the recommended value, this same trend was also observed in the month of December, 2015 in all the areas of study but in the month of January, 2016 the mean values were below NESREA (2009)/WHO (2011) standards.

LEAD (Pb)

The value of Pb during the study period showed that it had lower values in all the areas under study. For the first three months Pb had the least value, in some cases it was not detected which showed that it was below the international standards of NESREA (2009)/WHO (2011), the first three months of August, September and October, 2015 showed that the concentration of Pb was low in Ahmadu Bello Way, Old Panteka and New Panteka. During the remaining months of November, December, 2015 and January, 2016, there was increase in mean metal concentration which showed that there was low concentration of Pb in the wet season to the dry season and this agreed with the report of Mishra*et al.,* 2000, in his research on local industrial areas around King

Sejong Station that the Concentration of Lead was comparative low i.e. almost half of the commercial and industrial zone.

In the month of November, 2015 the highest value of Pb was from New Panteka followed by Old Panteka, this high mean metal concentration that was recorded maybe due to the commercial activities going on in these areas. Metal smelting and vehicular movement are associated with these areas under study and this report agreed with the work of Mishra*et al.*, 2000, that most probable sources of heavy metals example; Pb from commercial zone were automobile body workshops and vehicular activities while the probable sources for industrial zone was electroplating and small scale of galvanizing industries.

The higher Pb level in the ambient air of heavy traffic area was quite obvious and was due to the vehicular emission, apart from the other contributing sources. Anthropogenic activities, wind velocity and wind directions were the major contributing sources of air pollution around the areas under study and this was due to the high population of people around the area of study. Season had an impact in the concentration of these heavy metal in the areas under study because the results obtained showed that the wet season had lower mean metal values compared to the dry season and this may be due to the density of the metals in air and which agrees with report by Gotschi*et al*. (2005)an increase in density in one of these elements resulted in an increase in density in the other in air. The concentration of these heavy metal in the ambient air within the areas under study has to do with the size distribution of the metals within the two seasons and this trend agreed with report made by Karanasiou *et al*., (2007) in his study at Athens Urban Aerosol during Summerthat the size distribution trend of Pb concentration was noticed in the study.

IRON (Fe)

The mean concentration of Fe during the study period in the months of August, September and October, 2015 showed that the mean values for Fe were above those of international standards as set by NESREA (2009)/WHO (2011). Ahmadu Bello Way, Kaduna had the highest mean value of heavy metals in the first three months followed by Old Panteka and New Panteka respectively. This high value recorded might be due to the presence of commercial activities, variations in average levels of Fe exhibited the following pattern during the study period. Concentration of heavy metals was higher in the wet season than the dry season, manifesting a negative interaction with the temperature taking place in these areas under study.

Fe is one of the most frequently used element in this area where these local industrial activities are taking place and particularly prevalent in the roll andmelting industries as it was observed in results from both Old Panteka and New Panteka because these sites have local industrial activities taking place which agreed with similar report made by Querol*et al*., 2004, when he studied Metals in airborne particulate matter in industrialdistrict of Santa Cruz, Rio de Janeiro.

5.1 CONCLUSION

In conclusion, the concentration of heavy metals in ambient air in Chechenia Market along Ahmadu Bello Way Kaduna, Old Panteka, Kaduna and New Panteka, Kadunahas shown that most of the mean metal values obtained in comparison with NESREA (2009)/WHO (2011) were significantly highly($P>0.01$). In this study Pb, Zn and Fe content were the heavy metals of interest. There was seasonal trend of Pb concentrations during the period of study showing low concentrations during wet season and showed a significant high concentration during the dry season.

The main sources air pollution from the area of study isvehicular traffic, combustion of fuel, anthropogenic activities, local heating, wear and tear of tyres and dust resuspension.

The obtained results from this study has substantially improve our knowledge in estimating parameters that define transport distribution and interaction of pollutants from the sources of pollution to human population and with a sole aim of finding effective solutions to improve air quality and for a sustainable development in commercial areas and urban centers.

5.2 RECOMMENDATION

From this research, the following recommendations were made;

1. Studies should be carried out to develop and implement technological and management solutions for the reduction of heavy metals in suspended particulate matter.
2. Government should relocate some of these sites to areas that are not densely populated.
3. There should be routine checks on the air quality so as to know whether they are within international and national acceptable limits or limits of NESREA (2009)/WHO (2011).
4. Awareness should be created by regulatory agencies on the effect of glazed food containers.

5. Phasing out any remaining uses of heavy metal additives (e.g. lead) should be encouraged.
6. There is a need to develop effective framework by both the state and federal government that will initiate the integration and ensure implementation of safety regulations in this areas and also promote adherence to practice these safety guidelines (e.g. safety mask and goggles).
7. Further studies should be carried on other heavy metals in order to know their concentration in the atmosphere.

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APPENDIX



Plate 1: Old Air Sampler

APPENDIX II



Plate 2: New Air Sampler

APPENDIX III



Plate 3: Old Panteka



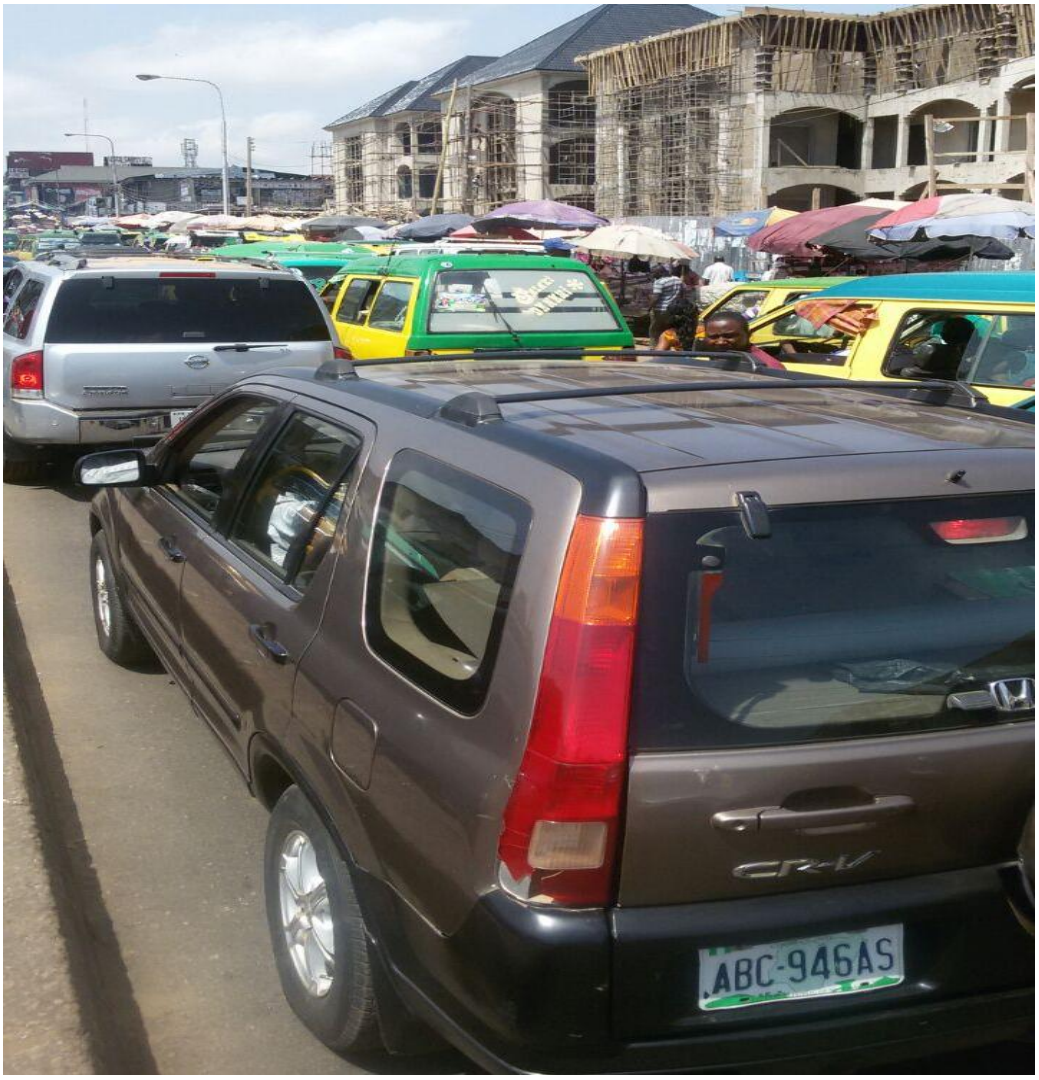
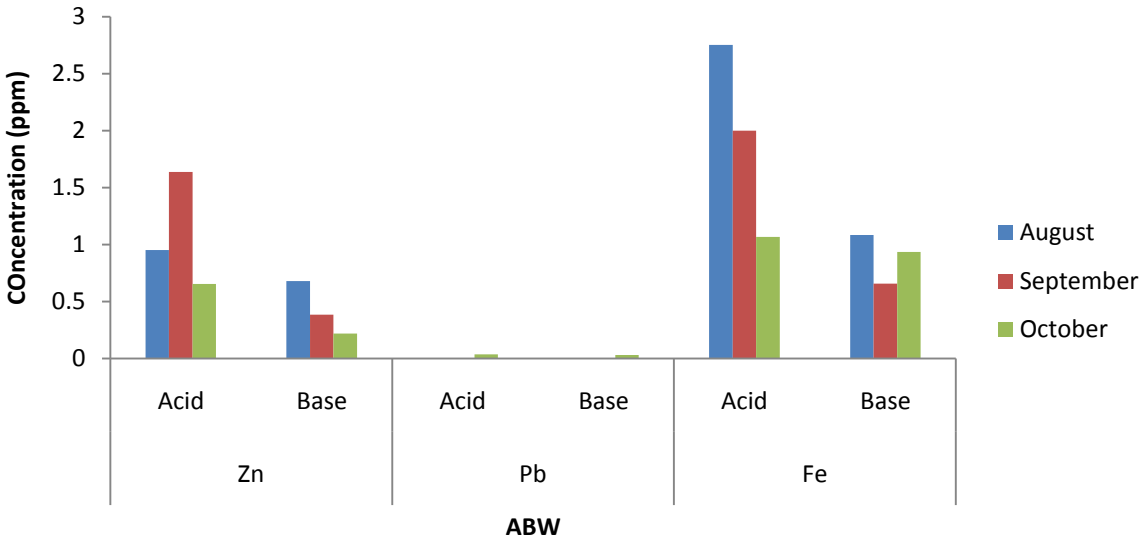


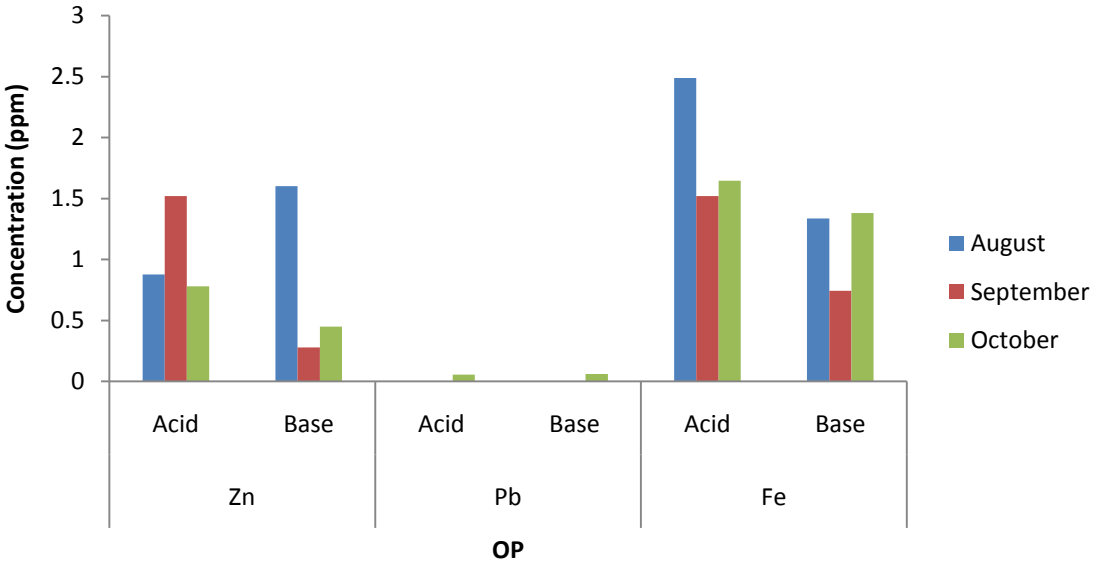
Plate 5: Ahmadu Belllo Way

APPENDIX V

Graph of Wet Season concentration of Zn, Fe and Pb (Ahmadu Bello Way)

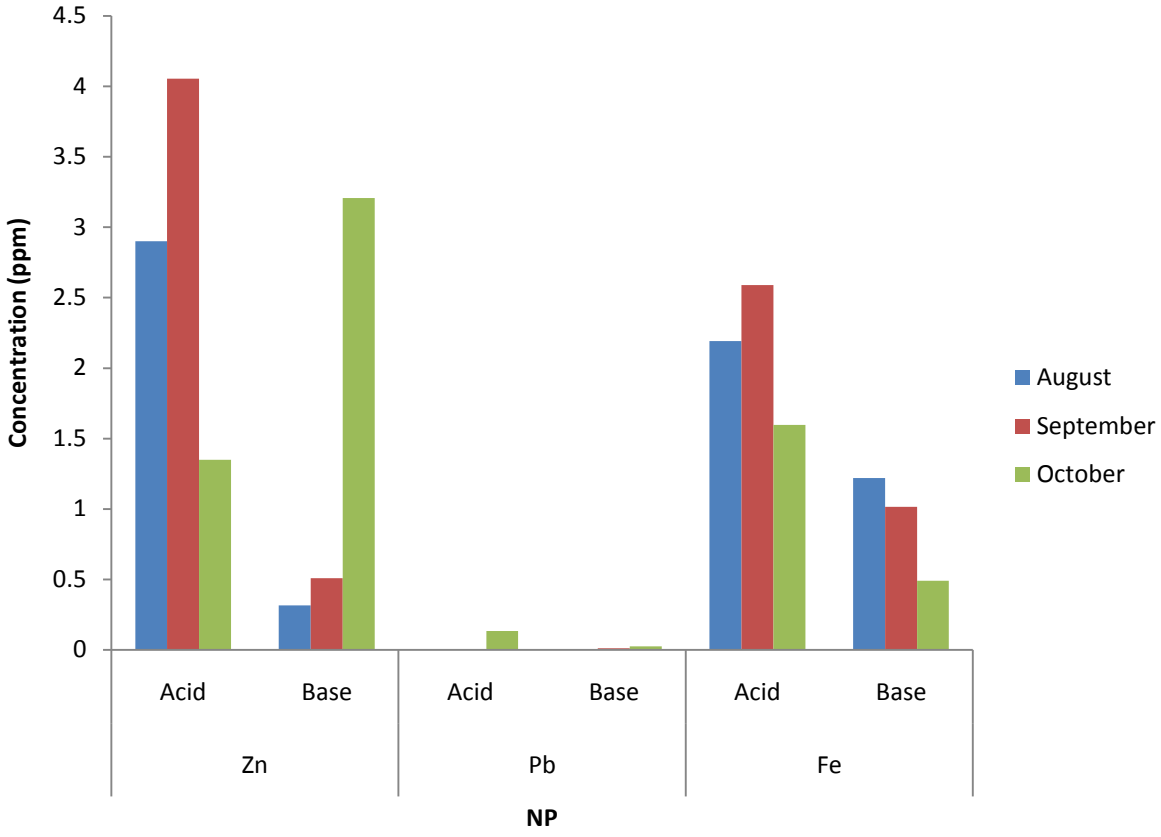


Graph of Wet Season concentration of Zn, Fe and Pb (Old Panteka)



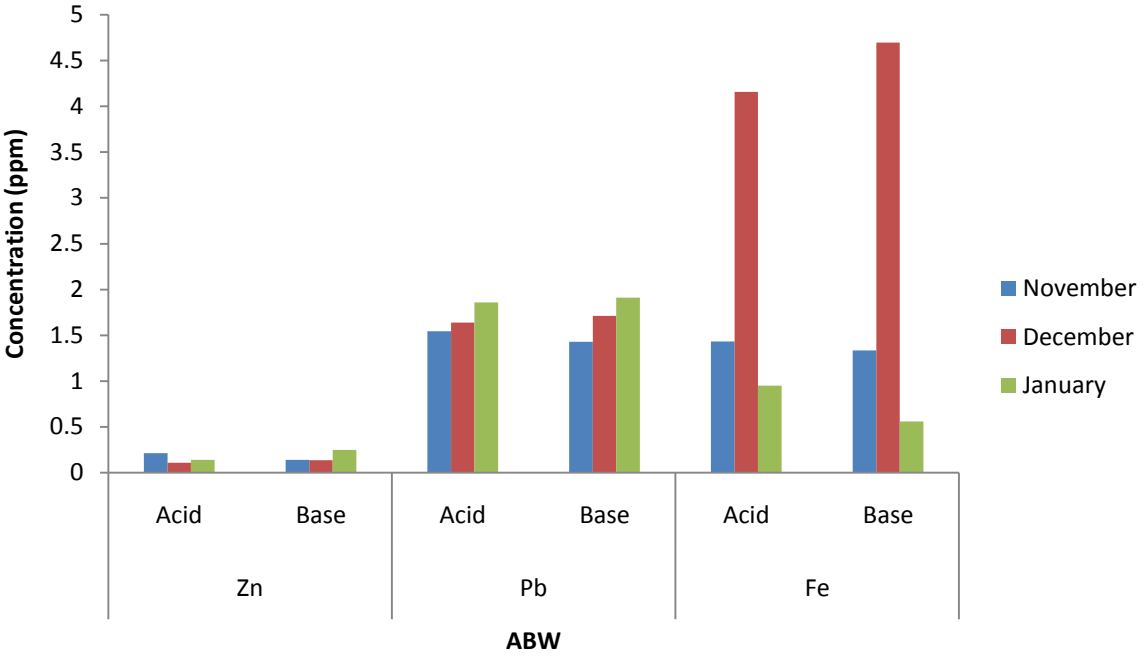
APPENDIX VI

Graph of Wet Season concentration of Zn, Fe and Pb (New Panteka)

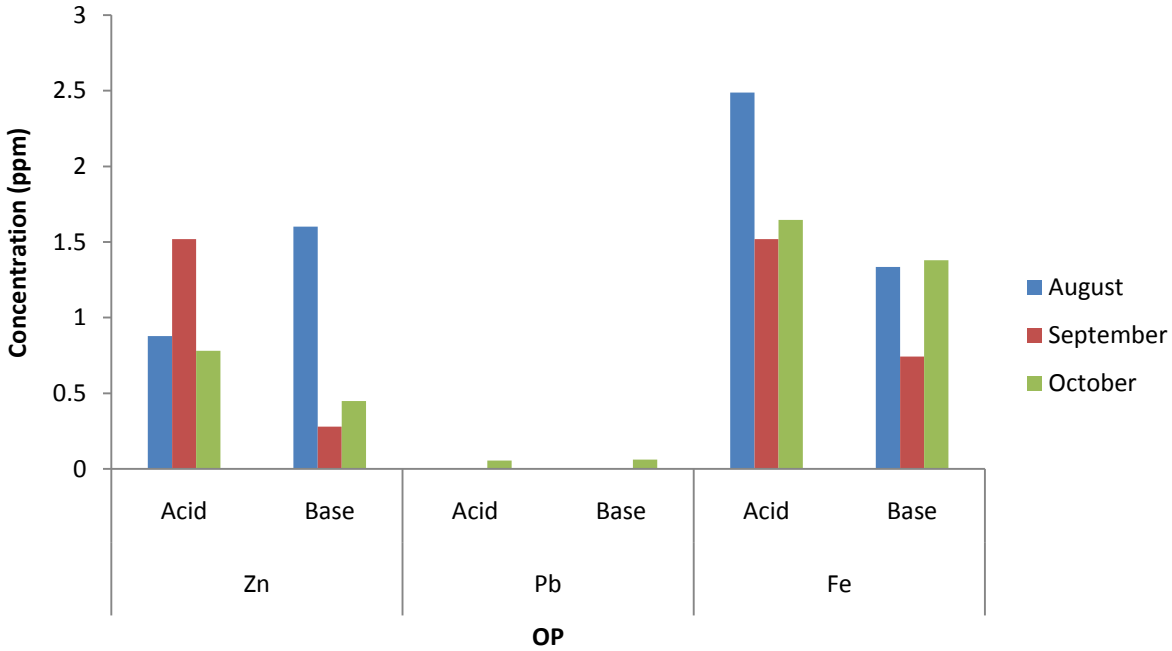


APPENDIX VII

Dry Season concentration of Zn, Fe and Pb (Ahmadu Bello Way)

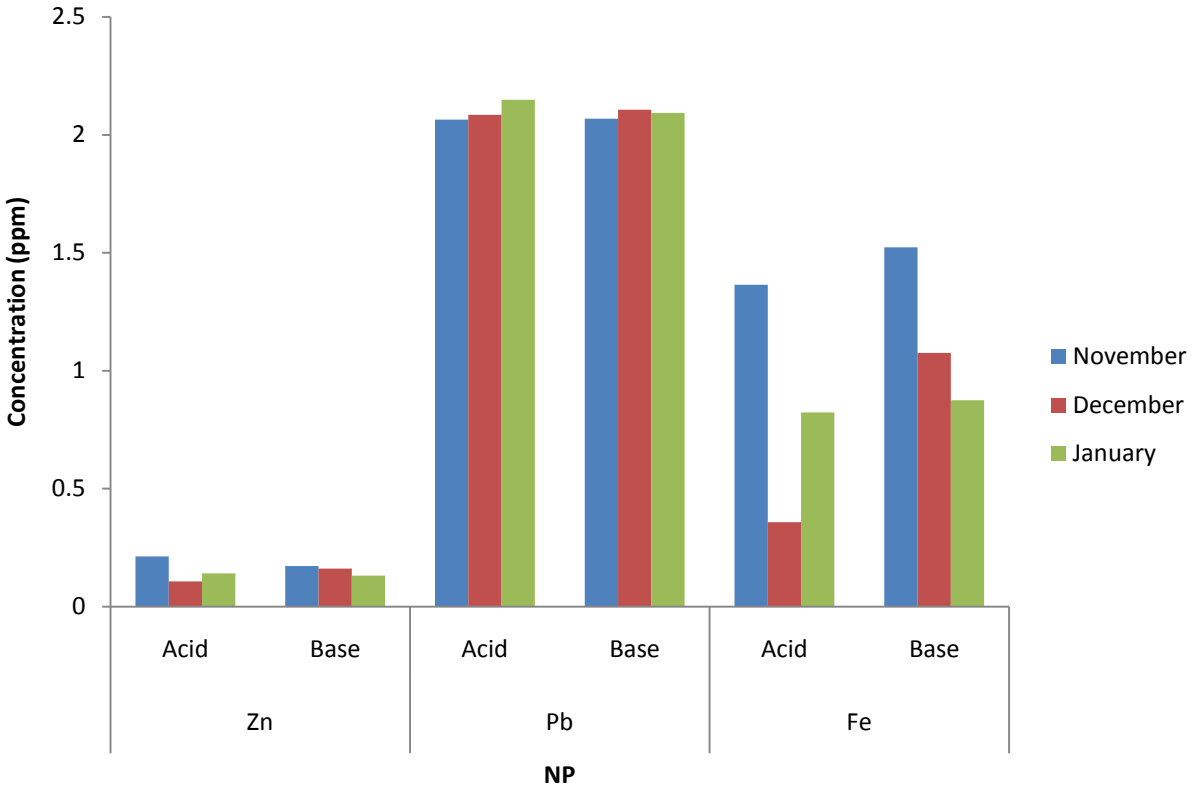


Dry Season concentration of Zn, Fe and Pb (Old Panteka)



APPENDIX VIII

Dry Season concentration of Zn, Fe and Pb (New Panteka)



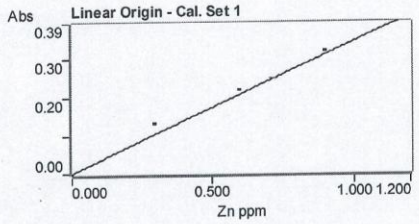
APPENDIX IX

AAS Read out of Zinc in wet season

SpectrAA Report. 12:22 PM 10/30/2015 Page 1 of 2

Analyst	MUSRL/ABU Zaria
Date Started	11:52 AM 10/30/2015
Worksheet	Zinc 001 40
Comment	Halima G Habib
Methods	Zn
Computer name	MUSRL-PC
Serial Number:	AA0904M046

Method: Zn Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	0.715	0.0014	0.2452
Sample 2	0.307	0.0005	0.1053
Sample 3	0.776	0.0012	0.2660
Sample 5	0.756	0.0011	0.2590
Sample 6	0.299	0.0003	0.1026
Sample 7	1.187	0.0000	0.4068
Sample 8	1.045	0.0020	0.3582
Sample 9	0.978	0.0023	0.3354
Sample 10	0.289	0.0010	0.0989
Sample 12	0.331	0.0006	0.1133
Sample 13	1.176	0.0000	0.4030
Sample 14	0.343	0.0012	0.1176
Sample 15	0.875	0.0021	0.3001
Sample 16	0.349	0.0006	0.1197
Sample 17	1.162	0.0000	0.3984
Sample 18	0.293	0.0005	0.1003
Sample 20	0.426	0.0021	0.1460
Sample 22	0.210	0.0007	0.0718
Sample 24	0.722	0.0021	0.2474
Sample 25	0.996	0.0025	0.3416
Sample 26	0.198	0.0007	0.0678
Sample 27	1.045	0.0018	0.3584
Sample 28	0.560	0.0014	0.1920
Sample 31	0.313	0.0024	0.1073
Sample 32	0.243	0.0006	0.0833
Sample 33	0.516	0.0011	0.1769
Sample 34	0.346	0.0012	0.1185
Sample 35	0.241	0.0009	0.0825
Sample 36	0.207	0.0015	0.0708
Sample 37	0.454	0.0010	0.1944
Sample 38	0.393	0.0021	0.1682
Sample 4	2.914m	0.0016	0.0999
Sample 11	5.047m	0.0015	0.1730
Sample 19	2.102m	0.0006	0.0720
Sample 21	2.163m	0.0015	0.0742
Sample 23	6.949m	0.0024	0.2382
Sample 29	2.456m	0.0008	0.0842
Sample 30	6.207m	0.0011	0.2128

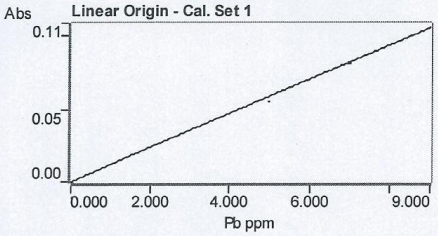
Appendix X

AAS Read out of Lead in wet season

	Sample 37	0.038	0.0002	0.0009
	Sample 38	0.028	0.0002	0.0007

SpectrAA
Analyst
Date Starte
Worksheet Lead 001 41
Comment Halima G Habib
Methods Pb
Computer name MUSRL-PC
Serial Number: AA0904M046

Method: Pb Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	0.000	0.0002	-0.0006
Sample 2	0.000	0.0003	-0.0008
Sample 3	0.000	0.0001	-0.0010
Sample 4	0.000	0.0003	-0.0010
Sample 5	0.000	0.0003	-0.0011
Sample 6	0.000	0.0002	-0.0011
Sample 7	0.000	0.0003	-0.0008
Sample 8	0.000	0.0001	-0.0014
Sample 9	0.000	0.0004	-0.0011
Sample 10	0.000	0.0002	-0.0009
Sample 11	0.000	0.0003	-0.0010
Sample 12	0.000	0.0003	-0.0007
Sample 13	0.000	0.0001	-0.0008
Sample 14	0.000	0.0003	-0.0007
Sample 15	0.000	0.0001	-0.0006
Sample 16	0.000	0.0002	-0.0007
Sample 17	0.000	0.0001	-0.0005
Sample 18	0.000	0.0001	-0.0005
Sample 19	0.000	0.0001	-0.0007
Sample 20	0.000	0.0001	-0.0009
Sample 21	0.000	0.0002	-0.0003
Sample 22	0.000	0.0002	-0.0002
Sample 23	0.002	0.0003	0.0000
Sample 24	0.021	0.0001	0.0002
Sample 25	0.000	0.0002	-0.0001
Sample 26	0.024	0.0003	0.0003
Sample 27	0.050	0.0001	0.0006
Sample 28	0.038	0.0002	0.0004
Sample 29	0.211	0.0003	0.0025
Sample 30	0.000	0.0003	-0.0001
Sample 31	0.072	0.0002	0.0008
Sample 32	0.037	0.0001	0.0004
Sample 33	0.062	0.0003	0.0007
Sample 34	0.083	0.0002	0.0010
Sample 35	0.059	0.0003	0.0007
Sample 36	0.050	0.0002	0.0006

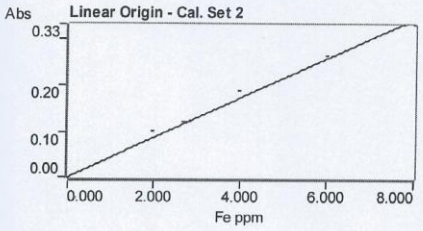
Appendix XI

AAS Read out of Iron in wet season

SpectrAA Report. **10:48 AM 10/30/2015** **Page 1 of 2**

Analyst	MUSRL/ABU Zaria
Date Started	9:58 AM 10/30/2015
Worksheet	Iron 001 31
Comment	Halima G Habib
Methods	Fe
Computer name	MUSRL-PC
Serial Number:	AA0904M046

Method: Fe Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	2.753	0.0016	0.1184
Sample 2	1.158	0.0005	0.0498
Sample 3	2.998	0.0003	0.1289
Sample 4	1.466	0.0006	0.0631
Sample 5	2.453	0.0008	0.1055
Sample 6	1.053	0.0002	0.0453
Sample 7	2.756	0.0007	0.1185
Sample 8	1.012	0.0007	0.0435
Sample 9	1.978	0.0011	0.0851
Sample 10	1.206	0.0006	0.0519
Sample 11	1.933	0.0006	0.0831
Sample 12	1.386	0.0005	0.0596
Sample 13	2.411	0.0018	0.1037
Sample 14	1.153	0.0011	0.0496
Sample 15	1.252	0.0006	0.0538
Sample 16	1.029	0.0008	0.0443
Sample 17	1.965	0.0004	0.0845
Sample 18	0.762	0.0004	0.0328
Sample 19	1.588	0.0004	0.0683
Sample 20	0.162	0.0010	0.0070
Sample 21	1.787	0.0006	0.0769
Sample 22	0.456	0.0003	0.0196
Sample 23	3.215	0.0009	0.1383
Sample 24	1.265	0.0003	0.0544
Sample 25	0.822	0.0006	0.0354
Sample 26	1.015	0.0008	0.0437
Sample 27	1.973	0.0006	0.0849
Sample 28	1.630	0.0010	0.0701
Sample 29	1.955	0.0014	0.0841
Sample 30	0.264	0.0001	0.0114
Sample 31	1.311	0.0006	0.0564
Sample 32	0.858	0.0005	0.0369
Sample 33	1.317	0.0007	0.0566
Sample 34	1.130	0.0006	0.0486
Sample 35	1.238	0.0005	0.0532
Sample 36	0.717	0.0005	0.0308
Sample 37	1.882	0.0348	0.0809
Sample 38	0.939	0.0168	0.0404

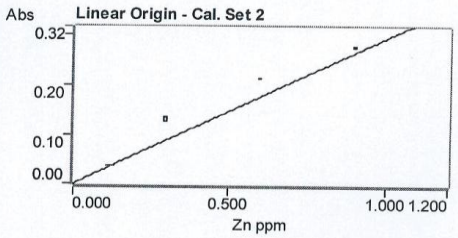
Appendix XII

AAS Read out for Zn in dry season

SpectrAA Report. **1:25 PM 2/19/2015** **Page 1 of 2**

Analyst	MUSRL/ABU Zaria
Date Started	12:58 PM 2/19/2015
Worksheet	Zinc 001 88
Comment	Haj. Halima Water Re.
Methods	Zn
Computer name	MUSRL-PC
Serial Number:	AA0904M046

Method: Zn Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	0.122	0.0016	0.0356
Sample 2	0.050	0.0008	0.0147
Sample 3	0.303	0.0009	0.0884
Sample 4	0.227	0.0001	0.0663
Sample 5	0.032	0.0007	0.0092
Sample 6	0.051	0.0007	0.0148
Sample 7	0.186	0.0007	0.0542
Sample 8	0.221	0.0004	0.0646
Sample 9	0.022	0.0004	0.0064
Sample 10	0.000	0.0010	-0.0091
Sample 11	0.259	0.0010	0.0757
Sample 12	0.494	0.0027	0.1444
Sample 13	0.291	0.0024	0.0851
Sample 14	0.095	0.0006	0.0277
Sample 15	0.377	0.0003	0.1101
Sample 16	0.226	0.0005	0.0661
Sample 17	0.116	0.0007	0.0339
Sample 18	0.176	0.0006	0.0515
Sample 19	0.123	0.0015	0.0360
Sample 20	0.316	0.0008	0.0922
Sample 21	0.214	0.0019	0.0624
Sample 22	0.020	0.0010	0.0059
Sample 23	0.429	0.0009	0.1252
Sample 24	0.258	0.0008	0.0753
Sample 25	0.087	0.0006	0.0255
Sample 26	0.218	0.0008	0.0636
Sample 27	0.334	0.0027	0.0975
Sample 28	0.126	0.0003	0.0367
Sample 29	0.036	0.0008	0.0107
Sample 30	0.066	0.0005	0.0194
Sample 31	0.179	0.0013	0.0524
Sample 32	0.257	0.0006	0.0751
Sample 33	0.155	0.0002	0.0454
Sample 34	0.123	0.0008	0.0361
Sample 35	0.127	0.0008	0.0372
Sample 36	0.139	0.0016	0.0405
Sample 37	0.086	0.0650	0.0251
Sample 38	0.033	0.0127	0.0095

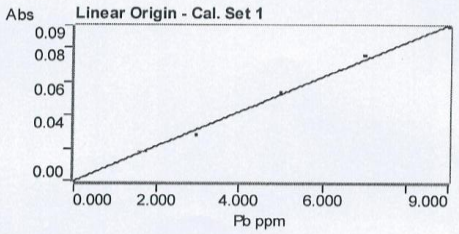
Appendix XIII

AAS Read out for Pb in dry season

SpectrAA Report. **12:57 PM 2/19/2015** **Page 1 of 2**

Analyst	MUSRL/ABU Zaria
Date Started	12:16 PM 2/19/2015
Worksheet	Lead 001 96
Comment	Haj. Halima Water Re.
Methods	Pb
Computer name	MUSRL-PC
Serial Number:	AA0904M046

Method: Pb Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	1.658	0.0008	0.0172
Sample 2	1.401	0.0006	0.0146
Sample 3	1.442	0.0001	0.0150
Sample 4	1.455	0.0004	0.0151
Sample 5	1.653	0.0008	0.0172
Sample 6	1.707	0.0004	0.0177
Sample 7	1.627	0.0001	0.0169
Sample 8	1.717	0.0003	0.0178
Sample 9	1.796	0.0001	0.0187
Sample 10	1.842	0.0002	0.0192
Sample 11	1.923	0.0004	0.0200
Sample 12	1.980	0.0004	0.0206
Sample 13	1.963	0.0005	0.0204
Sample 14	1.977	0.0003	0.0206
Sample 15	1.983	0.0002	0.0206
Sample 16	1.940	0.0001	0.0202
Sample 17	2.057	0.0002	0.0214
Sample 18	2.021	0.0003	0.0210
Sample 19	2.096	0.0004	0.0218
Sample 20	2.164	0.0001	0.0225
Sample 21	2.091	0.0001	0.0217
Sample 22	2.103	0.0003	0.0219
Sample 23	2.034	0.0004	0.0211
Sample 24	2.038	0.0006	0.0212
Sample 25	2.040	0.0007	0.0212
Sample 26	2.083	0.0001	0.0217
Sample 27	2.088	0.0010	0.0217
Sample 28	2.054	0.0003	0.0214
Sample 29	2.081	0.0004	0.0216
Sample 30	2.090	0.0004	0.0217
Sample 31	2.089	0.0001	0.0217
Sample 32	2.123	0.0007	0.0221
Sample 33	2.204	0.0002	0.0229
Sample 34	2.152	0.0005	0.0224
Sample 35	2.093	0.0006	0.0218
Sample 36	2.034	0.0003	0.0211
Sample 37	1.068	0.0004	0.0222
Sample 38	1.085	0.0001	0.0226

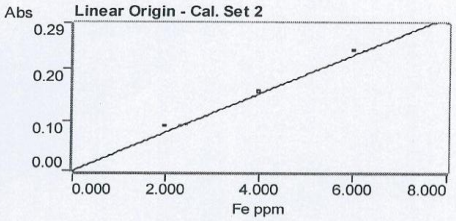
Appendix XIV

AAS Read out for Fe in dry season

SpectrAA Report. **12:14 PM 2/19/2015** **Page 1 of 2**

Analyst	MUSRL/ABU Zaria
Date Started	11:44 AM 2/19/2015
Worksheet	Iron 001 70
Comment	Haj. Halima Water Res.
Methods	Fe
Computer name	MUSRL-PC
Serial Number:	AA0904M046

Method: Fe Water (Flame)



Sample ID	Conc ppm	SD	Mean Abs
Sample 1	2.360	0.0015	0.0891
Sample 2	1.450	0.0014	0.0547
Sample 3	0.502	0.0002	0.0190
Sample 4	1.221	0.0013	0.0461
Sample 5	0.734	0.0011	0.0277
Sample 6	2.189	0.0041	0.0826
Sample 7	7.583	0.0010	0.2862
Sample 8	7.206	0.0008	0.2720
Sample 9	0.538	0.0005	0.0203
Sample 10	0.123	0.0008	0.0046
Sample 11	1.366	0.0006	0.0516
Sample 12	0.997	0.0007	0.0376
Sample 13	2.740	0.0018	0.1034
Sample 15	2.439	0.0018	0.0920
Sample 16	0.273	0.0003	0.0103
Sample 17	1.421	0.0008	0.0536
Sample 19	7.398	0.0021	0.2792
Sample 21	2.286	0.0010	0.0863
Sample 22	0.280	0.0007	0.0106
Sample 23	4.296	0.0016	0.1621
Sample 24	1.252	0.0008	0.0472
Sample 25	2.037	0.0010	0.0769
Sample 26	0.136	0.0010	0.0051
Sample 27	0.691	0.0008	0.0261
Sample 28	2.910	0.0012	0.1098
Sample 29	0.380	0.0009	0.0144
Sample 30	0.515	0.0006	0.0194
Sample 31	0.337	0.0003	0.0127
Sample 33	1.096	0.0010	0.0414
Sample 34	0.448	0.0002	0.0169
Sample 35	0.552	0.0002	0.0208
Sample 36	1.302	0.0005	0.0491
Sample 37	0.327	0.0037	0.0123
Sample 38	2.208	0.0045	0.0833
Sample 14	13.513m	0.0001	0.0510
Sample 18	23.015m	0.0005	0.0869
Sample 20	11.004m	0.0016	0.0415
Sample 32	16.371m	0.0008	0.0618

Appendix XV

DMRT for Zn in wet season

VAR00001	N	Subset for alpha = .05
	1	One
1.00	6	.4270
2.00	6	.7763
3.00	6	1.3432
Sig.		.338

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.

DMRT for Pbin wet season

VAR00001	N	Subset for alpha = .05
	1	One
1.00	6	.0102
3.00	6	.0118
2.00	6	.0202
Sig.		.520

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.

DMRT for Fein wet season

VAR00001	N	Subset for alpha = .05
	1	1
1.00	6	.8927
3.00	6	.9078
2.00	6	1.1528
Sig.		.300

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.

Appendix XVI

DMRT for Zn in dry season

VAR00001	N	Subset for alpha = .05
	1	1
3.00	6	.1548
1.00	6	.1738
2.00	6	.1818
Sig.		.738

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.

Appendix XIII

DMRT for Pb in dry season

VAR00001	N	Subset for alpha = .05	
	1	2	1
1.00	6	1.6837	
2.00	6		2.0405
3.00	6		2.0893
Sig.		1.000	.552

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.

Appendix XIV

DMRT for Fe in dry season

VAR00001	N	Subset for alpha = .05
	1	1
3.00	6	1.1580
1.00	6	2.1977
2.00	6	8.2228
Sig.		.054

Means for groups in homogeneous subsets are displayed.
a uses Harmonic Mean Sample Size = 6.000.