ELEMENTAL CHARACTERIZATION OF $PM_{2.5}$ AND TORAL SUSPENDED PARTICULATE (TSP) IN AUTO-MECHANIC WORSHOPS AROUND UWELU MOTOR SPARE PARTS MARKET, BENIN CITY.

BY

ERHAIGHEWU JENNIFER EFE

PG/PSC0707581

DEPARTMENT OF CHEMISTRY

FACULTY OF PHYSICAL SCIENCES

UNIVERSITY OF BENIN

BENIN CITY

JANUARY, 2020

ELEMENTAL CHARACTERIZATION OF $PM_{2.5}$ AND TORAL SUSPENDED PARTICULATE (TSP) IN AUTO-MECHANIC WORSHOPS AROUND UWELU MOTOR SPARE PARTS MARKET, BENIN CITY.

BY

ERHAIGHEWU JENNIFER EFE

PG/PSC0707581

A THESIS IN THE DEPARTMENT OF CHEMISTRY, SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (MSc.) IN INDUSTRIAL CHEMISTRY

UNIVERSITY OF BENIN

BENIN CITY

NIGERIA

JANUARY, 2020

CERTIFICATION

This is to certify that this research project was carried out by Miss. Erhaighewu Jennifer Efe under my in the Department of Chemistry, University of Benin, in partial fulfillment of the Award for the Degree of Master of Science (M.Sc) in Industrial Chemistry.

____________________	____________________
ERHAIGHEWU JENNIFER EFE (STUDENT)	**DATE**
____________________	____________________
PROF J.M OKUO (SUPERVISOR)	**DATE**
____________________	____________________
DR BALA ANEGBE (CO-SUPERVISOR)	**DATE**
____________________	____________________
PROF E.E UKPEBOR (HEAD OF DEPARTMENT)	**DATE**

DEDICATION

This project work is dedicated to God Almighty for his infinite mercies, grace, knowledge and guidance during the course of my schooling at University of Benin and to my beloved parents Pastor and Mrs. D.A Erhaighewu for their care, encouragement and their financial support.

ACKNOWLEDGEMENT

I thank the Almighty God for making it possible for me to be alive to complete this project work and for taking me through this program successfully.

Special appreciation goes to my supervisor Prof James Okuo for the unreserved direction, guidance and tolerance throughout my writing of this thesis, God richly bless you. Special thanks goes to the Head of Department, Prof E.E Ukpebor and to all the Lecturers and non-academic staff of Chemistry Department.

Special thanks also to Mr Greg Onaiwu for his support, care and assistance during the course of this project work.

I would extend a hand of gratitude to my family members Mr and Mrs. Lato, Mr Ernest David Nurse Abiodun, Osasere, Ernest, Emmanuel and my dearest Henry Efosa, for their prayers and encouragement during tough times may God bless you all.

Finally, I want to say a big thank you to all my course mates who turned friends, I wish to appreciate my very own sister and project partner Miss Ohonba Osasumwen for all her support during the course of this project work.

TABLE OF CONTENT

LIST OF PLATES

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Particulate matter (PM) are basically released into the environment through anthropogenic activities such as combustion processes which includes vehicular emissions, combustion of fossil fuel, metal smelting, which significantly pollutes the environment, thereby having negative effects on man and its environment. Particulate matter comprises of different particles size, ranging from ultrafine particles to total suspended particulates and various composition, the major components are the organic and the inorganic (metals) and these are the once that have cause for health concern. Metals have divers of adverse effects on the environment and on the human body

In this study, $PM_{2.5}$ and TSP were collected during the dry and wet season using APEX2IS Casella standard pump coupled with conical inhalable sampler (CIS) head at a flow rate 3.5L/min for a sampling period of 8 hours per day. The weight of the sample collected were determined gravimetrically and analyzed for heavy metal concentration in $PM_{2.5}$ and TSP using Atomic Absorption Spectroscopy (AAS) method. The results obtained were subjected to Statistical analysis such as principal component analysis (PCA) for source identification, cluster analysis and correlation matrix.

$PM_{2.5}$ concentration obtained ranged from 2604.16 - 7351.18 $\mu g/m^3$, while TSP levels obtained ranged from 10758.91 - 16458.34 $\mu g/m^3$. The highest concentrations for both $PM_{2.5}$ and TSP were obtained in February and the least concentrations in June. The heavy metals analysis showed that the highest value of lead (1.08 and 2.78 $\mu g/m^3$) and cadmium (0.73 and 1.36 $\mu g/m^3$) for $PM_{2.5}$ and TSP respectively in all sampling sites had values which exceeded those of the regulatory limits (0.5 $\mu g/m^3$ for lead) and (0.005 $\mu g/m^3$ for cadmium), while other like chromium, zinc, nickel, cadmium, iron, arsenic and manganese were below the regulatory limits. The PCA result identified vehicular emission, as a major source of emission into the environment. Correlation matrix revealed strong positive correlation among some metals, others negative correlation and some were not correlated. The concentration of $PM_{2.5}$ recorded in this study were higher than safe limit stated by regulatory bodies (WHO, FEPA, FMNEW).

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

In cities of most developing world, rapid economic growth together with ineffective transportation system is causing a raise in vehicular ownership and subsequent vehicular traffic, which is a main source of emissions of particulate matter pollution (Kinney *et al*., 2011).

Road transport has also been identified as the single largest source of air pollution with contributions from automobiles reported to fall within the range of 40 to 80% (Agyemang-Bonsu *et al.,* 2010; Goyal *et al*., 2006). According to the United Nations Environment Programme (UNEP), emissions from motor vehicles account for about 90% of air pollution in fast growing cities in most developing world (UNEP, 2013). Though there are many causes of ambient air pollution, including burning of domestic waste, biomass burning, re-suspended road dust and windblown dust as well as dry harmattan winds (Nerquaye-Tetteh, 2009; Zhou *et al*., 2013), motor vehicles contribute greatly to the air pollution problem. Emissions from motor vehicles include a wide range of pollutants such as carbon monoxide, particulate matter, oxides of sulphur and nitrogen (Kinney *et al*., 2011).

Automobiles constitute one of the major modes of transportation for conveying people and goods in any nation of the world. The usefulness of this mode of transportation is not without cost. The major cost is pollution of different magnitude. Ekong *et al*., (2012), classified the pollution cost of automobile transportation into two main groups such as operational and the maintenance cost. The operational cost of automobile transportation occurs when vehicles are driven from one place to the other while the maintenance dimension occurs during vehicle repairs. (Ekong *et al*., 2012), observed that 48% of total atmospheric pollution comes from these two forms of automobile activities. Their gaseous pollutants are sulphur dioxide, nitrogen oxide, ozone, carbon monoxide and hydrocarbons.

International fora such as Earth Summit focused more attention on the reduction of operational cost of automobile pollution by recommending the use of ethanol and hydrogen as alternative fuel for powering automobiles, removal of lead from gasoline, use of electric trains for inner city transportation, etc. Most of these suggestions have been implemented in some developed countries while some have been interpreted into local contents of some developing countries.

However, less attention is paid to pollution caused by the maintenance dimension of automobile transportation (auto-mechanic activities). Auto-mechanic activities are actually producing comparable amount of pollutants due to their intensive operations (Sax , 2001). Chemicals such as refrigerator gases used in vehicle air conditioners are made up of chlorofluorocarbons which when allowed to escape in larger quantities into the atmosphere can deplete the ozone layer and cause a greenhouse effect (Ekong *et al*., 2012). This situation cannot be allowed to continue especially with the current changes in climate within the region as shown by (Atser *et al*., 2010).

The increase in automobile repairs/workshops and their activities in Nigeria are partly due to the ever-increasing demand for personal vehicles, most of which are used “Tokunbo” vehicles. These have contributed remarkably to the problem of air pollution in most cities.

Automobiles activities involves working with and spilling of fresh and used oils petrol, grease, diesel, welding electrodes, iron filing machines, battery filing electrolyte etc. These used oil (waste) contains oxidation products, sediments, water and metallic particles resulting from machinery wears, used batteries, organic and inorganic chemicals used in oil additives and metals.(European Environment Agency, 2007). These activities and materials generates particulate matter which poses threats to the environment and leads to several health problem. Unfortunately, information on the impact of automobile mechanics activities on the ecosystem is still very scanty.

It has been reported by many researchers that particulate matter irrespective of its source has chemical composition which could be organic or inorganic. Hence this research is conducted to characterize the ambient air of auto-mechanic workshop activities, so that their impacts on the surrounding air quality can be known and preventive measures could be designed depending on its severity.

1.1.1 BACKGROUND OF STUDY

Gaseous pollutants and particulate matter are released into the atmosphere at concentrations above their normal ambient level. This is caused by the increasing human activities which eventually have a measurable effect on humans, animals and plants. (Okuo *et al*., 2017). Chemical free and serene air is a key requirement for human health. As consequence of numerous anthropogenic activities and physical processes such as auto-mechanic activities and combustion processes, various pollutants are released into the atmosphere. Thereby altering the ideal composition of air (Ekong *et al*., 2012). These pollutants are in the form of gases, particulates or mixture of gases and particulates. Particulates are of organic and inorganic composition, which leads to health effects and environmental degradation. Airborne particulate depending on their chemical composition can deplete nutrients in soil and waterways, harm forests and crops, and damage cultural icons such as monuments and statues.

Criteria air pollutant which is also called air pollutant of major concern for human health can be classified into six categories they include, nitrogen dioxide (NO_2), ozone (O_3), carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2), lead (Pb) and particulate matter (PM) (EPA, 2015).

Particulate matter (PM) which is inhaled into the human respiratory system is related to most serious health effects including pulmonary and cardiovascular illnesses, it causes environmental damages; Visibility impairment- fine particles are the main cause of reduced visibility (haze) in parts of the United States. Particles can be carried over long distances by wind and then settle on ground or water. Depending on their chemical composition, the effects of this settling may include: making lakes and streams acidic, contributing to acid rain, affecting diversity of ecosystems, depleting sensitive forests and farm crops, changing the nutrient balance in coastal waters and large river basin.

Particulate matter is greatly dependent on two factors which are;

- The Size
- The Composition

The size of particles is directly linked to their potential for causing health problems. Environmental Protection Agency (EPA) agencies such as Federal Ministry of Environment and United State Environmental Protection Agency are concerned about particles that are 2.5 micrometer in diameter ($PM_{2.5}$) or smaller because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health problems such as irregular heartbeat and decreased lung function. Particulate matter is classified into different size fractions due to the different health effects associated with particles of different sizes.

Of particular concern are the respirable particle ($PM_{2.5}$) and inhalable particles (PM_{10}) since these are the ones that can enter deep into the alveoli, bronchi and lungs and it results in serious health effects (Kura *et al.,* 2013), others are the total suspended particles (TSP), they are the large particles which are too big to pass through the nose and throats and so cannot enter the lungs. TSP samples may also contain small PM_{10} and $PM_{2.5}$ particles that may enter into the lungs.

The composition of particulate matter is complex and differs depending on the source and location, it can be classified into the organic and inorganic composition. The organic includes the polycyclic aromatic hydrocarbons (PAHs), volatile organic carbon (VOC) etc, while the inorganic includes the heavy metals. The co-existence of toxic heavy metals and hydrocarbons (HCs) at many of the auto-mechanics contaminated sites all over Nigeria and in other developing countries pose a severe threat to the environment. The source of airborne particulates includes natural and anthropogenic processes. The most noteworthy anthropogenic source with regards to quantity stem from incomplete combustion processes, such as fossil fuel and biomass burning (Okuo *et al*., 2017).

Particulate matter is a multi-component aerosol formed by anthropogenic and natural species. Its constituents may differ depending on the prevailing weather conditions, season and place of emissions.

In fact, the presence of heavy metals in air sample is increasingly becoming an issue of global concern especially as air constitutes a crucial component of rural and urban environment. Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) which are often used as additives in some lubricants and gasoline are non-degradable in the environment. Some of them have been classified as priority pollutants by United State Environmental Protection Agency (United States Department of Agriculture 2001). The occurrence of toxic heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) in particulates may contribute to substantial health effects (Safo-Adu *et al*., 2014). Some of these heavy metals in particulates are strong triggers of carcinogenesis, teratogenesis and mutagenesis (Awan *et al*., 2011).

1.1.2 STATEMENT OF PROBLEM

The dangers of ambient pollution cannot be overemphasized. Studies have shown that the prevalence of pollutant substances such as particulate matters, gases, vapours, etc, in the atmosphere can have detrimental effects on public safety in various ways. Specifically, epidemiological studies have iterated the lethal effects of particulate pollution, with resulting consequences that include respiratory dysfunctions and organ damages, thus leading to an increase in morbidity and mortality rate amongst human receptors (Okokon *et al*., 2018).

There is an increase in the rate of air pollution in auto-mechanic workshop due to the numerous activities carried out of which are vehicle repairs, panel beating and weathering. These activities releases gaseous pollutants into the atmosphere of these pollutant the most prominent are the particulate matters which comprises both the organic and inorganic particles. Consequently, vehicular emission and one prominent is vehicular exhaust emission releases a number of pollutants from exhaust pipes directly into the breathing zone of man and this in turn comprise of particulate matter which has a good number of health challenges which includes respiratory disorders, decreased lung function/lung disease, cardiovascular morbidity, cancer etc.

These fine particulates and TSP bound heavy metals are of particular concern due to their persistence in the environmental media and their human toxicity. (Okuo *et al*., 2017). The adverse health effects caused by particles have often been associated with particles of size fraction less than or equal to 10µm in diameter, or to the chemical composition. The chemical composition of fine particulate matter can reveal the hazards of this air pollutant for human health which is very important concerning the number of people at risk and the continuous nature of exposure (Talebi & Tavakoli-Ghinani, 2008).

Ultimately, this study does not only propose to identify current issue of air pollution in auto-mechanic workshop but to investigate the levels of heavy metal pollution in particulate matters in auto-mechanic workshop in Uwelu south-west, Benin City.

1.1.3 JUSTIFICATION

Since the occurrence of toxic heavy metals in $PM_{2.5}$ and TSP is assumed to contribute to substantial health effects and persist in the environment (Okuo *et al*., 2017), it is of particular interest to investigate the levels of heavy metals such as cadmium, lead, copper, zinc, nickel, arsenic, iron, chromium and manganese in particulate matter in the ambient air of selected auto mechanic workshop in Uwelu south-west, Benin City. The concentrations of particulate matter and characterization of heavy metals in $PM_{2.5}$ in industrial Area of different cities has been investigated (Okuo *et al*., 2017). However, little or no information is available on the heavy metal constituents of $PM_{2.5}$ and TSP in ambient air of auto-mechanic workshop in Benin City. These workshops may play host to different artisan such as panel beating, battery charges, spray painters etc. These artisans spend minimum of 8 hours daily on the workshop. $PM_{2.5}$ and TSP are release into the environment by these artisans during operation. Unfortunately these artisans depends on these polluted air for sustenance, thus this present studies tend to characterize the particulate matter ($PM_{2.5}$) and TSP in auto-mechanic workshop in Uwelu North West Benin City.

1.1.4 SCOPE OF WORK

This study was carried out in Benin City, Nigeria, in the months of February to June. Samples were collected from different auto-mechanic workshop around Uwelu motor spare parts market, Benin City. Concentration of total suspended and respirable particulate matter were measured. Meteorological conditions, represented by temperature, humidity and wind speed, wind direction, pressure, solar radiation and ultra-violet radiation were investigated as well. The Air samples collected using the $PM_{2.5}$ and TSP filter and foam were analyzed for heavy metals. Statistical analysis were carried with the data obtained.

1.1.5 AIM AND OBJECTIVES

The aim of the work is to characterize the level of heavy metals in particulate matter ($PM_{2.5}$) and total suspended particulate matter (TSP) in auto mechanic workshops around Uwelu motor spare parts markets, Benin City.

SPECIFIC OBJECTIVES

The specific objectives of this research were to:

- Measure the levels of $PM_{2.5}$ in an auto mechanic workshop in Uwelu.
- Measure the levels of TSP in an auto mechanic workshop in Uwelu.
- Measure meteorological conditions, such as temperature, humidity and wind speed.
- Investigate the concentration of heavy metals (Cadmium, Nickel, Zinc, Copper, iron, lead, Chromium, Manganese, Arsenic) in the $PM_{2.5}$ and TSP in an auto mechanic workshops in Uwelu.

1.2 LITERATURE REVIEW

1.2.1 AIR POLLUTION

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

Air pollution can be referred to as an impairment of air quality to an extent that it is no longer suitable for breathing, and which may cause undesirable changes in the physico-chemical characteristics of air of the atmosphere. This condition is usually due to the occurrence of contaminant substances in harmful concentrations. Air pollution is a cause of devastating environmental effects or outright harm on humans, animals, plants, and other biotic and abiotic entities that are in interaction with the atmosphere. These harmful contaminant substances are referred to as *air pollutants*. They exist in form of gases, solid particles, liquid droplets, vapour, ions or mixtures, basically suspended in the atmosphere in concentrations that may cause any harmful or undesirable change in the natural state of the atmosphere. Air pollutants may originate from either natural or anthropogenic sources, being released into the atmosphere through various mediums. On release, they are subject to further modification and/or dispersion in atmosphere by complex chemical processes and air flow patterns. After discharge, an air pollutant may be transported, diluted, degenerated, or become immobilized with time. Its exact fate in the atmosphere depends on its physical and chemical properties, as well as meteorological factors at play. Hence, the more persistent the air pollutant is, the higher its tendency to become a greater threat to the environment. Due to the increasing trend in air pollution as well as substantial evidence from scientific studies on the dangers of air pollution, the International Agency for Research on Cancer (IARC) classified ambient air pollution as a carcinogen. This classification according to a report by the Agency was very crucial and that there was need for the international community to take steps in order to curb the problem (IARC, 2013).

Air pollutants can be classified into two (2) major categories based on their mode of entry into the atmosphere, they are;

- Primary pollutants
- Secondary pollutants

Primary pollutants are the class of air pollutants that are emitted directly from a particular process; their source of emission could be either natural or anthropogenic, such as particulate matter, sulphur dioxide (SO_2) and ash being emitted from a volcanic eruption process, or carbon monoxide (CO) from the exhaust pipes of automobiles. The pollutants in this case are released directly into the air, and therefore, will have a direct environmental impact. On the other hand, secondary air pollutants are a class of pollutants which occur in the atmosphere as a result of their formation from reactants during chemical reactions or physical processes. The reactants, which could be primary pollutants, may originate from either natural or anthropogenic sources or both, and then undergo certain reactions in the atmosphere to produce secondary pollutants. An example of a secondary pollutant is ozone (O_3), which is formed in the atmosphere from photochemical activity of nitrogen dioxide (NO_2) and further reactions with oxygen (O_2) in the atmosphere.

Adequate knowledge of the type of pollutants present in the air is of major importance in determining primary sources of such pollutants, elucidating the chemical transformation pathways that may occur in the atmosphere due to the presence of such air pollutants, and in investigating their potential impact on the environment and its inhabitants. Such investigations may yield results which present implications for the formation of control strategies (Kumar & Kratoria, 2013; Prashant *et al*., 2015).

Air pollution did not just evolve in one day as we think but has come along as a result of the use of fossil fuels as well as other combustible materials such as wood. The growth of communities resulted in the exhaustion of wood supplies which in turn paved way for the use of coal and peat. The use of coal especially the sulfurous ones often hurled smoke into the ambient air thereby contaminating it and settling on local structures. Although early concerns about air pollution was based on the use of coal as well as emissions from manufacturing plants, the beginning of highway systems to convey traffic from expanding towns to industrial and urban centres added a new dimension to air pollution (Stanek *et al*., 2011).

1.2.2 CRITERIA AIR POLLUTANT

Criteria air pollutant which is also called pollutant of major concern are air pollutant that must be used in air quality assessment because their health impact has been studied and established. Air pollution contributes to a wide variety of adverse health effects. USEPA and EPA has established national ambient air quality standards (NAAQS) for six of the most common air pollutants— Particulate matter, carbon monoxide, lead, ground-level ozone, nitrogen dioxide, and sulfur dioxide—known as “criteria” air pollutants (or simply “criteria pollutants”) (USEPA, 2010). The presence of these pollutants in ambient air is generally due to numerous diverse and widespread sources of emissions. The primary NAAQS are set to protect public health. EPA also sets secondary NAAQS to protect public welfare from adverse effects of criteria pollutants, including protection against visibility impairment, or damage to animals, crops, vegetation, or buildings. Ambient air standards have been set and are regularly reviewed by local, foreign and international regulatory bodies such as the Federal Ministry of Environment (FMENV), Nigeria; the United States Environmental Protection Agency (USEPA), USA; the World Health Organization (WHO) in order to develop solution policies for air pollution, and to ensure that necessary efforts are put into regulating local and global air quality.

Air pollutants of various types have various impacts on the environment; some tend to reduce visibility, while others may initiate adverse climatic changes in the atmosphere. The toxic ones spread contamination, leading to health challenges from exposure to the toxins in the substances. Many atmospheric pollutants are complex in their composition, containing perhaps several different molecular species. An example of this is in the case of particulate matter, where the composition is dependent on the source of generation; for instance, particulate matter emitted from the combustion of firewood for cooking is usually made up of a mixture of gases such as carbon monoxide (CO) and nitrogen oxides (NOX), metallic particles such as lead (Pb) cadmium (Cd), zinc (Zn), as well as other particles ((Font & Fuller , 2017); (Ukpebor *et al*., 2012)).

1.2.3 SOURCES OF AIR POLLUTION

Air pollutants are introduced into the atmosphere through various activities. These activities may be either natural or anthropogenic. While man-driven contribution to poor air quality is of major environmental concern, there are many natural sources of air pollution which are often much greater than their man-made counterparts. Several natural phenomena, such as volcanic eruptions often cause a massive release of sulphur dioxide (SO_2) and other pollutants such as nitrogen oxides NO_X and particulate matter (PM) into the air. Also, naturally occurring forest fires may account for a major release of NO_2, smoke, PM, volatile organic compounds (VOCs), as well as various other pollutants into the atmosphere. Ground level ozone, a secondary pollutant, is formed as a product of photochemical reactions taking place between atmospheric gases under the influence of sunlight. Although volcanic eruptions, forest infernos, as well as dust storms are major natural sources of particulates, such sources do not account for the threatening levels of particulate pollution, because they only seldom occur over relatively short time frames. Other pollutants that are released naturally include, dust – often released from a large area of earth with little or no vegetation; CO and smoke – released from wild infernos.

Anthropogenic sources of air pollution are those man-driven sources that bring about air pollution. These activities which include various forms of combustion, manufacturing, reaction processes, etc, are carried out by humans, daily, in a quest for attaining a better standard of living. This is often done by the utilization of natural resources for the purpose of industrialization and urbanization. Unfortunately, these acts are sources and drivers of excessive air pollution (Phalen & Phalen, 2013). Anthropogenic sources of pollution are classified according to the USEPA (2010), into stationary and mobile sources.

Stationary sources include:

- ❖ Industrial plants that burn organic fuels;
- ❖ Chemical manufacturing;
- ❖ Metals processing;
- ❖ Petroleum industries;
- ❖ Other industries (agriculture, textile, wood rubber, electronic, construction, etc);

Mobile anthropogenic sources include:

- ❖ On-road petrol-powered automobiles, trucks, and motorcycles;

- On-road diesel-powered vehicles; and

- Off-road vehicles (petrol and diesel-powered automobiles and trucks, aircrafts, marine vessels, railroad engines, etc). Electric utilities that burn organic fuels;

- Solvent users (degreasing, graphic arts, dry cleaning, etc).

The concentrations of most criteria and non-criteria air pollutants are well correlated and they are often released from the same or similar forms of sources. Carbon monoxide (CO), a major pollutant from anthropogenic sources is released during the combustion of carbon-containing fuels, and since automobile engines are built to run on petroleum fuels, the release of CO into the atmosphere will remain consistent for as long as these automobiles are in use.

Similarly, automobiles emissions are also major sources of particulate matter, hence their prominence in regions where automobiles are used. Most heavy metals such as lead (Pb) and cadmium (Cd) are from metal processing, waste handling, stationary fuel-combustion sources, as well as vehicular activity. Particulate matter (PM) is raised from stationary and mobile fuel combustion activities, industrial processing activities, wood dust, agitation of earth, etc (Ukpebor *et al*., 2012); (Olayinka *et al*., 2015); (Ediagbonya *et al*., 2013); (Ukpebor *et al*., 2006).

1.2.4 IMPACTS OF AIR POLLUTION

The presence of harmful air pollutants that have numerous potential detrimental effects on the ecosystem and the emergence of evidence of the impact of air pollution on public health have raised a cause for serious concern. Global research suggests that ambient air pollution is a major contributor to risks of stroke, heart disease, lung cancer, and chronic and acute respiratory diseases including asthma and more than 85% of people living in urban areas are exposed to dangerous air quality levels.

There are Various Harmful Effects of the air Pollutants:

i. Carbon monoxide (source- Automobile exhaust, photochemical reactions in the

ii. Atmosphere, biological oxidation by marine organisms, etc.)- Affects the respiratory activity as haemoglobin has more affinity for CO than for oxygen. Thus, CO combines with haemoglobin and thus reduces the oxygen-carrying capacity of blood. This results in blurred vision, headache, unconsciousness and death due to asphyxiation (lack of oxygen).

iii. Carbon dioxide (source- Carbon burning of fossil fuels, depletion of forests (that remove excess carbon dioxide and help in maintaining the oxygen-carbon dioxide ratio) – causes global warming.

iv. Sulphur dioxide (source- Industries, burning of fossil fuels, forest fires, electric generation plants, smelting plants, industnal boilers, petroleum refineries and volcanic eruptions)- Respiratory problems, severe headache, reduced productivity of plants, yellowing and reduced storage time for paper, yellowing and damage to limestone and marble, damage to leather, increased rate of corrosion of iron, steel, zinc and aluminium.

v. Hydrocarbons Poly-nuclear Aromatic Compounds(PAC) and Poly-nuclear Aromatic Hydrocarbons(PAH) (source- Automobile exhaust and industries, leaking fuel tanks, leaching from toxic waste dumping sites and coal tar lining of some water supply pipes)- Carcinogenic (may cause leukaemia).

vi. Chloro-fluoro carbons (CFCs) (source- Refrigerators, air conditioners, foam shaving cream, spray cans and cleaning solvents)- Destroy ozone layer which then permits harmful UV rays to enter the atmosphere. The ozone layer protects the earth from the ultraviolet rays sent down by the sun. If the ozone layer is depleted by human action, the effects on the planet could be catastrophic.

vii. Nitrogen Oxides (source- Automobile exhausts, burning of fossil fuels, forest fires, electric generation plants, smelting plants, industrial boilers, petroleum refineries and volcanic eruptions)- Forms photochemical smog, at higher concentrations causes leaf damage or affects the photosynthetic activities of plants and causes respiratory problems in mammals.

viii. Particulate matter Lead halides (lead pollution) (source- Combustion of leaded gasoline products) – Toxic effect in man. Heavy metals associated with PM may result in airway and tissue damage from the formation of reactive oxygen species in body tissues; cell membrane destruction, oxidative stress and inflammation may also occur (Kim *et al*., 2014).

ix. Asbestos particles (source- Mining activities) – Asbestosis – a cancerous disease of the lungs.

x. Silicon dioxide (source- Stone cutting, pottery, glass manufacturing and cement industries) – Silicosis, a cancerous disease.

xi. Mercury (source- combustion of fossil fuel & plants)-brain & kidney damage.

xii. Air pollutants affect plants by entering through stomata (leaf pores through which gases diffuse), destroy chlorophyll and affect photosynthesis. During the day time the stomata are wide open to facilitate photosynthesis. Air pollutants during day time affect plants by entering the leaf through these stomata more than night.

Pollutants also erode waxy coating of the leaves called cuticle. Cuticle prevents excessive water loss and damage from diseases, pests, drought and frost. Damage to leaf structure causes necrosis (dead areas of leaf), chlorosis (loss or reduction of chlorophyll causing yellowing of leaf) or epinasty (downward curling of leaf), and abscission (dropping of leaves).

Particulates deposited on leaves can form encrustations and plug the stomata and also reduce the availability of sunlight. The damage can result in death of the plant. $S0_2$ causes bleaching of leaves, chlorosis, injury and necrosis of leaves. $N0_2$ results in increased abscission and suppressed growth. O_3 causes flecks on leaf surface, premature aging, necrosis and bleaching.

Peroxyacetyl nitrate (PAN) causes silvering of lower surface of leaf, damage to young and more sensitive leaves and suppressed growth. Fluorides cause necrosis of leaf-tip while ethylene results in epinasty, leaf abscission and dropping of flowers.

1.2.5 PARTICULATE MATTER (PM)

Particulate matter (PM) has become the primary pollutant of the atmosphere in recent years (Ji *et al*., 2014), with a serious impact on global and regional climate changes (Bytnerowicz *et al*., 2007), reduced visibility (Moosmuller *et al*., 2009), and human health effects, especially associated with cardiovascular disease and wheezing (Pope & Dockery, 2006); (Dunea *et al*., 2016). Particulate Matter is a fraction of air pollution which consists of extremely small particles and liquid droplets containing acids, organic chemicals, metals, and dust particles (Anderson *et al*., 2012).

PARTICULATE MATTER SIZE CLASSIFICATION

Particle size plays an important role on deposition rate of the inhaled aerosol in different regions of the respiratory system (Arhami *et al*., 2010). Coarse particles (PM_{10}, aerodynamic diameter ≤ 10µm) and fine particles ($PM_{2.5}$, aerodynamic diameter ≤ 2.5µm) have been associated with hospital admissions for respiratory (Brunekreef & Forsberg, 2005) and cardiovascular disease (Bell, 2012). Ultrafine particles ($PM_{0.1}$, aerodynamic diameter ≤ 0.1µm), carrying considerable amounts of toxic substance, can penetrate deep into pulmonary alveoli (Sioutas *et al.*, 2015).

Particulate matter are released from a range of sources which includes road dust, wood dust, agricultural dust, vehicular and non-vehicular combustion emissions, construction operations, as well as other sources (Ediagbonya *et al*., 2013); (Olayinka *et al*., 2015)).

Particulate Matter is categorized by size and can be described by its aerodynamic equivalent diameter. Its distribution in the ambient air can be described as tri-modal, including, ultrafine, fine and coarse particles (Okokon *et al.*, 2018).

Their classification has been done based on their size and their penetration ability into the following:

i. Inhalable (coarse) particulate matter, known as PM_{10} of diameter <10µm. This describes particles that are small enough to get inhaled through the nostrils but may only be deposited in the tracheobronchial tree. They can cause irritation and respiratory discomforts to the victim.

ii. Respirable (fine) particulate matter, PM 2.5, with a diameter of <2.5µm. Particles in this size range have more penetrability reaching even deeper within the lungs. PM2.5 sizes are small enough to take part in gas exchange, penetrate the lungs and eventually escape into the bloodstream resulting to significant health problems

iii. Ultrafine particulate matter, $PM_{0.1}$ are particulate matter of nano-scale size (less than 0.1µm) they are believed to have several more aggressive health implications than those larger particulates, they can penetrate deep into pulmonary alveoli.

Total suspended particulate matter, (TSP) is a name given to particles of sizes up to about 50µm. The larger particles in this class are too big to get past our noses or throats and so they cannot enter our lungs. Total suspended particulate matter is a complex mixture of extremely small particles and liquid droplets which includes: acids, organic chemicals, metals, fume, smoke, dusts and soil particles with diameters less than 100 micrometers.

It is worth noting that with particulate matter monitoring, sampling is often done using the size selective method. This means that particles above, below or within a particular size range are deliberately sampled. The size that is often selected has special relevance with regards to sources, toxicity, inhalation and deposition (Pope & Dockery, 2006).

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

Coarse particles in PM_{10} fraction often consist of combustion-derived and carbon-centered particles with associated hydrocarbons and metals (Yang *et al*., 2013).

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

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

Particles with size less than 0.1µm are often described as ultrafine particles. Ultrafine particles are often emitted into the ambient air in industrial environments from sources related to combustion. Examples of these combustion related sources are vehicular exhausts and atmospheric photochemical reactions. These primary ultrafine particles, however, have a short life and grow through coagulation or condensation or both to form larger complex aggregates which forms part of $PM_{2.5}$. In recent times, interest in ultrafine particles has gained more attention because they serve in part as a primary source of fine particle exposure and because, poorly soluble ultrafine particles may be more likely than larger particles to translocate from the lung to the blood and other parts of the body. In studies relating to particulate matter, it is important to acknowledge that $PM_{2.5}$ is made up of particles with a size fraction which is less than or equal to a 2.5µm and includes fine particles and total suspended particulate is, made up of particles which is less than or equal to 50µm (Pope and Dockery, 2006). Particulate matter (PM) in atmosphere on entering the respiratory system is reported to cause wide-ranging health effects including cancer and heart failures (Pope & Dockery, 2006).

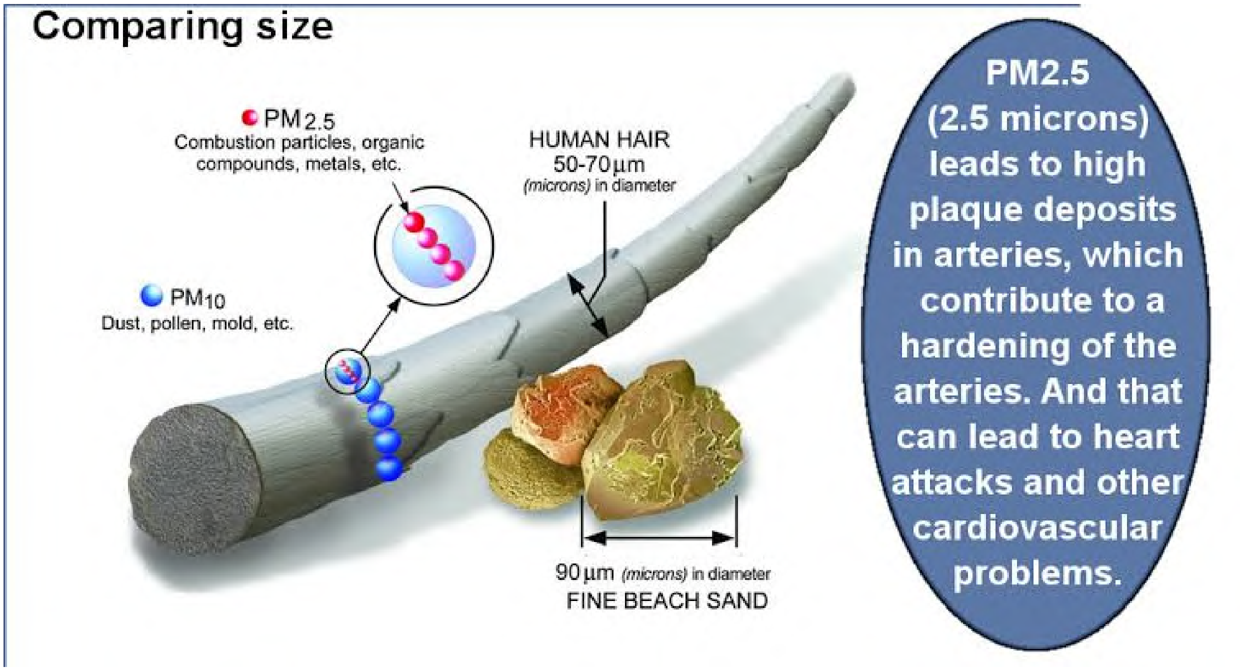

Figure 1.1: Size Classification of Particulate Matter

1.2.5.1 PARTICULATE MATTER STUDIES CARRIED OUT IN DIFFERENT REGIONS OF THE WORLD

1.2.5.1a Particulate matter in some part of Nigeria.

(Okuo & Okolo, 2011) Studied the levels of heavy metals in suspended particulate matter in ambient air of Artisan workshop in Benin City, Nigeria and found out that suspended particulate matter concentration ranged from 583-20,166µg/$m^{3.}$

(Ediabonya *et al*., 2016) did studies on the determination of exposure of total, inhalable and respirable particles in welder in Benin City, Edo State at various location Agbor, Oluku, New Benin, Second east circular and Sokponba and measured the highest value of total suspended particulate in Sokponba (7430.56µg/m^3) and lowest at Oluku (3958.33µg/m^3). For the respirable particulate matter, the highest measured particulate was in Sokponba (3020.84µg/m^3). And least values were in Agbor and Oluku (1284µg/m^3).

(Okuo *et al*., 2017) did a study on elemental characterization and source identification of fine particulate matter in an industrial Area of Lagos State, Nigeria. Based on study conducted, the concentration of $PM_{2.5}$ at different locations varied with respect to anthropogenic activities. The $PM_{2.5}$ levels obtained ranged from 14.00 to 32.67μg/m^3 during wet season and 18.67 to 34.67μg/m^3 during the dry season.

(Vincent, 2014), studied the TSP concentration in six different land use areas of Port Harcourt and reported high concentrations of TSP in most locations. This is as a result of anthropogenic factor like the presence of heavy industrial activities especially at the Eleme industrial zone where the Eleme Petro-chemical plants, Port Harcourt Refinery, One Oil and Gas Free Zone. These industries emit volumes of Particulate Matters into the urban cities of Port Harcourt.

1.2.5.1b Particulate matter in other parts.

(Yu-Cheng Chen *et al*., 2015) Carried out a study in Taiwan to investigate the characteristics of concentrations and metal compositions of $PM_{2.5}$ and $PM_{2.5-10}$ in Yunlin County, Taiwan during Air quality deterioration. The concentrations of twenty trace metals in ambient fine and coarse particles were characterized during the period of air quality deterioration of elevated particulate matter (PM episode) in winter in the suburban area, Yunlin County, Taiwan.

In Brazil, (Ingrid P.S Araujo *et al*., 2014) carried out studies on identification and characterization of particulate matter concentration at construction jobsites and found that PM concentration from construction sites activities pose challenges due to the diverse characteristic related to different aspects, such as concentrations, particle size and particle composition. And noted that characterization of particulate matter is influenced by meteorological conditions including temperature, humidity, rainfall and wind speed.

1.3 IMPACT OF PARTICULATE MATTER

1.3.1 Health Impact of Particulate matter

The size of particles is directly linked to their potential for causing health problems. Small particles less than 10µm in diameter pose the greatest problems because they get deep into the bloodstream. Exposure to such particles can affect both your lungs and your heart. It is believed to be responsible for many cerebrovascular as well as cardiovascular diseases through the processes of direct and indirect coagulation activation and systemic inflammation (Anderson *et al*., 2012).

Numerous scientific studies have linked particle pollution exposure to variety of problems, including;

1. Premature death in people with heart or lung disease.
2. Non-fatal heart attacks
3. Irregular heart beats
4. Decreased lung function
5. Increased respiratory symptoms, such as irritation of the airways, coughing or difficulty breathing.

Generally, PM_{10} include inhalable particles that are small enough to penetrate the thoracic region of the respiratory system the health effect of inhalable PM are well documented. They are due to exposure over both short term (hours, day) and long term (months, years) and include;

- ❖ Respiratory and cardiovascular morbidity such as aggravation of Asthma, respiratory symptoms and an increase in hospital admission

- Mortality from cardiovascular and respiratory disease and from lung cancer.

$PM_{2.5}$ is a stronger risk factor than PM_{10}. Long term exposure to $PM_{2.5}$ is associated with an increase in the long-term risk of cardiopulmonary mortality by 6-13% per μ/m^3 of $PM_{2.5}$.

Particulate Matter affects lung development in children including reversible deficits in lungs function as well as chronically reduced lung growth rate and a deficit in long-term lung function.

Black carbon part of $PM_{2.5}$ which result from incomplete combustion has attracted the attention of air quality and detrimental to health and climate. Many of its components are responsible for health effect that is organics such as PAHs that are known carcinogens and directly toxic to the cells as well as metals and inorganic salts are carcinogenic (lung cancer). Particulate matter reduces the life expectancy of the population.

1.3.2 Impact of Particulate matter on Climate

PM has been recognized as a major factor in determining global climate change. (IPCC, 2007). It also plays vital role in earth's climate by changing the amount of incoming solar radiation and the outgoing terrestrial long wave radiation retained in the earth's system. (Forster *et al.,* 2007)

1.3.3 Impact of particulate matter on Vegetation

Particulate Matter can block the openings of plants stomata and therefore interfere with their photosynthesis function and this may lead to stunted growth in the plant (Hogan, 2010). High or prolonged exposure to higher level of pollution can leads to damage from diseases, pests, drought and frost.

1.4 HEAVY METALS

Although there is no specific definition of a heavy metal, literature has defined it as a naturally occurring element having a high atomic weight and high density which is five times greater than that of water. Heavy metal refers to group of metals or metalloids or metallic element that has a relatively high density greater than $5gcm^{-3}$ (Duruibe *et al.*, 2007). Heavy metal(s) are widespread pollutants of great concern as they are non-degradable, toxic, persistent and/or bioaccumulative. As they are elements, heavy metals cannot be broken down and will therefore persist in the environment. Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, especially in lake, estuarine or marine sediments. Metals can be transported from one environment compartment to another. Heavy metals become toxic when they are not metabolised by the body and accumulate in the soft tissues. They may enter the human body through food, water, air or absorption through the skin when they come in contact with humans in agriculture, manufacturing, pharmaceutical, industrial or residential settings. Heavy metals are commonly associated with pollution and toxicity problems. They are classified according to their effect into three categories: the toxic, the nutritive and the essential nutritive metals (Lennutech, 2004). However, according to report by expert committee on metals (WHO, 2000), all essential elements become toxic at high intake and the margin between levels that are beneficial and those that are harmful may be small. Copper, zinc, cobalt, nickel, chromium, manganese, iron, selenium, silicon, tin, fluorine, iodine, molybdenum and vanadium are essential trace elements, while lead, cadmium, mercury are non-essential.

Heavy metals are natural component of the earth crust, they enter our bodies via air, food and drinking water (WHO, 2000). Some heavy metals (such as copper, selenium and zinc) are essential to maintain the metabolism of the human body. However at higher concentration they can lead to poisoning. Heavy metal poisoning could result, for instance from, high ambient air concentration near emission sources, drinking contaminated water such as lead pipes, or intake via the food chain (WHO, 2000). The heavy metals essential to plants include Cobalt, Copper, iron, Molybdenum and Zinc and for animals are Chromium, Nickel and Tin. The heavy metals Cadmium, Mercury and Lead have not been shown to be essential for either plants or animals (Misra & Mani, 2009). Heavy metals are non-biodegradable and once they enter into an environment, they will stay there for a long time (Voet *et al*., 2018)

Heavy metals are peculiar to air and all kinds of soils, sediments waters and living organisms in a range of normal background levels but when they exceed an optimum range of safe exposure then the term "heavy metal pollution" is used (Petrovic *et al*., 1999). Thus, of concern are their emissions into the environments as a result of increase in industrial, agricultural and urban activities, which give rise to anomalous high concentration of the metals relative to the normal background levels. Hence many heavy metals are essential to life, but they can be toxic at high levels while Cadmium, mercury and lead have been found to possess toxicity effect even at very low levels. They destroy the vital organs like the liver, kidney and central nervous system.

1.4.1 SOURCES OF HEAVY METALS

Various heavy metals are emitted into the air from both natural and man-made (anthropogenic) sources. The quantities may range from hundreds to millions of tonnes annually. Natural air pollution stems from various biotic and abiotic sources such as plants, radiological decomposition, forest fires, volcanoes and other geothermal sources. These result in a natural background concentration that varies according to local sources or specific weather conditions.

The emission of toxic substances in the environment has been spread from industrialized countries. Many industrial plants and also heavy traffic may produce heavy metal into atmosphere. Traffic pollutants include potentially toxic metals for health like lead, cadmium and zinc.

Anthropogenic sources

The conventional sources of heavy metal pollution are spent oil lubricant, industrial waste, oil spills, mining operation, combustion emission, garbage and metallurgical activities. Metals have a wide range of uses from which they find their way into the environment. Raw materials used in the cottage industries where operations like welding, soldering are undertaken contain these metals.

Another source is atmospheric pollution from motor vehicle. The use of leaded petrol has been responsible for the global dispersion of lead aerosol. The use of lead in paints and organic Pb compounds in gasoline has caused lead to be wide spread in the environment. Combustion of fossil fuel leads to the dispersion of many elements in the air over a large area.

1.4.2 EFFECTS OF SELECTED HEAVY METALS IN $PM_{2.5}$ AND TSP FRACTION

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

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

1.4.2.1 LEAD

Lead has been known since ancient times. It is naturally present in the earth's crust in small concentration, but for centuries it has been mined and disseminated throughout the environments from where it has gradually become incorporated into the structural tissue of animals, plants and humans. Lead exists as Pb_{+2} ion during the chemical reaction. Lead is well known to be a highly toxic metal and a cumulative poison. The common industries that deal with lead are the motor vehicle repair, battery manufacturing, cable making and metal grinding industries and it is also used in piping, conducting materials, accumulators, lead chambers, printing characters, soldering, anti-knock substances, colored pigments, radiation shielding, wrappings for food, tobacco and as an additive in gasoline.

Lead is a bluish grey metal which is found in the earth‘s crust. It occurs naturally in the form of leaded compounds rather than a metal, making it a less common metal compared to oxygen and silicon which are the two most abundant metals in the earth‘s crust (ATSDR, 2007). Lead can be emitted into the atmosphere during the combustion of lead-bearing fuels such as coal containing lead and other impurities because coal and fuel oil contain lead, also through burning of oil, coal or waste as well as emissions from factories that use lead or leaded compounds. In the atmosphere, its concentrations vary greatly, with the highest concentrations observed near stationary sources like lead smelters.

1.4.2.1a Toxicity of lead

Lead is among the majority toxic heavy metal ions affecting the environment. Poisoning can also occur from inhalation of fumes from burning storage batteries or solder or from air around polluted auto mechanic workshop.

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

However, there is no doubt that lead is seriously poisonous to human beings and evidence is accumulating that considerable differing effects result in different human beings who have absorbed similar amounts. Most of the absorbed lead is stored in the bones, blood or brain. Lead colic (painter's cramps) is characterized by severe abdominal pain. Damage to the brain can occur in children it is known to cause convulsions, mental retardation and even death. It is also known that lead is harmful to the kidney and permanent neurological injury. Lead can reason several unwanted effects, such as disorder of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, declined fertility of men through sperm damage and behavioural disruptions of children, such as aggression, impulsive behavior and hyperactivity. Lead can enter a foetus through the placenta of the mother and it can cause serious damage to the nervous system and the brains of unborn children. Lead is known to cause precipitation of protein, through the interaction of lead ions with the sulphydryl (-SH) groups of proteins. Lead has a negative influence on both children and adults. For children, Pb reduces the physical growth and mental growth (Simeonov *et a* 2010). The intelligent quotient of children is diminished and symptoms of irritability and fatigue could be observed. Chronic exposure can affect physical growth and can cause anemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al*., 2010). It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Simeonov *et al*., 2010).

Toxicity due to lead exposure is called lead poisoning. Lead poisoning is mostly related to the gastrointestinal tract and central nervous system in children and adults. Lead poisoning can be either acute or chronic. Acute exposure of lead can cause headache, loss of appetite, abdominal pain, fatigue, sleeplessness, hallucinations, vertigo, renal dysfunction, hypertension and arthritis while chronic exposure can result in birth defects, mental retardation, autism, psychosis, allergies, paralysis, weight loss, dyslexia, hyperactivity, muscular weakness, kidney damage, brain damage, coma and may even cause death. Although lead poisoning is preventable, it still remains a dangerous disease as it can affect most of the organs of the body. Exposure to elevated levels of lead can cause the plasma membrane of the blood brain barrier to move into the interstitial spaces leading to edema. Also, lead exposure can disrupt the intracellular second messenger systems and alter the functioning of the central nervous system.

Developing fetuses and children are most vulnerable to neurotoxic effects due to lead exposure. A number of prospective epidemiologic studies in children less than 5 years of age have shown that low-level of lead exposure (5–25 µg/dL in blood) resulted to the impairment of intellectual development which was manifested by the loss of intelligence quotient points. As such, the Centers for Disease Control (CDC) in the United States has reduced the tolerable amount of lead in children's blood from 25 to 10 µg/dL and recommended universal screening of blood lead for all children.

1.4.2.2 CADMIUM

Cadmium is generally a non-essential element with teratogenic, carcinogenic and highly nephrotoxic effects on living organisms (Antonin *et al*., 2010). It is considered non-essential for living organisms. Cadmium is often found in the earth's crust in association with other metal ores like lead and zinc. It is usually found as a mineral combined with other elements such as oxygen, chlorine and sulphur to form oxides and chlorides) and sulphate and sulphide respectively. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings and plastics. In the atmosphere, it exists in the form of particulates and sometimes vapour (ATSDR, 2012). Cadmium is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides (Wieczorek *et al.,* 2004). Among the sources of Cadmium in the environment include; mining and smelting of metal ores, fossil fuel combustion (Challan & Kumar, 2009). Cadmium is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. The other sources of Cd are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Adeleken &

Abegunde, 2011). Small quantities cause adverse changes in the arteries of human kidney. It also replaces zinc biochemically and causes high blood pressures and kidney damage, lung disease which has been linked to lung cancer and may also produce bone defects (osteomalcia, osteoporosis) in humans (Adeleken and Abegunde, 2011). Prolonged exposure to cadmium may cause renal dysfunction which may in turn lead to devastating bone disease in people with risk factors like poor nutrition. Populations that live in places polluted with cadmium often suffer from diseases like osteoporosis and increase risk of fractures. However, a link between exposure to cadmium and bone effects has also been noticed in people exposed to high concentrations of cadmium but not living in cadmium polluted areas (ATSDR, 2012). The exposure to Cadmium and especially chronic exposure can cause renal calcium metabolism disorders and increased incidence of some forms of cancer.

1.4.2.2a HEALTH EFFECT OF CADMIUM

The health effects of cadmium are well documented. The IARC and the USEPA both classify it as being carcinogenic to humans. Cadmium is a heavy metal with a high toxicity and bio-accumulation. Cadmium is toxic at very low exposure levels and has acute and chronic effects on health and environment. Cadmium is not degradable in nature and will thus, once released to the environment, stay in circulation. New releases add to the already existing deposits of cadmium in the environment. Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate. Chronic cadmium exposure produces a wide variety of acute and chronic effects in humans. Cadmium accumulates in the human body and especially in the kidneys. According to the current knowledge kidney damage (renal tubular damage) is probably the critical health effect. Other effects of cadmium exposure are disturbances of calcium metabolism, hypercalciuria and formation of stones in the kidney. High exposure can lead to lung cancer and prostate cancer.

1.4.2.2b ENVIRONMENTAL EFFECT OF CADMIUM

The major issues of concern related to cadmium may be summarised as follows:

- Atmospheric deposition seems continuously to cause the content of cadmium in agricultural top soil to increase, which by time will be reflected in an increased human intake by foodstuffs and therefore in an increased human risk of kidney damages and other effects related to cadmium.
- In the marine environment levels of cadmium may significantly exceed background levels causing a potential for serious effects on marine animals and in particular birds and mammals.
- Significant quantities of cadmium are continuously stockpiled in landfills and other deposits and represent a significant potential for future releases to the environment.

1.4.2.3 COPPER

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

Copper resists the action of the atmosphere and seawater; exposure for long periods to air, however, results in the formation of a thin green protective coating (patina) that is a mixture of hydroxocarbonate, hydroxosulphate and small amounts of other compounds. Copper is a moderately noble metal, being unaffected by non-oxidizing or non-complexing dilute acids in the absence of air; it will however, dissolve readily in nitric and sulphuric acids in the presence of oxygen (Frit *et al.,* 2000).

Copper is among heavy metals that are essential to life but could be toxic at elevated levels (Rogers *et al*., 2009). All heavy metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants at low but critical concentrations (Bose & Hemantaranjan, 2005).

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

1.4.2.3a HEALTH EFFECT OF COPPER

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

1.4.2.4 CHROMIUM

Chromium is one of those heavy metals in the environment whose concentration is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries (Adeleken and Abegunde, 2011). Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below. People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. The most common forms of chromium are chromium (VI) and chromium (III).

Chromium (III) is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipid metabolism in humans while chromium (VI) is carcinogenic (Hilgenkamp, 2006).

Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effect as well, for instance skin rashes.

Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. Other health problems that are caused by Chromium (VI) are;

- Respiratory problems
- Kidney and liver damage
- Lung cancer
- Death

1.4.2.4a HEALTH EFFECT OF CHROMIUM

Although chromium toxicity in the environment is rare, it still presents some risks to human health since it can be accumulated in skin, lungs, muscle, in liver, hair, nails and placenta where it is traceable to various health problems (Adeleken and Abegunde, 2011). The health effects brought about by the exposure to chromium (VI) include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Sarkar, 2005). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported (Adeleken and Abegunde, 2011). The sources of chromium in the environment include, cement, leather, plastics, dyes, textiles, paints, printing ink, cutting oils, photographic materials, detergents and wood preservatives (Hilgenkamp, 2006). Other sources of chromium are power plants, liquid fuels, brown and hard coal, industrial and municipal wastes.

Chromium, in its hexavalent form, is the most toxic species of chromium though some other species such as Chromium (III) compounds are much less toxic and cause little or no health problems. Chromium (VI) has the tendency to be corrosive and also to cause allergic reactions to the body. Therefore, breathing high levels of chromium (VI) can cause irritation to the lining of the nose and nose ulcers. It can also cause anemia, irritations and ulcers in the small intestine and stomach, damage sperm and male reproductive system. The allergic reactions due to chromium include severe redness and swelling of the skin. Exposure of extremely high doses of chromium (VI) compounds to humans can result in severe cardiovascular, respiratory, hematological, gastrointestinal, renal, hepatic, and neurological effects and possibly death. Exposure to chromium compounds can result in the formation of ulcers such as nasal septum ulcer which are very common in chromate workers.

Exposure to higher amounts of chromium compounds in humans can lead to the inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methemoglobin to hemoglobin. *In vivo* and *in vitro* experiments have shown chromate compounds to induce DNA damage in many different ways and can lead to the formation of DNA adducts, chromosomal aberrations, alterations in replication sister chromatid exchanges, and transcription of DNA. Thus, there are substantial evidence of chromium to promote carcinogenicity of humans as increase stomach tumors have been observed in animals and humans who were exposed to chromium (VI) in drinking water.

1.4.2.4b ENVIRONMENTAL EFFECT OF CHROMIUM

The environmental effect of chromium is that most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water chromium will absorb on sediment and become immobile. Non biodegradability of chromium is responsible for its persistence in the environment and once mixed with soil, it undergoes transformation into various mobile forms before ending into environmental sink (Adeleken and Abegunde, 2011).

1.4.2.5 MANGANESE

Manganese is a pinkish-gray, chemically active element. It is a hard metal and is very brittle. It is hard to melt, but easily oxidized. Manganese is essential for normal physiological functioning of humans and animals and exposure to low levels in the diet is considered nutritionally essential in humans. However chronic exposure to higher doses is detrimental to human health (Calkins, 2009). In higher doses it is toxic and its toxicity varies with route of exposure, chemical species, age, sex and animal species (EPA, 2004).

1.4.2.5a HEALTH IMPACT OF MANGANESE

The nervous system has been determined to be the primary target organ with neurological effects generally observed (EPA, 2004). Syndrome called manganism may result from chronic exposure to higher levels of manganese (EPA, 2004; Calkins, 2009). Manganism is characterized among other symptoms with, weakness, tremors, a masklike face and psychological disturbance (Calkins, 2009). Human activities are also responsible for much of this manganese contamination in air, soil and water in some areas (EPA, 2004). Sources of manganese due to human activities in the environment include; combustion of coal, residential combustion of wood, iron and steel production and power plants (Calkins, 2009). Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will occur. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis.

Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in people exposed to dust or fume of Manganese compounds.

1.4.2.5b ENVIRONMENTAL IMPACT OF MANGANESE

Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. These usually settle to earth within a few days. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water.

1.4.2.6 ZINC

Zinc is an essential trace element for plants, animals and humans found in virtually all air samples, foods and potable water in the form of salts or organic complexes (Miculescu *et al*., 2011). It is used in the formation of connective tissues like ligaments and tendons (Miculescu *et al*., 2011). Zinc toxicity is rare but at concentrations of up to 40 mg/L, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008). Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.

1.4.2.7 IRON

Iron is a lustrous, ductile, malleable, silver-gray metal. It is known to exist in four distinct crystalline forms. Iron rusts in damp air, but not in dry air. It dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compounds. Iron is an essential part of hemoglobin; the red colouring agent of the blood that transports oxygen through our bodies. Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues.

1.4.2.7a HEALTH EFFECT OF IRON

Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. It is corrosive to the lining of the gastrointestinal tract including the stomach and so, the first indication of iron poisoning by ingestion is a stomach pain.

1.4.2.7b ENVIRONMENTAL EFFECT OF IRON

Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment.

1.4.2.8 NICKEL

Pure nickel is a hard, silvery-white metal, which has properties that make it very desirable for combining with other metals to form mixtures called alloys. Nickel combined with other elements occurs naturally in the earth's crust. It is found in all soils and is also emitted from volcanoes (ATSDR, 2005b). It is the 24th most abundant element. Nickel is released into the atmosphere during nickel mining and by industries that make or use nickel, nickel alloys or nickel compounds. These industries might also discharge nickel in waste water. Nickel is also released into the atmosphere by oil burning and coal-burning power plants and trash incinerators (ATSDR, 2005).

1.4.2.8a HEALTH EFFECTS OF NICKEL

The most serious harmful health effects from exposure to nickel, such as chronic bronchitis, reduced lung function and cancer of the lung and nasal sinus, have occurred in people who have been exposed to dust containing certain nickel compounds (ATSDR, 2005b). Nickel exposure has been linked to breast cancer. It is believed to bind to estrogen receptors and mimic the actions of estrogen (Aquino *et al*., 2012). Nickel has been identified as a toxin that severely damages reproductive health and can lead to infertility, birth defect and miscarriages.

1.4.2.8b ENVIRONMENTAL EFFECT OF NICKEL

Nickel may be released into the environment from the stacks of large furnaces used to make alloys or from power plants and trash incinerators. The nickel that comes out of the stacks of power plants binds to small particles of dust that settle to the ground or are taken out of the air in rain or snow. It usually takes many days for nickel to be removed from the air. If the nickel is attached to very small particles, it can take more than a month to settle out of the air. Nickel can also be released in industrial waste water. A lot of nickel released into the environment ends up in soil or sediment, where it strongly attaches to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and might seep into groundwater. Studies show that some plants can take up and accumulate nickel. However, it has been shown that nickel does not accumulate in small animals living on land that has been treated with nickel containing sludge (ATSDR, 2005b).

1.5 AIR QUALITY GUIDELINES

Episodes of air pollution such as the methyl isocyanate disaster in Bhopal and the London smog in London brought about a great change in the history of air pollution. Public awareness on the effects of air pollution grew and mounted pressure on governments and states to form legislations that would protect public health and environment (Stanek *et al*., 2011).

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

The USEPA have National Ambient Air Quality Standards (NAAQS) for pollutants like lead, particulate matter, carbon monoxide, sulphur dioxide, nitrogen dioxide, and ozone. The Environmental Protection Agency also has guideline values for pollutants such as particulate matter, nitrogen dioxide and sulphur dioxide amongst others. For particulate matter, the WHO has 24-hour guideline value of 25µg/m^3 for $PM_{2.5}$ and 50µg/m^3 for PM_{10} and 125µg/m^3 for TSP. Most metals found in particulates do not have guideline values from NAAQS since most of them are considered as hazardous air pollutants. The WHO however has guideline values for some of these heavy metals (USEPA, 2013).

1.6 METEOROLOGICAL PARAMETERS AND THEIR IMPACT ON AIR POLLUTION DISPERSION

During Air pollution studies, weather parameter of the area should be studied this is because the fate of the pollutant can be influenced by the movement and characteristic of air mass into which they are emitted. If the air in the environment is calm, pollutants builds up but if the air is strong, turbulent wind blowing, generated pollutant will be rapidly dispersed into the atmosphere and will result in lower concentration of pollutant near the pollution source.

Meteorological Parameters includes the following;

i. Temperature
ii. Humidity
iii. Rainfall
iv. Wind speed and wind direction
v. Pressure
vi. Solar radiation
vii. Ultra-violet radiation

1.6.1 TEMPERATURE

Temperature and sunlight play a vital role in chemical reactions that occur in the atmosphere to form photochemical smog from other pollutants. Favourable conditions can lead to increased concentration of smog (EPA Meteorological Data, 2008).

1.6.2 RAINFALL

Rainfall has a scavenging effect, when it washes particulates matter out of the atmosphere and dissolve gaseous pollutants. Reduced particle concentration after rainfall improves visibility. Rainfall acts as a solvent for gaseous pollutants, such as sulphur (iv) oxide, forming acid rain resulting in potential damage to materials or vegetation where it falls. Rainfall can be measured with a rain gauge (EPA Meteorological Data, 2008)

1.6.3 HUMIDITY

The water vapour content of air is generally measured as a percentage of the saturation vapour pressure of water at a given temperature and is called relative humidity. The amount of water vapour in the atmosphere is highly variable, it depends on geographical location, wind direction and ambient air temperature. Relation humidity is generally higher during the wet season than during dry season. Water vapour plays vital role in many thermal and photochemical reactions in the atmosphere. As water molecules are small and highly polar, they can absorb strongly to many substances. If attached to particles suspended in the air they can significantly increase the amount of light scattered by the particles. If the molecules are attached to corrosive gases such as sulphur (iv) oxide, the gas will dissolve in the water and form an acid solution that can cause damage to health and property. The environmental protection agency measures humidity by using a thin polymer film that either absorbs or emits water vapour as the relative humidity of the ambient air increase or decreases (EPA Meteorological Data, 2008).

1.6.4 WIND SPEED AND DIRECTION

Wind speed and direction are direction are important for any air quality monitoring. If the air is calm and pollutants cannot disperse then the concentration of pollutant will build upon the other hand, if a strong, turbulent wind is blowing any pollutant generated will be rapidly dispersed into the atmosphere and will result in lower concentrations near the pollutant source (EPA Meteorological Data, 2008)

1.6.5 SOLAR RADIATION

The intensity of sunlight is an important influence on the rate of the chemical reactions that produces photochemical smog in the atmosphere. The intensity of sunlight can be affected by the cloudiness of the sky, time of day and geographical location. Solar radiation can be measured using a device called pyranometer. It measures the energy, which radiates onto the surface of the instrument, or the intensity of the sunlight (EPA Meteorological Data, 2008).

CHAPTER TWO

2.0 MATERIALS AND METHODS

2.1 STUDY AREA

This study was carried out in twenty (20) auto-mechanic workshops randomly chosen around Uwelu Motor Spare Parts Market which is located in the North-West zone of Benin City, Edo state, Nigeria. The metropolis lies between latitude 6^{o}2355N to 6^{o}2739N and longitude 5^{o}3618E to 5^{o}4430E, it has a tropical climate characterized by two distinct conditions of wet and dry seasons. The dry season starts in October and lasts till March while the wet season starts in April and lasts till September. Temperature across the state is relatively high with a very narrow variation in seasonal and diurnal range; 22°C - 36°C and an annual rainfall of above 600mm with mean relative humidity of above 80%. The sampling locations are shown in the map displayed in figure 2.1.

SAMPLING LOCATION DESCRIPTION

All sampling locations were fairly similar. They were chosen based on the following criteria

1. Presence of at least 3 mechanical activities such as general engine repair and servicing, welding, panel beating, electrical repair, paint/body repair, A/C repair etc
2. Absence of trees at least 50m from the repair shop
3. Minimum distance of 100m from major roads

Table 2.1: Coordinates of sampling locations

S/no	Latitude	Longitude
1	6.3721090	5.584539
2	6.3779350	5.589140
3	6.3779148	5.589063
4	6.3774468	5.588533
5	6.3775565	5.588315
6	6.3803503	5.588568
7	6.3803460	5.588568
8	6.3806094	5.588077
9	6.3724543	5.583226
10	6.3801628	5.588145
11	6.3816280	5.587822
12	6.3770366	5.589735
13	6.3769261	5.589826
14	6.3783252	5.589822
15	6.3791364	5.590729
16	6.3791558	5.591252
17	6.3800378	5.591703
18	6.3802184	5.592307
19	6.3804487	5.592692
20	6.3704570	5.588049

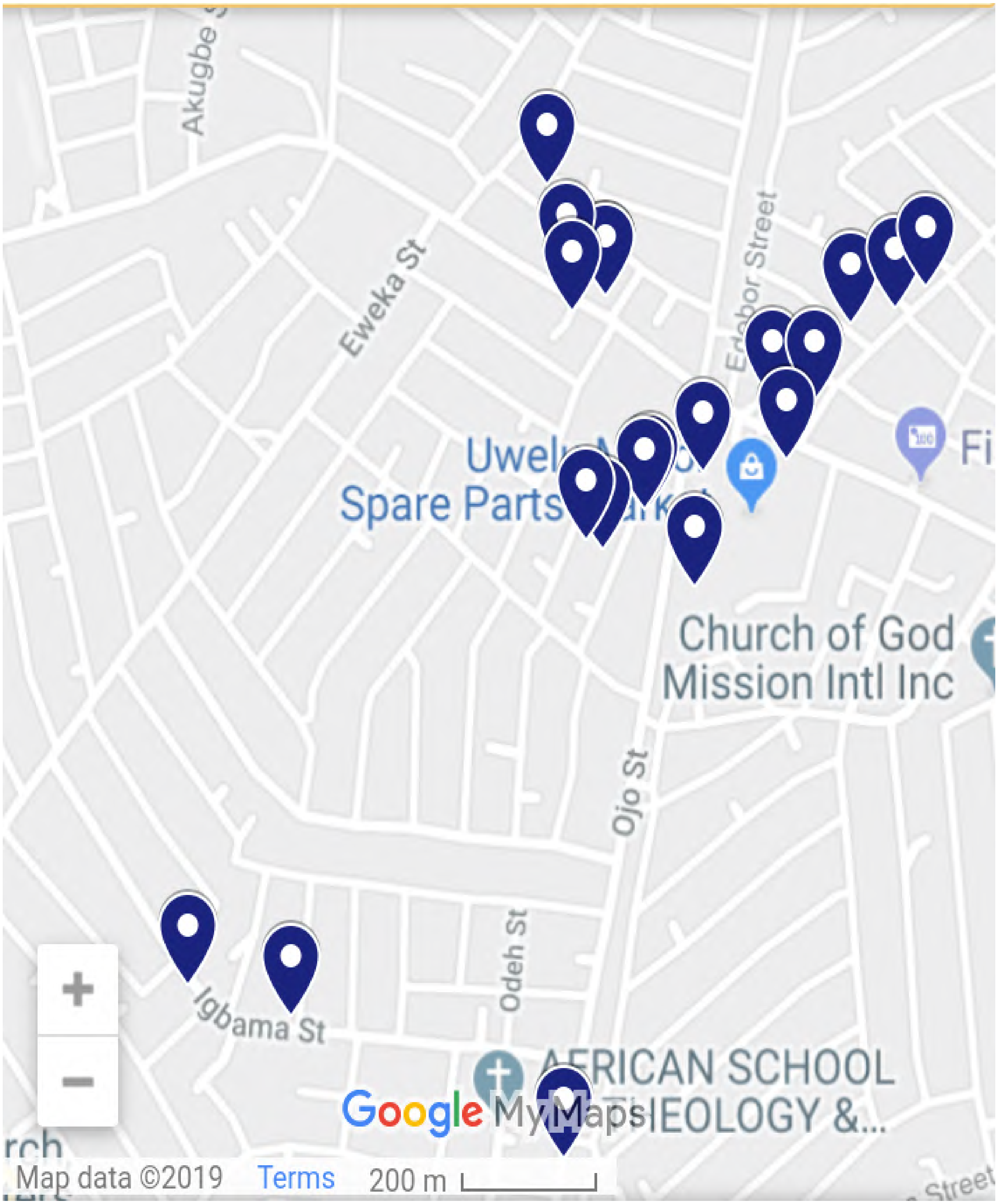

Figure 2.1 Map of Uwelu environ showing sampling locations

Source: google maps 2019

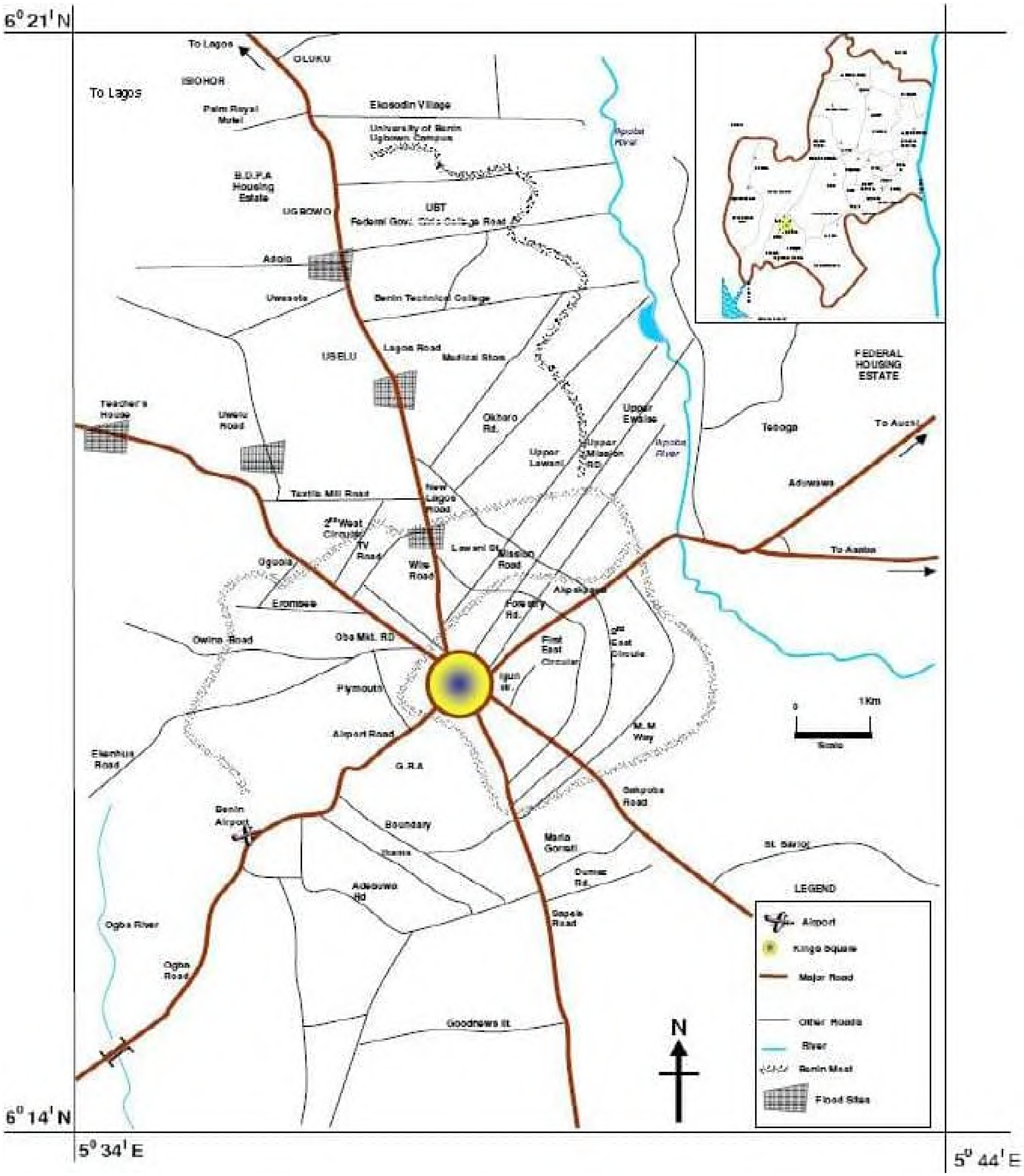

Figure 2.2 Map of Benin city

2.2 MATERIALS

2.2.1 CHEMICALS/REAGENTS

- Hydrochloric acid (HCL) Analar grade
- Nitric acid HNO_3 Analar grade
- Acetone
- Dichloromethane (HPLC grade)
- Distilled water
- Standard stock solutions (Buck)
- Nitrogen gas

2.2.2 INSTRUMENTS/APPARATUS

- Analytical weighing balance (Ohaus)
- Laboratory glass wares (pyrex)
- Apex2IS Casella Standard Pump (Bedford, UK)
- Dessicator
- Conical Inhalable Sampler CIS (Bedford, UK)
- Polyurethane foams (PUF)
- Atomic Absorption Spectrophotometer (Buck Scientific model-VGP-210)
- Fume cupboard

- Kjeldahl Digester
- Whatman filter papers
- Quartz filter

2.3 PREPARATION OF QUARTZ FILTER AND POLYURETHANE FOAM (PUF) FOR SAMPLING

The quartz filters were baked at 450°C for 4 hours in a muffle furnace and stored in a dichloromethane pre-treated dark plastic bag to prevent photo-oxidation and sealed.

Polyurethane foam (PUF) for sampling were pre cleaned with dichloromethane in an ultrasonic bath for 15 minutes and purged at room temperature with nitrogen gas till it was dried prior to field sampling. (USEPA, 2006).

The quartz filter and PUF were equilibrated in a desiccator for 48 hours before sampling to eliminate the effect of humidity and weighed in a weighing balance to obtain accurate PM and TSP measurements.

2.4 FIELD SAMPLING

2.4.1 CALIBRATION OF PUMP FOR SAMPLING

Pre and post field calibration was carried out for each field sampling to meet the recommended flow rate for each of the sampling period. (NIOSH, 2017).

2.4.2 SAMPLING PROCEDURE FOR $PM_{2.5}$ AND TSP (SAMPLE COLLECTION)

$PM_{2.5}$ and TSP was collected at a height 1.5-2.0 metres above the ground using Apex2IS Casella standard pump coupled with conical inhalable sampling (CIS) head at a flow rate of 3.5LPM

(Litre per minute) for 8 hours (NIOSH, 2017). The sampler was monitored closely throughout the duration of sampling to ensure accurate sample collection, timing, prevent battery failure and vandalism. Sampling was carried out during working hours (8.00am-4.00pm). After sampling, the filter cassette containing the $PM_{2.5}$ fine particles and the PUF was coded and conditioned in a desiccator overnight. Weighed three times and immediately transferred into a 100 ml brown bottle containing 25 ml acetone/dichloromethane (1:1) to prevent photolytic degradation. Sealed and wrapped in aluminium foils and stored at 4°C until analysis.

The difference of the initial and final weights of the mass concentration of $PM_{2.5}$ and TSP was calculated.

PUF (containing coarse particles + $PM_{2.5}$=TSP

Plate 2.1: Casella pump and conical inhalable sampler

2.4.3 DETERMINATION OF PARTICULATE MATTER (PM) MASS CONCENTRATION

The particle mass concentration was determined using gravimetric method of analysis. This was done by subtracting the initial average mass of the sampled filter. Filters were repeatedly weighed using an electric weighing balance (Denver instrument) until a constant value was obtained. The total volume of air collected by the sampler was determined from the measured flow rate and the sampling time (USEPA, 1999). The mass concentration of PM in the ambient air was then determined by the following equation

$$M_{2.5} = M_{f.(2.5)} - M_{i.(2.5)} \times 10^6 \qquad 1$$

$$M_{tsp} = M2.5 + M_{f(inh)} - M_{i(inh)} \times 10^6 \qquad 2$$

Where;

$M_{2.5}$= mass of fine particulate matter collected during sampling period (µg)

$M_{f.(2.5)}$= final mass of conditioned filter after sample collection (g)

$M_{i.(2.5)}$= initial mass of conditioned filter after sample collection (g)

M_{tsp}= mass of total suspended particulate during sampling period (µg)

$M_{f(inh)}$= mass of conditioned PUF before sample collection (g)

$M_{i(inh)}$= initial mass of conditioned PUF before sample collection (g)

10^6= unit conversion factor for grams (g) to micrograms (µg)

Therefore

$$PM_{2.5} = \frac{M_{2.5}}{V} \qquad 3$$

$$PM_{TSP} = \frac{M_{TSP}}{V} \quad 4$$

$PM_{2.5}$= Mass concentration of $PM_{2.5}$ (µg\m^3)

PM_{TSP}= mass concentration of total suspended particulates (µg\m^3)

V= total volume of air sampled (m^3)

$V = Q_{avg} \times t \times 10^{-3}$

Q_{avg}= average flow rate over the entire duration of the sampling period 3.5 Litre per min

t= duration of sampling period in minutes

10^{-3}= unit factor for litre (L) into cubic metre (M^3)

2.4.4 MONITORING OF METEOROLOGICAL PARAMETERS

Meteorological data such as ambient temperature, rainfall, relative humidity (RH), wind speed (WS), wind direction (WD), solar radiation and ultra-violet was recorded through an automatic weather monitoring system (professional weather station) mounted 2.5-3.0 meters above the ground level at the sampling site. It was programmed to collect data at 5 minute interval and stored in memory to be downloaded to a computer using software and average of 1 hour calculate (Lie *et al.*, 2016).

Plate 2.2: Professional weather station equipment

2.5 SAMPLE PREPARATION AND ANALYSIS

2.5.1 SAMPLE DIGESTION AND HEAVY METALS ANALYSIS

A 250 ml digestion flask washed with detergent, rinsed thoroughly with distilled water and allowed to dry in an oven. The quartz filter containing the fine particulate left inside 100 ml brown bottle and the remaining particles on the 47 mm Millipore filter after the extraction of PAHs was rinsed with 10 ml Aqua regia (mixture HCl and HNO_3, ratio 3:1), three consecutive times in to a digestion flask and the mixture heated in a kjeldahl digester at 70°C for 2 hours for complete digestion. The digest was allow to cool and filtered using whatman filter paper into a 100 ml volumetric flask (Okuo *et al.,* 2017). An unexposed filter paper was prepared as a blank using the same method described for the exposed filter paper.

The digested samples were analysed for heavy metals such as Lead Pb, Cadmium Cd, Chromium Cr, Nickel Ni, Iron Fe, Copper Cu, Manganese Mn, Zinc Zn, Arsenic As, using Atomic Absorption Spectrophotometer (Buck Scientific model-VGP-210)**.**

2.5.2 ATOMIC ABSORPTION SPECTROSCOPY

In analytical chemistry, atomic absorption spectroscopy technique is a technique for determining the concentration of a particular metal element. The technique can be used to analyse the concentration of over 70 different metals in a solution.

2.5.2.1 PRINCIPLES OF ATOMIC ABSORPTION SPECTROSCOPY

It is a technique for measuring the concentration of various elements in the sample through the absorption of light. It is a relatively simple and reliable technique which uses absorption of optical radiation by free atoms to determine the content of different elements. The samples were vaporized and dissociated into their elements in the gaseous state. The elements being measured is aspirated into a flame and atomized. The atoms in the unionized or ground state absorb energy, become excited and advance to a higher energy level. A light beam containing the corresponding wavelength of the energy required to raise the atoms of the analyte from the ground state to the excited state is directed through the flame. This wavelength is observed by a monochromator and a detector through the flame. Each wavelength is observed by a monochromator and a detector that measures the amount of light absorbed by the element, hence, the number of atoms in the ground state in the flame is measured. A hollow cathode lamp for the element been determined provides a source of metal’s particular absorption wavelength. Determination of metal concentrations was performed from prepared calibration curves and each samples were analysed in triplicates and the mean concentration was calculated.

The results obtained from trace metal analysis were converted from mg/L or ppm to µg/m^3 using the formula below as reported by Muhammed *et al,* 2011.

$$Cs = \frac{(\mathrm{Ci} - \mathrm{Cb})\mathrm{V}}{\mathrm{Vo}} \qquad 5$$

Where

Cs = concentration of metal in µg/m^3

Ci = metal concentration in solution of sample in mg/L

Cb = metal concentration in the solution of blank in mg/L

V = volume of the sample solution in 100ml

V_o = sampling air volume in m^3 at standard condition

$$Vo = \frac{Vr \times 298}{1000\mathrm{T}} \qquad 6$$

Where

Vr = sampling air volume at ambient condition (L/min)

T = Average temperature during sampling (K).

2.5.2.2 INSTRUMENTATION

Beer- Lamberts Law

This law tells us about (quantitatively) how the amount of alternation depends on the concentration of the absorbing molecules and the path length over which absorption occurs.

It states that there is a logarithmic dependence between the transmission T, of light through a substance and the product of the absorption coefficient of the substance, α, and the distance the light travels through the materials (i.e the path length), I. The absorption coefficient can in turn be written as a product of either a molar absorptivity of the absorber, E, and the concentration C of the absorbing species in the material or an absorption cross and the density N of absorbers.

For liquids, these relation are usually written as I_O

$$T = \frac{I}{IO} = 10^{\alpha L} = 10^{-ELC}$$

Where I_O and I are the intensity of the incident light and the transmitted light respectively.

The transmission is expressed in terms of an absorbance which for liquids is defined as:

$$A = -\log_{10} (I/I_O)$$

This implies that the absorbance becomes linear with the concentration according to

$$A = ELC = \alpha l$$

This is the path length and the molar absorptivity are known and the absorbance is measured, the concentration of the substance can deduced.

Although several expressions are often used as Beer-Lamberts law, the name should strictly speaking only be associated with the name should strictly speaking only be associated with the latter two. The reason is that historically, the Lambert law states that absorption is proportional to the light path length, whereas the Beers law states that absorption is proportional to the concentration of absorbing species in the material.

If the concentration is expressed as a molar fraction i.e a dimensionless fraction, the molar absorptivity (E) takes the same dimension as the absorption coefficient, i.e reciprocal length (e.g. cm^{-1}). However, if the concentration is expressed in moles per unit volume, the molar absorptivity (E) is used in $mol^{-1}\,cm^{-1}$.

2.6 QUALITY CONTROL

1) Clear forceps were used to handle the filters and PUF to avoid any contamination
2) Filters and PUF used for sample collection were equilibrated before and after sampling
3) Flow rate was well monitored during the 8 hours sampling
4) All the glass wares used for experiment were washed and rinsed properly and then oven dried before use
5) All reagents used were of analytical reagent grade.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

3.1 $PM_{2.5}$ and Total Suspended Particulate (TSP) Concentration in the study area

The particulate matter ($PM_{2.5}$ and TSP were sampled for at an auto-mechanic workshop in Uwelu, Benin City and the concentration of the $PM_{2.5}$ and TSP is reported in Tables below.

Table 3.1a: Concentration of $PM_{2.5}$ and TSP ($\mu g/m^3$) obtained in the various sampling locations from February to June.

Month	Locations	TSP	$PM_{2.5}$
February	1	17202.38	7440.47
	2	15892.85	6845.23
	3	17321.48	8630.95
	4	15416.66	6488.09
	Mean and SD	**16458.34 ± 822.11**	**7351.185 ± 813.43**
March	5	14404.76	5357.14
	6	14880.95	5238.09
	7	14166.67	4464.29
	8	13988.09	4821.43
	Mean and SD	**14360.11 ± 386.90**	**4970.23 ± 408.07**
April	9	13630.95	4702.38
	10	13095.24	3273.8
	11	13750.47	3630.95
	12	13690.47	3690.47
	Mean and SD	**13541.66± 301.55**	3824.4± 613.56
May	13	12440.47	3571.42
	14	11964.28	3035.71
	15	13392.85	3035.71
	16	12619.05	2916.67
	Mean and SD	**12604.16 ± 593.99**	**3139.87 ± 293.11**
June	17	11964.25	2976.19
	18	11011.9	2678.57
	19	10357.14	2440.47
	20	9702.38	2321.43
	Mean and SD	**10758.91 ± 965.14**	**2604.16 ± 289.06**

From Table 3.1 above, it was observed that $PM_{2.5}$ values obtained from the various sampling locations from the month of February to June ranged from 2321.43 to 8630.95 $\mu g/m^3$.

In February, location 3 had the highest concentration (8630.95 $\mu g/m^3$) while the lowest concentration was obtained in location 4 (6488.09 $\mu g/m^3$).

In March, location 5 had the highest concentration with $PM_{2.5}$ value of 5357.14 $\mu g/m^3$ and location 7 had the lowest concentration of 4464.29 $\mu g/m^3$.

For the month of April, location 9 recorded the highest concentration (4702.38 $\mu g/m^3$) and location 12 recorded the least concentration (3690.47 $\mu g/m^3$).

In May, the highest concentration was in location 13 having $PM_{2.5}$ value of 3571.42 $\mu g/m^3$ and location 16 had the least concentration of 2916.67 $\mu g/m^3$.

In the month of June, location 17 recorded the highest concentration 2976.19 $\mu g/m^3$ and the least in location 20 (2321.43 $\mu g/m^3$).

From Table 3.1 above, TSP values ranged from 9702.38 to 17321.48 $\mu g/m^3$. February had the highest concentration of TSP while June had the lowest concentration.

In February, location 3 measured TSP concentration of 17321.48 $\mu g/m^3$ which was the highest and the least was in location 4 which had TSP value of 15416.66 $\mu g/m^3$.

In March, the highest concentration was recorded in location 6 (14880.95 $\mu g/m^3$) and the lowest in location 8 (13988.09 $\mu g/m^3$).

April had TSP values lower than those in February and March, its highest concentration was obtained in location 12 having TSP levels of 13690.47 $\mu g/m^3$ and lowest concentration in location 10 (13095.24 $\mu g/m^3$).

In the month of May, location 15 recorded the highest TSP concentration of 13392.85 $\mu g/m^3$ and the lowest concentration in location 14 (11964.28 $\mu g/m^3$).

For June, TSP concentration in location 17 had the highest value of 11964.25 $\mu g/m^3$ and location 20 recorded the lowest value of 9702.38 $\mu g/m^3$

These values of $PM_{2.5}$ and TSP are high compared with the statutory limits of 250$\mu g/m^3$ limit for particulate matter stipulated by Federal ministry of Environment (FMNEW, 2000) and 150-230 $\mu g/m^3$ limit stipulated by the world health organization (WHO, 2005) and 250 $\mu g/m^3$ limit set by federal environmental protection agency (FEPA), also high compared with the 24 hours air quality threshold value for $PM_{2.5}$ (25$\mu g/m^3$) and TSP (125$\mu g/m^3$).

These concentration of $PM_{2.5}$ range from February to June measured 2321.43 to 8630.95 $\mu g/m^3$ respectively. These are 9 and 34-folds the value of 250 $\mu g/m^3$ standard for Particulate Matter.

Those of the TSP ranged from February to June measured 9702.38 to 17321.48 $\mu g/m^3$ respectively, these are 38 and 69-folds the value of 250 $\mu g/m^3$ for particulate matter by the regulatory bodies.

The reason for our high values particularly for the TSP and then for $PM_{2.5}$ in the month of February might be as a result of the season when the samples were obtained and the location too. February is part of the dry season and as a result of that many particulates are suspended in the air, samples were collected from auto-mechanic workshop where so many activities like repair and maintenance of vehicles are carried out. Also activities from welding and motor spray painting which was a major factor considered during the site location. Emissions from generators used during welding activities, all these activities releases particulates into the environment. Emissions from vehicles which are driven in and out of the mechanic workshop also plays vital role in increasing the level of TSP and $PM_{2.5}$ obtained. As most of these vehicles are either gasoline or diesel vehicles also the start-up of the engine which can be high combustion engine releases pollutants to the environment and this contributes to the high level of TSP and $PM_{2.5}$ recorded in the sampling site.

The high levels of TSP and $PM_{2.5}$ in the air is certainly from both natural and anthropogenic source. Basically, all these activities listed above are anthropogenic activities, so we can say that variations in anthropogenic activities in the various mechanic workshops could be a major contributing factor to the observed differences in particulate matter level in the various sites.

TSP and $PM_{2.5}$ values decreased coming down to June this is as a result of the month of June being part of the wet season and this had significant effect on the levels of TSP and $PM_{2.5}$obtained, the environment has the ability to cleanse itself during the wet season, as the rainfall increases, the particulate level drops to lower values.

Generally, the high values may also be attributed to meteorological factors such as frequency in the variation of rainfall, wind direction, humidity.

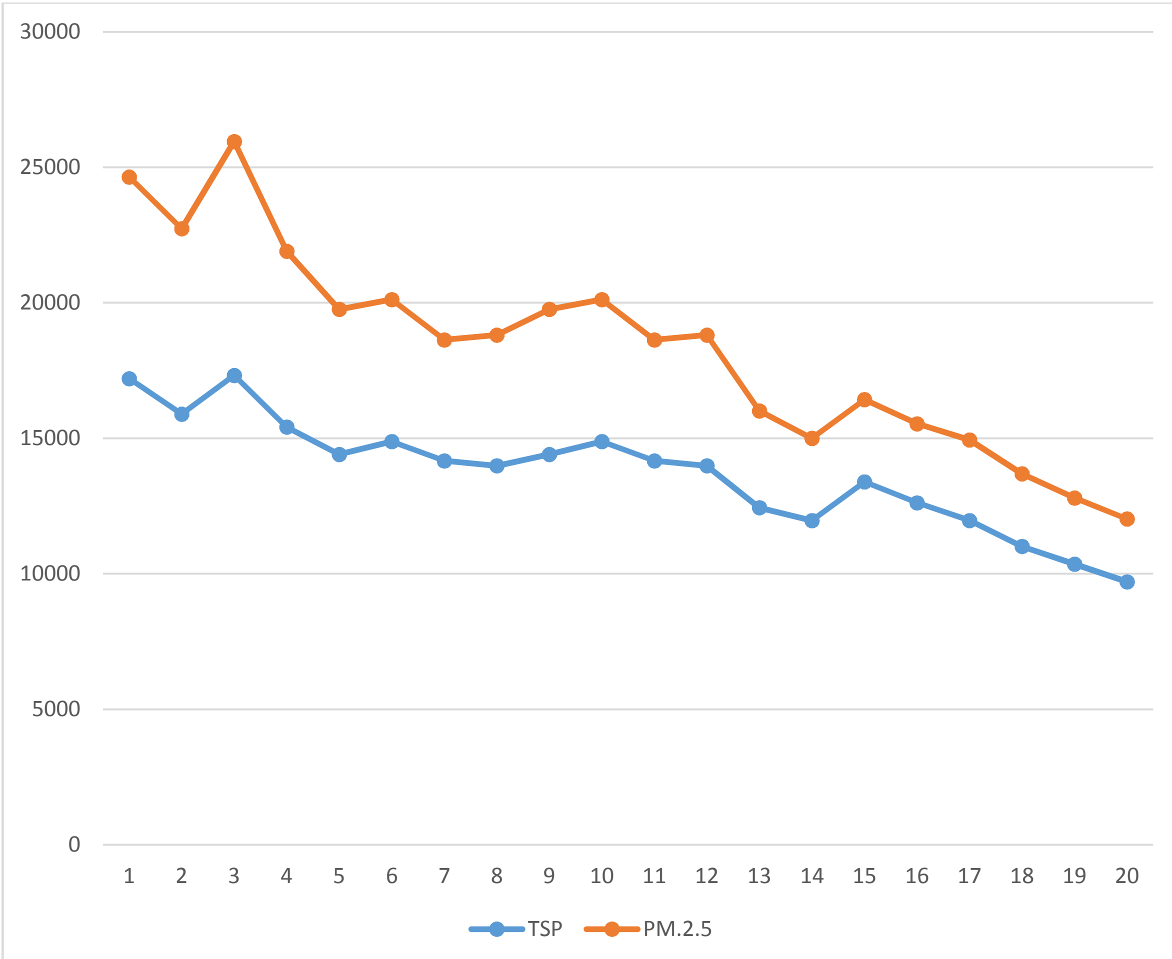

Figure 3.1: Line graph showing the trend of concentration of TSP and $PM_{2.5}$ for the sampling period presented as weekly locations.

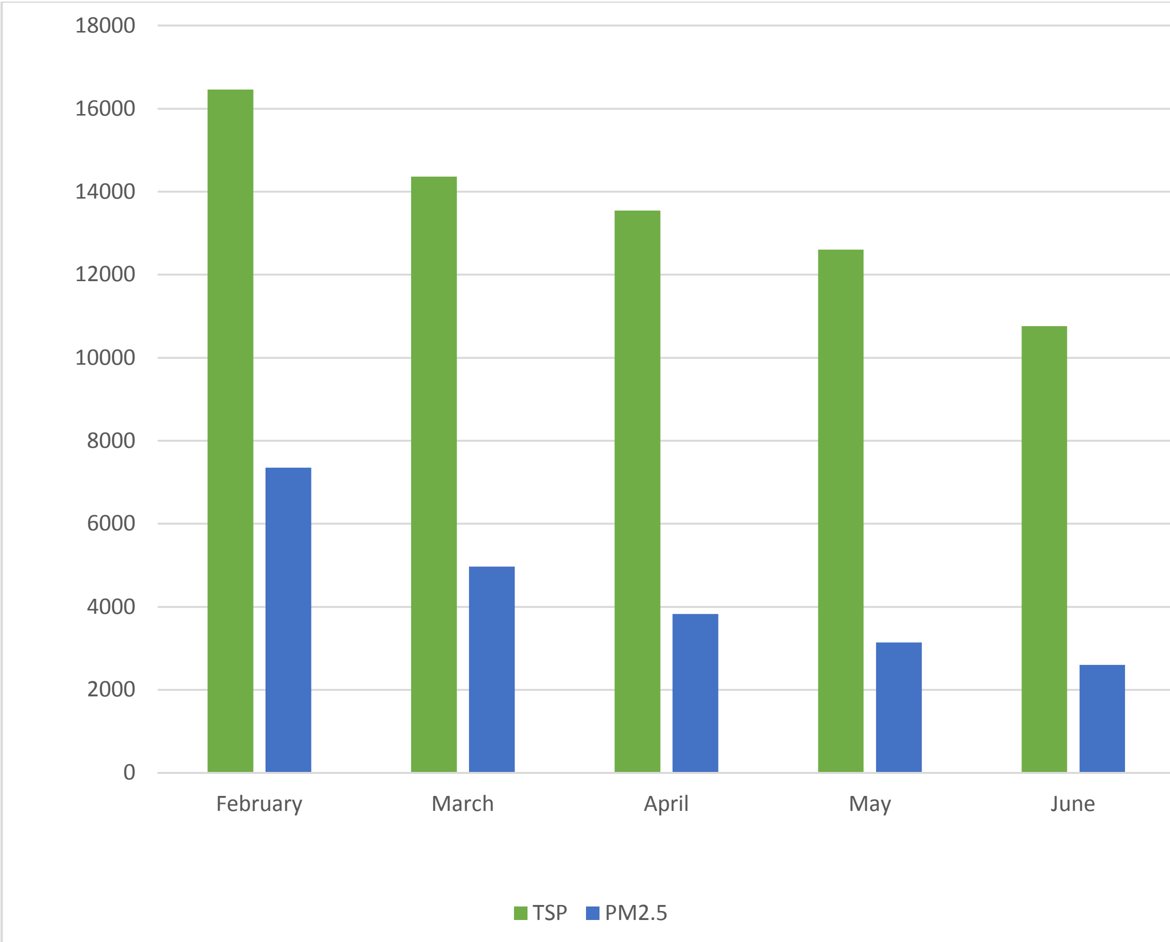

Figure 3.2: Bar chart showing the trend of concentration of TSP and $PM_{2.5}$ for the sampling period presented as monthly average (mean of four locations).

Figure 3.2 above, clearly shows the trend of concentration of TSP and $PM_{2.5}$ in the month of February to June in this sequence: February>March>April>May>June.

February and March recorded values higher in concentration as it was part of the dry season, April had values lower than those of February and March but values greater than those of May and June, this might be due to the fact that in April the dry season is partly fading away and the wet season gradually coming in. the TSP and $PM_{2.5}$ concentrations in May was lower than those recorded in April as in May the rain had already started but was not so much, June had the lowest concentration this might be because it was collected during the wet season.

Table 3.1b: Comparison of Total Suspended Particulate and $PM_{2.5}$ of this study with other studies.

S/N	SITE/LOCATIONS	VALUES (µg/m³)	$PM_{2.5}$/TSP	REFERENCES
1	Urban/Benin City	583.00-20,166.67	TSP	Okuo *et al.,* 2011
2	Urban/Benin City	3958.33-7430.56	TSP	Ediagbonya *et al.,* 2016
3	Urban/Benin City	1284.72-3020.84	$PM_{2.5}$	Ediagbonya *et al.,* 2016
4	Rural/Calabar	108.98	TSP	Ikamaise *et al.,* 2013
5	Nigeria	1033-40,000	TSP	Taiwo *et al.,* 2015
6	Urban/Lagos	For wet season- 14.00-32.67 For dry season- 18.67-34.67	$PM_{2.5}$	Okuo *et al.,* 2017
7	Urban/Benin City	2321.43-8630.95	$PM_{2.5}$	Current Study
8	Urban/Benin City	9702.38-17321.48	TSP	Current Study

In Benin, Okuo *et al.,* 2011, the highest concentration TSP recorded exceeds the highest concentration of this study and with about 1-fold and about 80-folds the 250µg/m^3 stipulated by the FMNEV and FEPA.

In Lagos, Okuo *et al.,* 2017, the highest concentration of $PM_{2.5}$ recorded during dry season was 34.67µg/m^3 and during the wet season 32.67µg/m^3. This value was below regulatory limit but differs greatly from those obtained from this study, this might be as a result of the activities been carried out in the various sampling site. Studied conducted at Lagos was in an Industrial area where less anthropogenic activities that releases particulates into the environment unlike this study which is sited at an auto-mechanic workshop where so many anthropogenic activities are carried out, as earlier stated.

3.2 Heavy Metal Concentration

In the case of high concentration of heavy metals in ambient air particulate matter, it become of environmental and health concerns. This is due to their persistence in the environmental media and their human toxicity. Particularly, the non-biodegradability of heavy metals lead to their accumulation in the environment.

The mean concentration of the heavy metals- nickel Ni, copper Cu, iron Fe, zinc Zn, manganese Mn, lead Pb, chromium Cr, cadmium Cd and arsenic As in the TSP and $PM_{2.5}$ samples obtained in the various locations (mean of four location) were taken and summarized on a table 3.2a and 3.2b. This was done because mechanic workshops around Uwelu spare part market are clustered areas hence slight differences in the heavy metal concentration obtained in the various sampling locations.

Table 3.2a: Concentration of heavy metals in $PM_{2.5}$ ($\mu g/m^3$) represented as Mean and Standard Deviation.

Heavy Metals	February	March	April	May	June
Ni	**0.45±0.31**	**0.81±0.40**	**1.03±0.63**	**0.61±0.34**	**0.47±0.09**
Cu	**0.08±0.04**	**0.10±0.08**	**0.21±0.23**	**0.19±0.08**	**0.04±0.00**
Fe	**0.71±0.22**	**0.92±0.65**	**1.31±0.65**	**1.18±0.73**	**0.41±0.06**
Zn	**0.14±0.04**	**0.32±0.04**	**0.23±0.15**	**0.60±0.55**	**0.05±0.00**
Mn	**0.44±0.11**	**0.49±0.11**	**0.58±0.40**	**0.31±0.08**	**0.08±0.00**
Pb	**1.08±0.58**	**0.57±0.25**	**0.78±0.34**	**0.34±0.17**	**0.33±0.30**
Cr	**0.18±0.13**	**0.38±0.16**	**0.48±0.36**	**0.09±0.03**	**0.12±0.00**
Cd	**0.34±0.16**	**0.61±0.16**	**0.73±0.30**	**0.06±0.00**	**0.06±0.01**
As	**0.12±0.05**	**0.25±0.09**	**0.32±0.18**	**0.15±0.04**	**0.07±0.01**

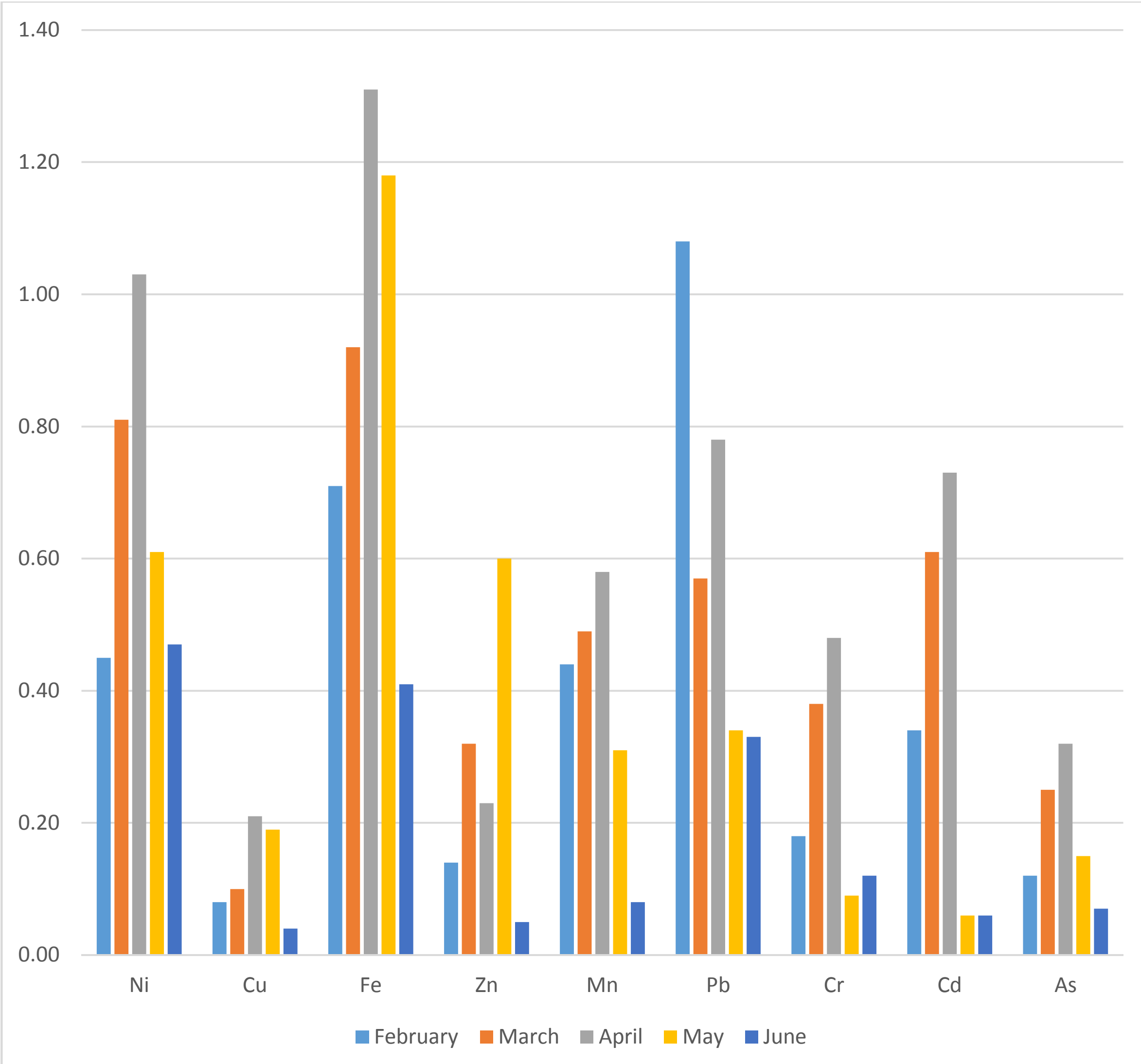

Figure 3.3: Bar chart showing the mean concentration of heavy metals in $PM_{2.5}$ from February to June.

The bar chart show that lead in the month of February had the highest concentration, followed by iron, nickel, manganese, cadmium, chromium, zinc, arsenic while the lowest was copper. Represented by Pb>Fe>Ni>Mn>Cd>Cr>Zn>As>Cu.

In the month of March, iron had the highest concentration, then nickel, cadmium, lead, manganese, chromium, zinc, arsenic and the lowest was copper. Represented by the trend Fe>Ni>Cd>Pb>Mn>Cr>Zn>As>Cu.

In the month of April, iron recorded the highest concentration followed by nickel, lead, manganese, chromium, arsenic, zinc and copper had the lowest concentration. Represented by the trend Fe>Ni>Pb>Cd>Mn>Cr>As>Zn>Cu.

Bar chart shows that in the month of May, iron recorded the highest concentration while the next was nickel, zinc, lead, manganese, copper, arsenic, chromium and the least concentration was cadmium. The heavy metals are represented in the following sequence: Fe>Ni>Zn>Pb>Mn>Cu>As>Cr>Cd.

In the month of June, the chart showed that nickel had the highest concentration followed by iron, then lead, chromium, manganese, arsenic, cadmium, zinc and the least been copper. Represented in this sequence: Ni>Fe>Pb>Cr>Mn>As>Cd>Zn>Cu.

Copper had the least concentration for all the months except in May.

Table 3.2b: Mean concentration of heavy metals in TSP (µg/m^3) represented as Mean and Standard Deviation.

Heavy Metals	February	March	April	May	June
Ni	1.20±0.54	1.40±0.11	1.62±0.46	0.29±0.29	0.56±0.25
Cu	0.46±0.24	1.34±0.94	1.14±0.48	0.13±0.09	0.39±0.34
Fe	1.85±0.90	3.18±1.36	4.29±1.32	3.73±1.83	1.37±1.03
Zn	0.93±0.70	0.71±0.09	0.93±0.31	0.41±0.23	0.28±0.20
Mn	1.40±0.40	1.41±0.84	1.82±0.70	0.54±0.28	0.19±0.13
Pb	1.73±0.87	1.85±0.68	2.78±0.78	0.92±0.67	0.87±0.71
Cr	0.89±0.63	0.81±0.19	1.29±0.41	0.30±0.12	0.29±0.22
Cd	1.20±0.22	1.04±0.20	1.36±0.23	0.13±0.04	0.14±0.09
As	0.31±0.21	0.54±0.24	0.65±0.23	0.19±0.15	0.13±0.07

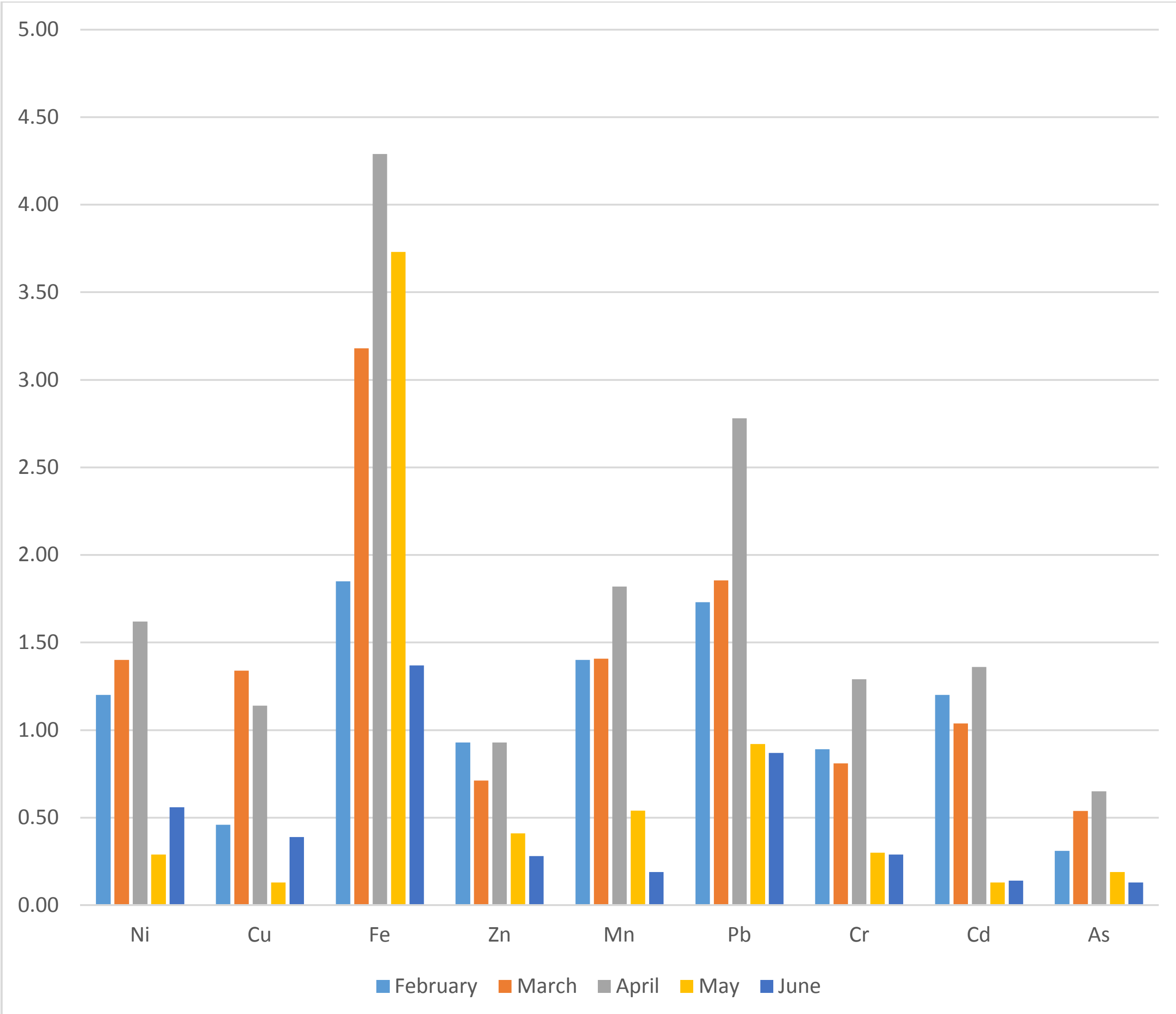

Fig 3.4: Bar chart showing the mean concentration of heavy metals in TSP from February to June.

The bar chart showed that the highest heavy metal concentration in the month of February was iron, next was lead, manganese, nickel, cadmium, zinc, chromium, copper and the least concentration recorded was arsenic. Represented in this trend: Fe>Pb>Mn>Ni>Cd>Zn>Cr>Cu>As.

In the month of March iron had the highest concentration, followed by lead, nickel, manganese, copper, cadmium, chromium, zinc and the least concentration arsenic. Represented as: Fe>Pb>Ni>Mn>Cu>Cd>Cr>Zn>As.

In April, iron recorded the highest concentration, next was lead, manganese, nickel, cadmium, chromium, copper, zinc and lowest concentration arsenic. Represented in this sequence: Fe>Pb>Mn>Ni>Cd>Cr>Cu>Zn>As.

The bar chart shows that iron recorded the highest concentration in May, followed by lead, manganese, zinc, nickel, chromium, arsenic, cadmium and the least concentration was copper. Represented as: Fe>Pb>Mn>Zn>Ni>Cr>As>Cd>Cu.

In the month of June, iron recorded the highest concentration, followed by lead, nickel, copper, chromium, zinc, manganese, cadmium and the least concentration arsenic. Represented as Fe>Pb>Ni>Cu>Cr>Zn>Mn>Cd>As.

In all months iron was the highest and the next was lead, arsenic recorded the least concentration in all months except in May.

From Table 3.2a, concentration of heavy metals in $PM_{2.5}$, in February, Nickel had concentration of 0.45 $\mu g/m^3$, nickel concentration in March was 0.81 $\mu g/m^3$, in April it recorded 1.03 $\mu g/m^3$, in May and June it was 0.61 $\mu g/m^3$ and 0.47 $\mu g/m^3$ respectively. April had the highest concentration of nickel while February recorded the lowest concentration. The measured concentrations were lower than the US OSHA (2009) limit of 1.0mgm^{-3} and FEPA 1991 limit of 3.5mgm^{-3}. The iron metal might have been released into the environment through anthropogenic sources like diesel/gasoline fuel and residual oil, brake emissions and corrosion of vehicle steel parts.

The concentration of copper in February was 0.08 μg/m^3, in March it recorded 0.10 μg/m^3, in April 0.21 μg/m^3, in May 0.04 μg/m^3 and in June 0.19 μg/m^3. April measured the highest concentration and lower was in June. However all the concentration were below the air quality guideline stated by US OSHA 2009 and FEPA 1991 1.0mgm^{-3}. The concentration of copper might be as a result of vehicular emissions. Vecchi *et al.,* (2007), showed that brake wear and tear causes significant particulate matter emission characterised by high concentration metals of which copper is prominent. Study also showed that a large portion of copper comes from the wearing out of vehicular brakes which is in a way related to this study.

The concentration of iron in February was 0.71μg/m^3, in March 0.92 μg/m^3, April 0.21 μg/m^3, in May 1.18 μg/m^3 and June 0.41 μg/m^3. Iron was found to be more in April and the least concentration in June. The concentration of iron for all the months were within the typical concentration of urban concentration of iron metal in the air which is about 0.1-10.0 μg/m^3 Radojevic and Bashkin 2007.

The source of iron into the environment is from vehicles since it is present in brake wear particles (Giet *et al.,* 2009) and from activities of welding which involves use of electrodes and metal plates. Although main source of iron metal into the environment is mainly from earth crust as it is an abundant element in the earth crust.

In the month of February, the concentration of zinc was 0.41 μg/m^3 in March 0.3 2μg/m^3, April 0.23 μg/m^3, May recorded 0.60 μg/m^3 and June 0.05 μg/m^3. Zinc was found to be much in the month of May and least concentration in June. The measured values were within the WHO standard for zinc (0.1-0.50 μg/m^3) except for the one in May which had a value of 0.60 μg/m^3 which was slightly above the WHO limit.

Zinc is known to be an important nutrient for mammals and occurs naturally in soil and ambient air. However the presence of zinc in the ambient air across the sampling sites may be due to re-suspended dust or windblown dust around the auto-mechanic workshop.

Concentration of manganese in February 0.44 μg/m^3, March 0.49 μg/m^3, April 0.58 μg/m^3, May had 0.31 μg/m^3 and June 0.08μg/m^3. Manganese values recorded in the various sampling months were all below EPA standard value of 1μg/m^3 and US OSHA (5.0mgm^{-3}). Manganese can be present due to the Methylcyclopentadienyl Manganese Tricarbonyl (MMT) additive in fuels. The main source of manganese in the ambient air of auto-mechanic workshop may be due to emissions from fuel combustion.

The concentration of lead in February was 1.08, March 0.57, April 0.78, May 0.34 and June 0.33μg/m^3. Lead concentration was found to be much in February and the least concentration in June. The lead level measured in February, March and April was higher compared to those measured in May and June. This was influenced by emission activities and meteorological parameters. During the wet season, there was higher amount of wind speeds and rainfall. These helped to wash down pollutants from the atmosphere and the wind speed enhanced the dispersion of pollutants hence the reduction in concentration of the lead.

The lead level measured for February, March and April were higher than the WHO limit (0.5μg/m^3) while for those in May and June was below WHO limit. Lead detected in this samples could be from emissions from automobile exhaust, tyre wear, bearing wear, automobile batteries, lubricating oil and grease.

The concentration of chromium in February was 0.18μg/m^3, in March it was 0.38μg/m^3, April 0.48 μg/m^3, May 0.09μg/m^3 and June 0.12μg/m^3. The highest concentration was observed in the month of April. The measured values of chromium were all below the US OSHA limit (0.5mgm^{-3}).

The concentration of cadmium in February was 0.34 μg/m^3, March 0.61 μg/m^3, April 0.73 μg/m^3, May 0.06 μg/m^3 and June 0.06 μg/m^3. The concentration of the metal measured were higher than WHO limit for cadmium (0.005 μg/m^3). Possible source of cadmium in the auto-mechanic workshop environment is the vehicular exhaust emission and can be from dust particles around the sampling site. Other anthropogenic sources are vehicular emission including tyre abrasion, brake emission, diesel/gasoline fuel and residual oil. (Awan *et al.,* 2011).

Arsenic concentration for February was 0.12 μg/m^3, March was 0.25 μg/m^3, April 0.32 μg/m^3, May 0.15 μg/m^3 and June 0.07 μg/m^3. The highest concentration was measured in April and March.

From table 3.2b, TSP mean concentration of nickel in the month of February was 1.20μg/m^3, March 1.40 μg/m^3, April 1.62μg/m^3, May recorded 0.29 μg/m^3 and June 0.56 μg/m^3. The highest concentration of nickel was recorded in the month of April (1.62μg/m^3) while February recorded the lowest concentration (1.20 μg/m^3). The measured concentrations were higher than the US OSHA (2009) limit of 1.0mgm^{-3}.

The concentration of copper for February was 0.46 μg/m^3, March 1.34 μg/m^3 April 1.14μg/m^3, May 0.13 μg/m^3 and June 0.39μg/m^3. The highest concentration was recorded in the month of March (1.34 μg/m^3). However all the concentration were below the air quality guideline stated by US OSHA 2009 and FEPA (1991) 1.0mgm^{-3}. The concentration of copper is as a result of vehicular emissions.

The concentration of iron in February was 1.85 μg/m^3, March 3.18 μg/m^3, April 4.29 μg/m^3, May 3.73μg/m^3 and June 1.37μg/m^3. It was within the typical concentration of urban concentration of iron metal in the air which is about 0.1-10.0 μg/m^3 (Radojevic & Bashkin, 2007).

The source of iron into the environment is from vehicles since it is present in brake wear particles (Gietl *et al.,* 2010) and from activities of welding which involves use of electrodes and metal plates.

In February the concentration of zinc was 0.93 μg/m^3, March 0.71μg/m^3, April 0.93μg/m^3, May 0.41 μg/m^3 and June 0.28 μg/m^3. The highest value was obtained in the wet season in the month of February and April. The measured values were higher than the WHO standard for zinc (0.1-0.50 μg/m^3) for February, March and April while May and June recorded value within the WHO limit.

Concentration of manganese in February was 1.40 μg/m^3, March 1.41μg/m^3, April 1.82 μg/m^3, May 0.54 μg/m^3 and June 0.19 μg/m^3.The highest concentration was in the month of April (1.82μg/m^3) and the lowest was in June (0.19 μg/m^3). Manganese values recorded for the month of May and June were below EPA standard value of 1 µg/m^3 while those recorded in February, March and April were higher than the EPA standard value of 1 µg/m^3

The concentration of lead in February was 1.73 µg/m^3, March 1.85 µg/m^3, April 2.78 µg/m^3, May 0.92 µg/m^3 and June 0.87 µg/m^3. The lead level measured in was lower than those measured during the dry season. The lead level measured for both dry and wet season were higher than the WHO limit (0.5µg/m^3). Lead detected in this samples could be from emissions from automobile exhaust, tyre wear, bearing wear, automobile batteries, lubricating oil and grease.

The concentration of chromium in February was 0.89 µg/m^3, March 0.81 µg/m^3, April 1.29 µg/m^3, May 0.30 µg/m^3 and June 0.29 µg/m^3. The highest was observed in the month of April (1.9 µg/m^3). The measured values of chromium were all below the US OSHA limit (0.5mgm^{-3}).

The concentration of cadmium in February was 1.02µg/m^3, March 1.40µg/m^3, April was 1.36 µg/m^3, May was 0.13µg/m^3 and June was 0.14 µg/m^3. The concentration of the metal measured in all the months were higher than the WHO limit for cadmium (0.005 µg/m^3). Possible source of cadmium in the auto-mechanic workshop environment is the vehicular exhaust emission and can be from dust particles around the sampling site.

Arsenic concentration for February was 0.31 µg/m^3, March was 0.54 µg/m^3, April recorded 0.65 µg/m^3, May had 0.19 µg/m^3 and June was 0.13 µg/m^3. The highest concentration was measured in April.

3.3 Meteorological Parameters.

Table 3.3: Meteorological parameters obtained during sampling from February to June

Meteorological parameters	February	March	April	May	June
Ultra-violet radiation (μW/m^2)	944.12±65.31	1,034.97±96.57	1135.44±80.43	801.41±35.62	651.25±85.06
Pressure (mmHg)	749.8±0.76	748.81±0.33	748.18±0.10	749.72±0.53	750.82±0.30
Solar radiation (W/m^2)	589.45±140.78	656.44±145.49	777.95±133.95	526.59±101.73	529.80±90.15
Wind Direction (o)	191.81±19.68	184.91±6.49	194.28±20.81	183.84±30.44	190.78±49.75
Humidity (%)	75.09±2.35	72.91±1.42	69.25±1.51	74.06±1.72	74.91±1.49
Temperature (°C)	30.51±0.45	31.17±0.26	31.91±0.20	30.10±0.25	29.84±0.35
Wind Speed (km/h)	6.01±0.46	5.5±0.24	5.45±0.51	5.68±0.43	6.69±0.63

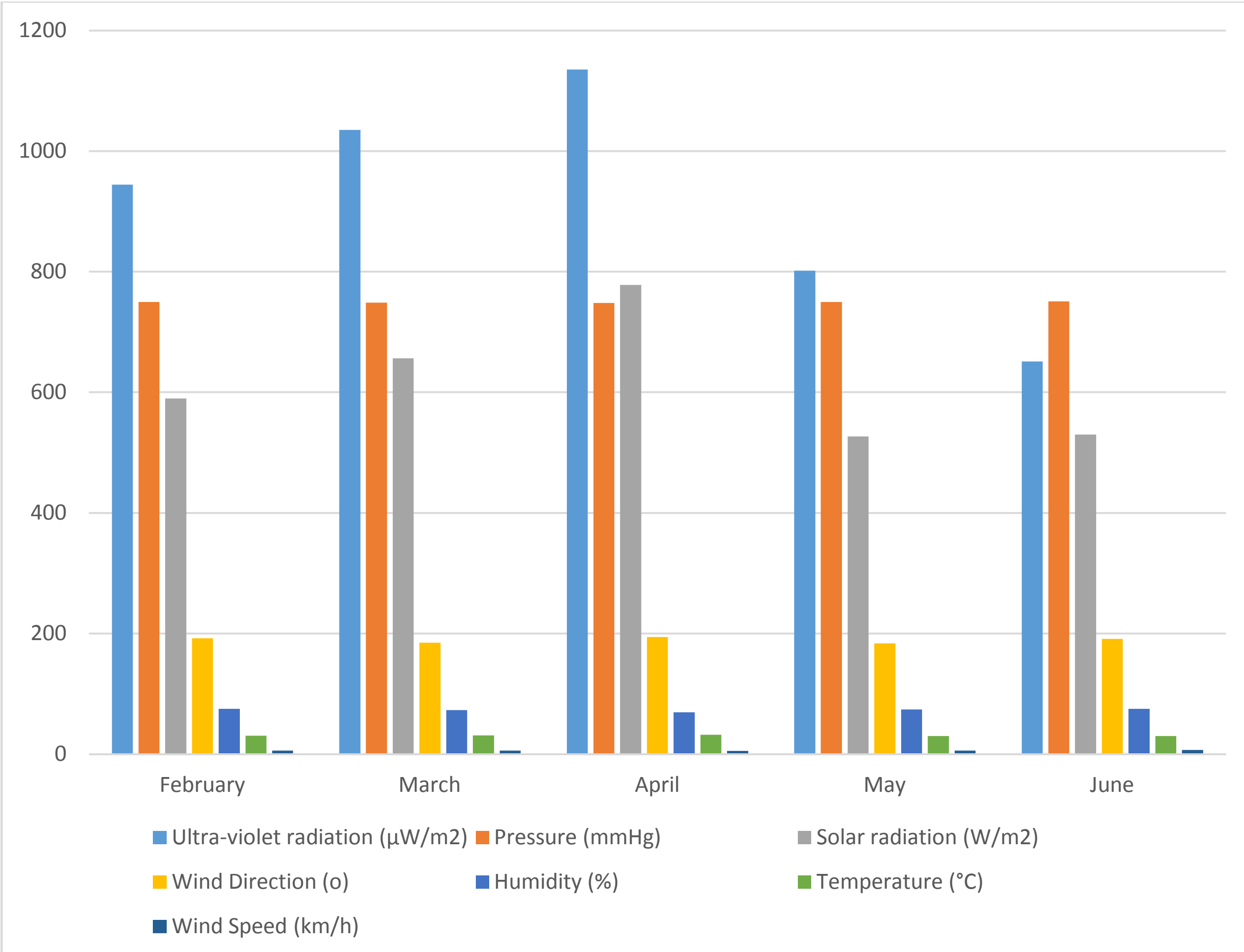

Figure 3.5: Bar Chart showing Meteorological parameter

3.4 STATISTICAL ANALYSIS

3.4.1 PRINCIPAL COMPONENT ANALYSIS (PCA)

Source identification analysis of $PM_{2.5}$ and TSP was performed based on the PCA method which is widely used to factorize the input concentration data of different species having a linear relationship between total mass concentration and the individual concentrations (Okuo *et al.,* 2017).

A Principal Component Analysis is often used in data analysis to study the correlation among a large number of interrelated quantitative variable by grouping the variable into a few factors. It interpret each factors according to the meaning of the variable and summarize variable by few factors.

PCA with varimax rotation was used in order to identify the possible sources contributing to the heavy metals in ambient air particles. Factors with Eigen values greater than 1.0 were used to identify major elements associated with different sources (Okuo *et al.,* 2017).

Table 3.4a: Principal Component Analysis for $PM_{2.5}$

Observation	Factor 1	Factor 2	Final communality
Ni	2.0204	0.3073	2.3278
Cu	-2.0577	0.2748	-1.7829
Fe	3.2180	0.9522	4.1702
Zn	-0.9071	1.0233	0.1163
Mn	-0.3893	-0.2640	-0.6533
Pb	1.6134	-1.6745	-0.0611
Cr	-1.1781	-0.1604	-1.3385
Cd	-0.6884	-0.5618	-1.2502
As	-1.6313	0.1031	-1.5282

Factor 1 explains 74.37% of the total variance and loads heavily on iron (Fe) and as well as nickel (Ni) and lead (Pb). This is likely from anthropogenic sources of emission such as diesel/gasoline emissions, brake emission, emissions from automobile exhaust.

Factor 2 explains 14.86% of the total variance and is loaded primarily by zinc, iron, nickel, copper and arsenic. This source may be attributed to vehicular emission as copper and iron is a marker element for brake, tyre and car parts wear and tear (Amato *et al.,* 2009). It can also be from wind-blown dust as zinc is predominant in dust samples.

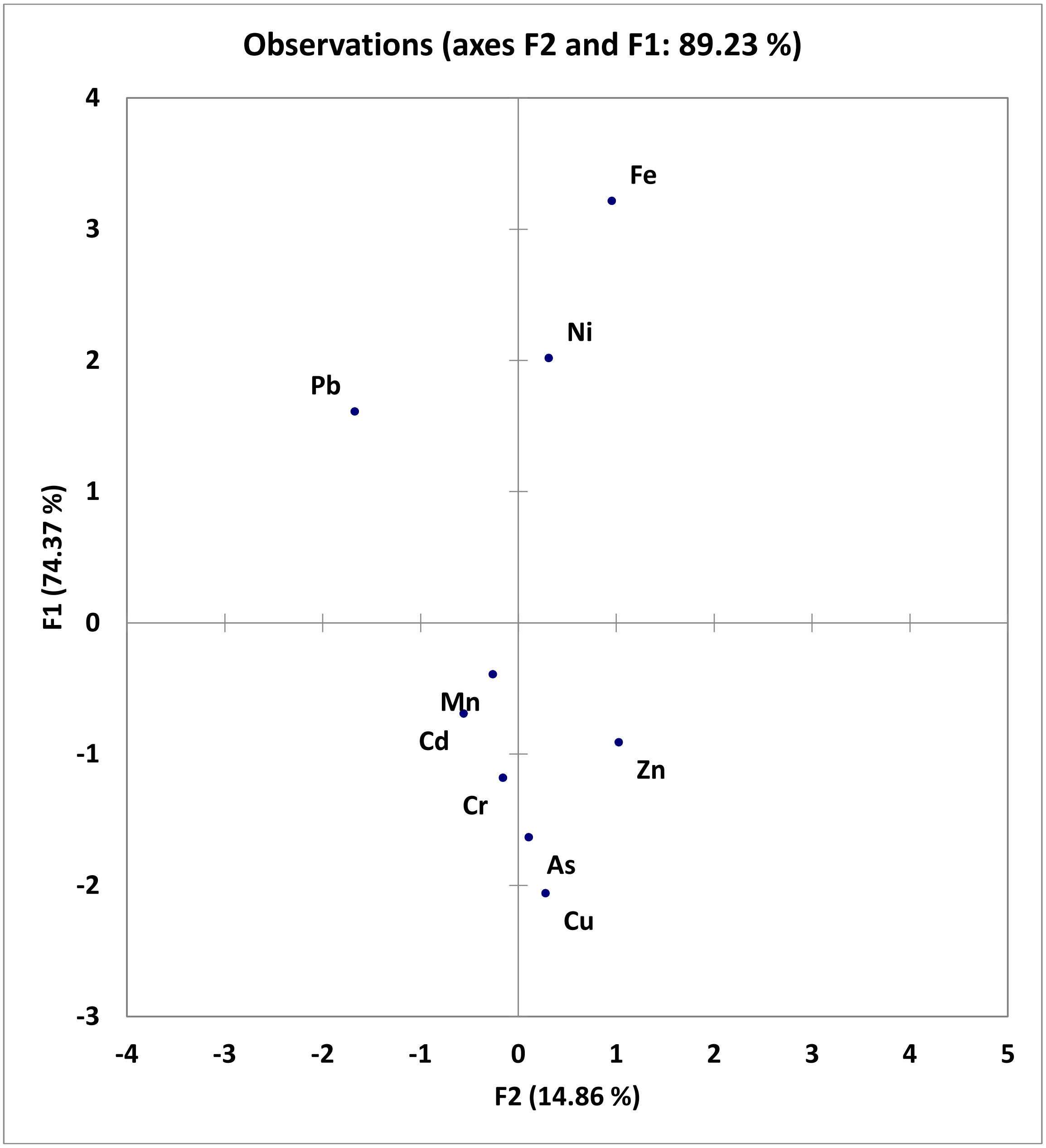

Figure 3.6: PCA plot for $PM_{2.5}$

Table 3.4b: Principal Component Analysis for TSP

Observation	Factor 1	Factor 2	Final communality
Ni	0.0217	0.2590	0.2807
Cu	-0.9994	-0.8722	-1.8716
Fe	4.5444	-0.6550	3.8894
Zn	-1.0256	0.0301	-0.9955
Mn	-0.1618	0.7742	0.6123
Pb	1.5284	0.6927	2.2212
Cr	-1.0301	-0.0228	-1.0529
Cd	-0.8624	0.6574	-0.2050
As	-2.0152	-0.8634	-2.8786

Factor 1 (PC1) explains (85.92%) of the total variance and it is loaded primarily by iron, lead and nickel. This is most likely from anthropogenic source as it is heavily loaded with iron and iron metals in the environment can be from vehicles since it is present in brake wear and from mechanical activities. Other anthropogenic activities includes automobile batteries, tyre wearing.

Factor 2 (PC2) explains (9.76%) of the total variance and loads primarily on manganese, cadmium, zinc, nickel and lead. This may be related to dust, vehicular activities.

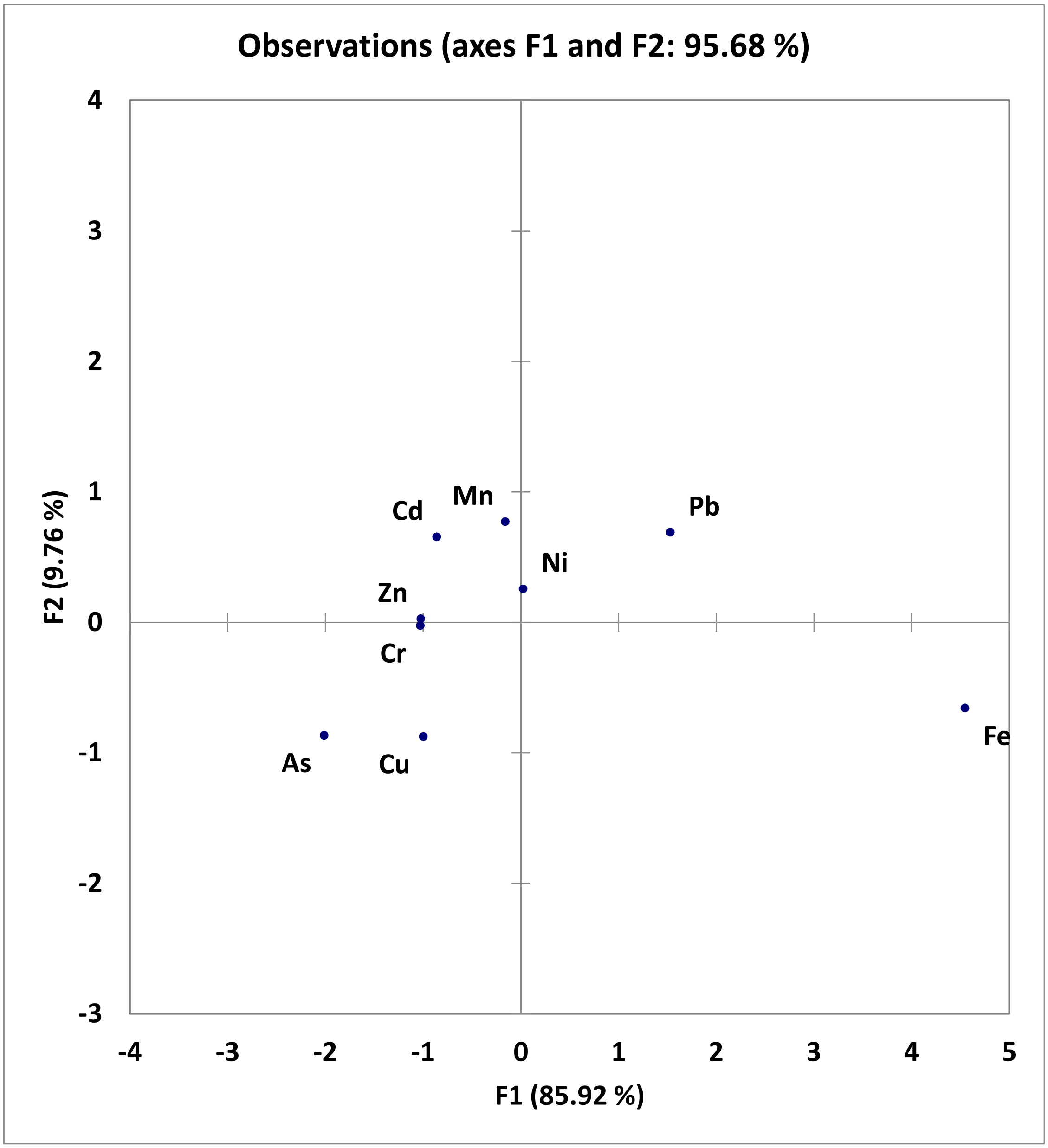

Figure3.7: PCA plot for TSP

3.4.2 CLUSTER ANALYSIS

A cluster analysis is an explanatory data analytical tool that yield groups of elements that have common sources controlling their concentration (Han *et al.,* 2001).

The heavy metal result from characterization of $PM_{2.5}$ and TSP were subjected to cluster analysis

Table 3.5a: Cluster analysis for $PM_{2.5}$

Class	**1**	**2**	**3**
Objects	2	6	1
Sum of weights	2	6	1
Within-class variance	0.2041	0.0930	0.0000
Minimum distance to centroid	0.3195	0.1577	0.0000
Average distance to centroid	0.3195	0.2666	0.0000
Maximum distance to centroid	0.3195	0.3771	0.0000
	Ni	Cu	Pb
	Fe	Zn	
		Mn	
		Cr	
		Cd	
		As	

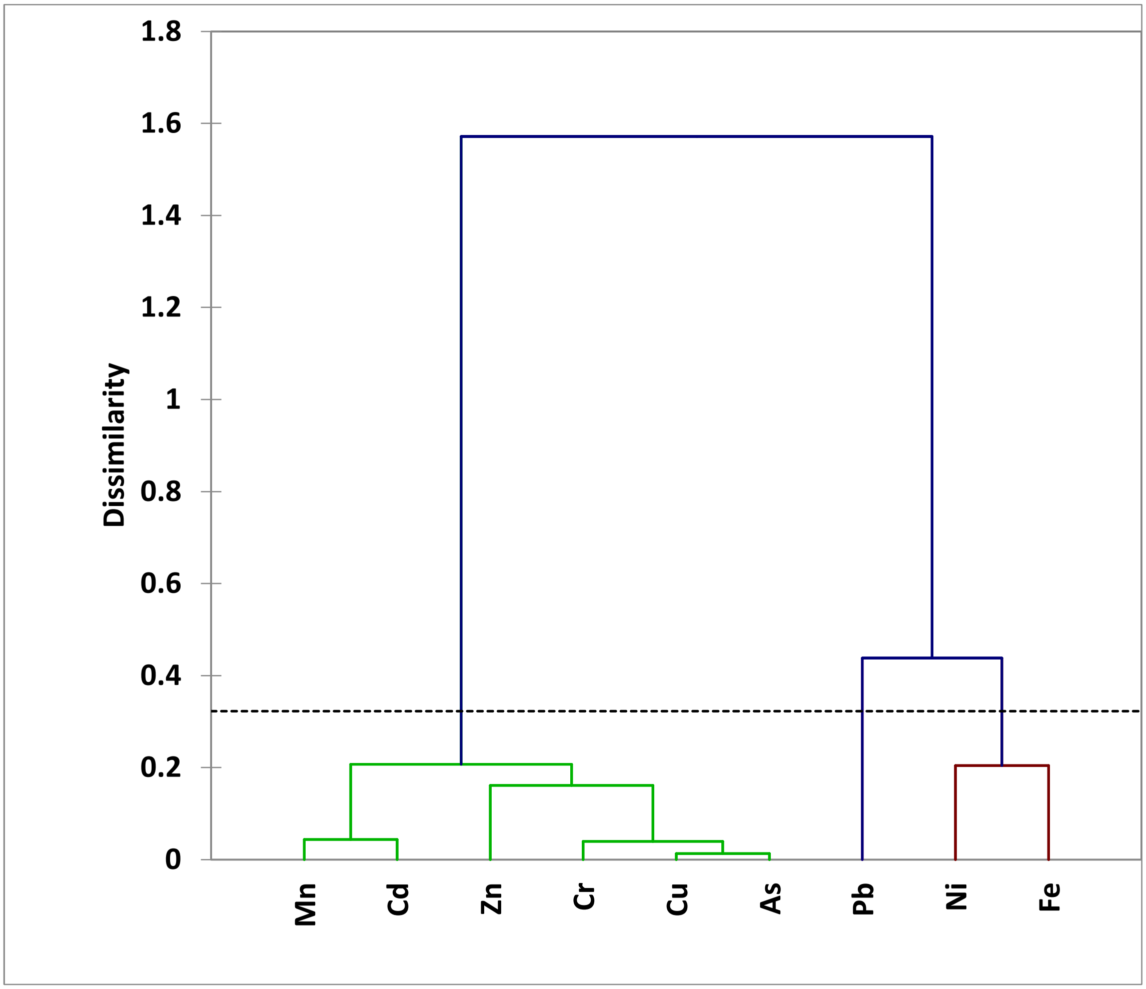

Figure 3.8: Dendogram of $PM_{2.5}$ samples

The result of $PM_{2.5}$ gave three clusters. Cluster 1 showed a significant clustering of nickel and iron. Cluster two showed significant clustering of manganese, cadmium, zinc, chromium, copper and arsenic. Cluster three showed clustering in lead. These metals are mainly from anthropogenic activities and may have been released into the environment from vehicles and mechanical activities.

Table 3.5b: Cluster analysis of TSP

Class	1	2	3	4
Objects	2	5	1	1
Sum of weights	2	5	1	1
Within-class variance	0.1198	0.2564	0.0000	0.0000
Minimum distance to centroid	0.2447	0.1734	0.0000	0.0000
Average distance to centroid	0.2447	0.4240	0.0000	0.0000
Maximum distance to centroid	0.2447	0.5805	0.0000	0.0000
	Ni	Cu	Fe	Pb
	Mn	Zn		
		Cr		
		Cd		
		As		

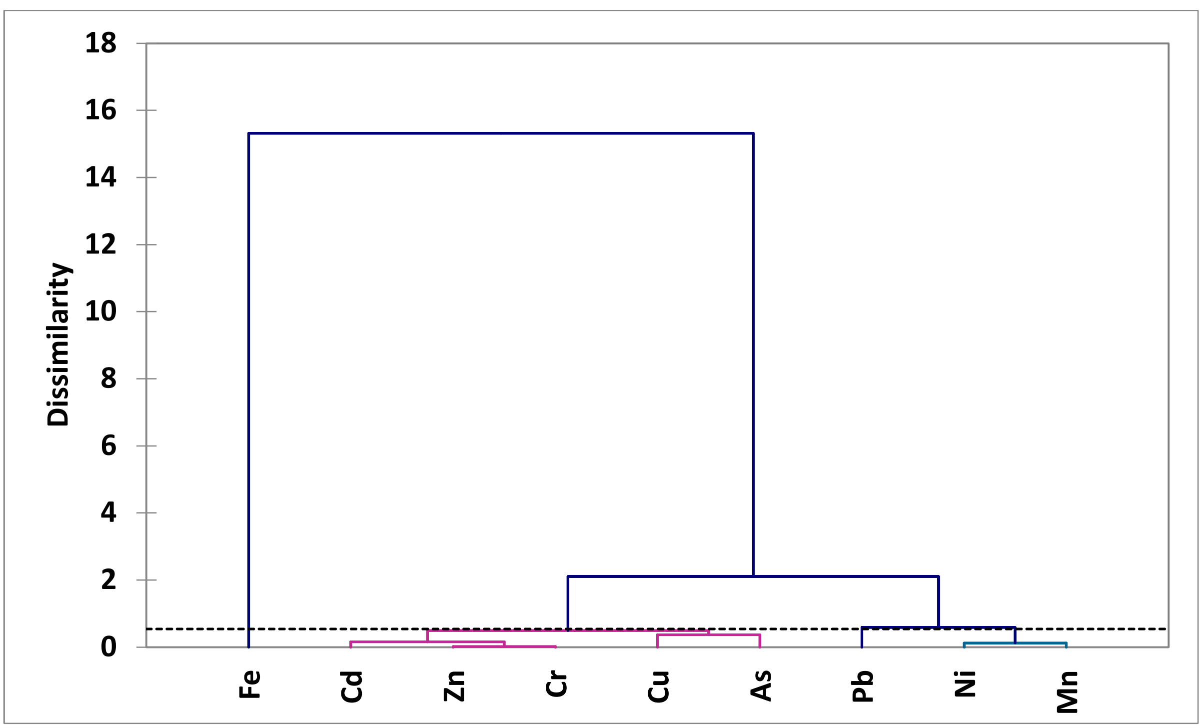

Figure 3.9: Dendogram of TSP samples.

For the TSP, the result of the cluster analysis gave four major clusters.

Cluster one showed significant clustering in nickel and manganese, these metals are mainly of anthropogenic source and may have been released into the environment through vehicular emissions.

Cluster two showed significant clustering in cadmium, zinc, chromium, copper and arsenic. These metals are mainly anthropogenic and may have been released into the atmosphere from vehicles or waste combustion.

Cluster three showed significant clustering of iron. This metal is of both natural and anthropogenic and may have been released into the environment naturally as it is abundant in the earth crust. While anthropogenically released into the environment from vehicles since it is present in brake wear particles and other activities like welding.

The cluster four showed a significant clustering in lead. The metal is mainly of anthropogenic source and may have been released into the environment through vehicular emissions.

3.4.3 CORRELATION MATRIX

Correlation coefficient is a measure of the linear correlation between the variables and given a value between two variables +1 and -1. Where 1 is the total positive correlation, 0 is no correlation and -1 is the total negative correlation. The closer a correlation goes to -1 or 1, the stronger the correlation. The closer a correlation coefficient gets to zero, the weaker the correlation is between the two variables. The correlation matrix is constructed based on the Pearson correlation coefficient obtained from a correlation analysis of related components. A positive correlation indicates that when one variable is increasing, the other variable is increasing while negative correlation indicates that both variables are decreasing.

A correlation analysis was performed between all variables to see if some of the metals are interrelated with each other, and to see if there is correlation between TSP, $PM_{2.5}$ and Meteorological Parameters.

Table 3.6: Correlation analysis for TSP, $PM_{2.5}$ and Meteorological Parameters

Correlation matrix (Pearson):

Variables	TSP (µg/m3)	$PM_{2.5}$ (µg/m^3)	Ultra-violet radiation (µW/m^2)	Pressure (mmHg)	Solar radiation (W/m^2)	Wind Direction (o)	Humidity (%)	Temperature (°C)	Wind Speed (km/h)
TSP (µg/m3)	**1.00**								
$PM_{2.5}$ (µg/m3)	**0.96**	**1.00**							
Ultra-violet radiation (µW/m^2)	0.63	0.45	**1.00**						
Pressure (mmHg)	-0.42	-0.18	**-0.95**	**1.00**					
Solar radiation (W/m^2)	0.32	0.15	**0.91**	**-0.90**	**1.00**				
Wind Direction (o)	0.12	0.18	0.25	-0.11	0.49	**1.00**			
Humidity (%)	-0.01	0.20	-0.76	**0.87**	**-0.92**	-0.36	**1.00**		
Temperature (°C)	0.39	0.21	**0.95**	**-0.95**	**0.99**	0.36	**-0.90**	**1.00**	
Wind Speed (km/h)	-0.46	-0.21	**-0.84**	**0.92**	-0.66	0.23	0.67	-0.76	**1.00**

Values in blue are different from 0 with a significance level alpha=0.05

Values in purple are different from 0 with a significance level alpha=0.1

Values in red are different from 0 with a significance level alpha=0.01

Table 3.6 above displays the Pearson Correlation Report, it was observed that there was strong positive correlation between TSP and $PM_{2.5}$, r=0.96 (p<0.01), correlation between solar radiation and temperature was found to be statistically significant, r=0.99, P<0.01. There was a negative correlation between ultra violet radiation and pressure at r=-0.95, P<0.05. The correlation between ultra-violet radiation and solar radiation was found to be statistically significant, r=0.91, P<0.05. Strong positive correlation exist between ultra-violet radiation and temperature, r=0.95, P<0.05. Negative correlation exist between ultra-violet radiation and wind speed, r=-0.84, P<0.1. Negative strong correlation exist between pressure and solar radiation, r=-0.90, P<0.05. Correlation exist between pressure and humidity at r=0.87, P<0.1, negative correction between pressure and temperature r=-0.95, P<0.05, correlation between pressure and wind speed was found to be statistically significant, r=0.92, P<0.05. Negative correlation exist between solar radiation and humidity at r=-0.92, P<0.05, strong positive correlation exist between solar radiation and temperature r=0.99, P<0.01 while strong negative correlation exist between humidity and temperature, at r=-0.99, P<0.0.

Other values in the table indicates no correlation at P<0.01, 0.05 and 0.1.

Table 3.7a: Correlation analysis for Heavy Metals in $PM_{2.5}$

Correlation matrix (Pearson):

Variables	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Ni	**1**								
Cu	0.699	**1**							
Fe	0.770	**0.973**	**1**						
Zn	0.219	0.671	0.686	**1**					
Mn	0.726	0.574	0.713	0.199	**1**				
Pb	0.078	0.006	0.089	-0.363	0.653	**1**			
Cr	**0.904**	0.402	0.521	-0.123	0.800	0.371	**1**		
Cd	**0.828**	0.357	0.502	-0.126	**0.884**	0.533	**0.976**	**1**	
As	**0.976**	0.685	0.789	0.234	**0.854**	0.246	**0.931**	**0.901**	**1**

Values in red are different from 0 with a significance level alpha=0.01
Values in blue are different from 0 with a significance level alpha=0.05
Values in purple are different from 0 with a significance level alpha=0.1

Table 3.7a above displays the Pearson Correlation Report between Heavy Metal in $PM_{2.5}$, correlation between nickel and Chromium was found to be statistically significant, r=0.904, P<0.01. There was correlation between nickel and cadmium, at r=0.828, P<0.1. Between nickel and arsenic there was strong positive correlation, r=0.976, P<0.01, and also between copper and iron, r=0.973, P<0.01. Correlation between manganese and cadmium was found to be statistically significant at r=0.884, P<0.05. Positive correlation was observed between manganese and arsenic at r=0.854, P<0.1. Strong positive correlation is revealed between chromium and cadmium, r=0.976, P<0.01. Correlation between chromium and arsenic was found to be statistically significant at r=0.931, P<0.05. Correlation exist between cadmium and arsenic at r=0.901, P<0.05.

The strong correlation between all these metals strongly suggest similar sources of emission in the sampling sites.

Positive correlation indicates that there is no significant influence of one metal on the other.

There was weak positive and negative correlation from the correlation table.

Table 3.7b: Correlation analysis **of Heavy Metals in TSP**

Correlation matrix (Pearson):

Variables	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Ni	**1**								
Cu	**0.869**	**1**							
Fe	0.303	0.405	**1**						
Zn	**0.871**	0.560	0.325	**1**					
Mn	**0.931**	0.739	0.505	**0.960**	**1**				
Pb	**0.935**	0.776	0.547	**0.872**	**0.947**	**1**			
Cr	**0.947**	0.724	0.450	**0.933**	**0.966**	**0.987**	**1**		
Cd	**0.960**	0.719	0.298	**0.973**	**0.973**	**0.920**	**0.964**	**1**	
As	**0.914**	**0.908**	0.646	0.765	**0.912**	**0.945**	**0.902**	**0.848**	**1**

Values in red are different from 0 with a significance level alpha=0.01

Values in blue are different from 0 with a significance level alpha=0.05

Values in purple are different from 0 with a significance level alpha=0.1

Table 3.7b above displays the Pearson Correlation Report between Heavy Metal in TSP, correlation between nickel and Copper was found to be statistically significant, r=0.869, P<0.1. There was correlation between nickel and zinc, at r=0.871, P<0.1. Between nickel and manganese there was positive correlation, r=0.931, P<0.05, correlation between nickel and lead was found to be statistically significant, r=0.935, P<0.05. There was correlation between nickel and chromium, at r=0.947, P<0.05. Between nickel and cadmium there was strong positive correlation, r=0.960, P<0.01, and also between nickel and arsenic there was correlation at r=0.914, P<0.05. Between copper and arsenic, there was positive correlation, at r=0.908, P<0.05. Correlation between zinc and manganese was found to be statistically significant at r=0.960, P<0.01. Positive correlation was observed between zinc and lead at r=0.872, P<0.1. Positive correlation exist between zinc and chromium at r=0.933, P<0.05. Strong positive correlation is revealed between zinc and cadmium, r=0.973, P<0.01. Correlation between manganese and lead was found to be statistically significant, r=0.947, P<0.05. There was strong positive correlation between manganese and chromium, at r=0.966, P<0.01. Between manganese and cadmium there was strong positive correlation, r=0.973, P<0.01, correlation between manganese and arsenic was found to be statistically significant, r=0.912, P<0.05. There was strong positive correlation between lead and chromium, at r=0.987, P<0.01. Between lead and cadmium there was positive correlation, r=0.920, P<0.05, and also between lead and arsenic there was correlation at r=0.945, P<0.05. Strong positive correlation exist between chromium and cadmium at r=0.964, P<0.01. Correlation between chromium and arsenic was found to be statistically significant at r=0.945, P<0.05. Correlation exist between cadmium and arsenic at r=0.848, P<0.1.

Positive correlation indicates that there is no significant influence of one metal on the other. The correlation between metals suggest vehicular source of emission type. Since the metals are mainly emitted either from diesel/gasoline, corrosion of car steel parts, welding/panel beating, wear/tear or automobile sources.

The negative correlation suggest that the changes in the level of these metals affects the concentration of the others in the same locations.

Other values in the table where positive or negative indicates no correlation at P<0.01, 0.05 and 0.1 that is there was a weak correlation among other variables.

CONCLUSION

The results obtained from this current study revealed that the ambient air in some selected auto-mechanic workshop around Uwelu motor spare parts market, Benin City were heavily polluted with $PM_{2.5}$ and TSP. The concentrations of the particulate matter were higher than the regulatory limit stated by the regulatory bodies, this can have deleterious effect on the environment and on human health. The $PM_{2.5}$ and TSP contains heavy metals of which some were of very low concentration which are not likely to pose threat to human health and environment, however some were of high concentrations higher than the safe limit which can pose threat to human health and the environment. The major source of this particulate and heavy metals were vehicular emissions, wear/tear of brake linings, automobile batteries, spilling of used oil/ lubricants.

Principal component analysis explained the sources contributing to $PM_{2.5}$ and TSP, such as vehicular emission and other emission source such as gasoline/diesel emission, brake emissions. Cluster analysis was able to obtain the various clustering in metals hence suggested their sources. Correlation matrix justified that some of the elements were strongly correlated while some were negatively correlated and others showed no correlation.

FINDINGS

The following findings were obtained from this studies;

- The levels of $PM_{2.5}$ in auto-mechanic workshop around Uwelu were higher and violates the regulatory limits.

- The levels of TSP in auto-mechanic workshop around Uwelu were higher than those of the regulatory limits.
- Some of the toxic heavy metals concentration (lead, cadmium) were higher than the regulatory limits stated by regulatory bodies.
- Vehicular emissions, brake emission, welding/panel beating activities were identified to be a contributing source of pollutant in the ambient air.

RECOMMENDATION

- Although the $PM_{2.5}$ and TSP concentration recorded in this study were high as well as few of the heavy metals constituent, however, it was observed that some of the heavy metals were very low in concentration and below the limits of the regulatory bodies. Therefore, there is need for further studies or research to be carried out to see what this high concentration of $PM_{2.5}$ and TSP is composed of, studies to be determined can be ionic and organic constituents of the $PM_{2.5}$ and TSP.
- Efforts should be made to reduce the levels of $PM_{2.5}$ and TSP around these mechanic workshops in other to protect the environment and human health at large.
- Long term studies should be carried out to determine the effects of $PM_{2.5}$ and TSP on public health.

CONTRIBUTION TO KNOWLEDGE

- This study provided base-line information of heavy metal concentration of $PM_{2.5}$ and total suspended particulate (TSP) in auto-mechanic workshops around Uwelu environs.
- The study also revealed the various possible sources of pollutant in the environment.

REFERENCES

Adeleken, B., & Abegunde, K. (2011). Heavy metal contamination of soil and ground water at auto mobile mechanic village in Ibadan, Nigeria. *International Journal of the Physical Sciences, 6*; 1045-1058.

Agyemang-Bonsu, K., Dontwi, I., Tutu-Benefoh, D., Bentil, D., Boateng, O., Asuobonteng, K., & Agyemang, W. (2010). Traffic-data driven modelling of vehicular emissions using COPERT III in Ghana: A case study of Kumasi. *American Journal of Scientific and Industrial Research,1*(1); 32-40.

Agency for Toxic Substances and Disease Registry (ATSDR) (2004). Toxicological profile for copper. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry (ATSDR) (2005a). Toxicological profile for zinc (Update). Atlanta, GA: U.S. Department of Public Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry (ATSDR) (2005b). Toxicological profile for nickel. Atlanta, GA: Agency for Toxic Substances and Disease Registry.

Agency for Toxic Substances and Disease Registry (ATSDR) (2007). Toxicological profile for Arsenic. (Update) Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry (ATSDR) (2012). Toxicological profile for Cadmium. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Al-Weher, M. (2008). Levels of heavy metals Cd, Cu and Zn in three Fish species collected from the Northern Jordan Valley. *Jordan Journal of Biological Sciences, 1*, 41-46.

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pay, J., Hokpe, P. (2009). Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF2. *Atmos Environ, 43*, 2770-2780. doi:10.1016/j.atmosenv.2009.02.039

Anderson, J., Thundiyil, J., & Stolbach, A. (2012). Cleaning the air: A review of the effects of particulate matter air pollution on human health. *Journal of Medical Toxicology, 8*, 166-175.

Aquino , N., Sevign, M., & Louie , M. (2012). The role of cadmium and nickel in estrogen receptor signaling and breast cancer: metalloestrogens or not ?. *Journal Environmental Science Health Enivronment Carcinogenic Ecotoxicology, 30*(3), 189-224.

Arhami, M., Minguillon, M., Polidori, A., Schaver, J., Delfino, R., & Sioutas, C. (2010). Organic compound characterization and source apportionment of indoor and out door quasi-ultrfine particulate matter in retirement homes of the Los Angeles Basin. *Indoor Air, 20*, 17-30.

Atser, J., Etim, N., Ofem, B., & Ekong, F. (2010). "An overview of the changing pattern of rainfall and its implications for environmental and Agricultural Development in AKS, Nigeria: A case study". *Journal of Agriculture and Social Science, 6*(3), pp65-72.

Awan, M., Ahmed, S., Aslam, M., & Qazi, I. (2011). Determination of total suspended particulate matter and heavy metals in ambient air of four cities in Pakistan. *Iranica Journal of Energy and Environment, 2*(2), 128-132.

Bell, M. (2012). *Assessment of the health impacts of particulate matter characteristics.* Health Effects Institute.

Bose, B., & Hemantaranjan, A. (2005). *Developments in Physiology, biochemistry and molecular biology of plants, New Delhi.* India New India Publishing Agency.

Brunekreef, B., & Forsberg, B. (2005). Epidemiological evidence of effects of coarse airborne particles on health. *Eur. Respir. J., 26*, 309-318.

Bytnerowicz, A., Omasa, K., & Paolletti, E. (2007). Intergrated effect of air pollution and climate change on forest: A northern hemisphere and perspective. *Environ. pollut., 147*, 438-445.

Calkins, M. (2009). *Materials for sustainable sites: A complete guide to evaluation.* New Jersery: John Wiley.

Challan, S., & Kumar, R. (2009). Nano structued oxides. *Weinheim, Germany Wiley*, 29.

Dunea, D., Iordache, S., Liu, H., Bohler, T., & Pohoata, A. (2016). Quantifying the impact of PM2.5 and associated heavy metals on respiratory health of children near mettallurgical facilities. *Environ. Sci. Pollut. Res., 23*, 15395-15406.

Duruibe, J., Ogwuebu, M., & Egwurugwuu, J. (2007). Heavy metal pollutions and human Biotoxic Effects. *Int. physical Sci., 2*(5), 112-118.

Ediabonya, T., Tobin, A., Olumayede, E., Okungbwa, G., & Iyekowa, O. (2016). The determination of Exposure to Total, Inhalable and Respirable Particle in Welders in Benin City, Edo State. *Journal of Pollution Effeccts and Control, 4*, 152.

Ediagbonya, T., Tobin, A., & Ukpebor, E. (2013). The level of suspended particulate matter (SPM) in wood industry (sawmills) in Benin city. *Nigerian Journal of Environment chemistry and Ecotoxicology, 5*(1), 1-6.

Efe, S.I (2008). Spatial distribution of particulate air pollution in Nigerian cities: implication for human health. *Journal Environmental Health Resources*, 7:2

Ekong, F., Michael, G., & Michael, U. (2012). Assessing the effects of mechanic activities on uyo air environment. *Ethiopian journal of environmental studies and management, 5*(1), 74-85.

Font, A., & Fuller , G. (2017). *Airbone Particles from wood burning in UK cities.* Kings college London: National physical laboratory.

Forster, P. V., Venkatachalam, R., Paulo, A., Terje, B., Richard, B., David, F. and James, H. (2007). "Contribution of working Group I to the Fourth Assessment Report of the intergovernmental Panel on Climate Change in Climate Change 2007: The Physical Science Basis". In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averty.

Frit, R., Vegas, G., & Perez, L. (2000). Important chemical properties of metals. *CRC Press Inc.*, 22-25.

Gietl, J., Lawerence, R., Thorpe, A., & Harrison, R. (2010). Identification of brake wear particles and derivation of a quantitative tracer for brake dust at major road. *Atmos Environ., 44*, 141-146. doi:10.1016/j.atmosenv.2009.10.106

Goyal, S., Ghatge, S., Nema, P., & Tamhane, S. (2006). Understanding Urban vehicular pollution problem vis-a-vis ambient air quality: case study of a mega city (Delhi India). *Environmental Monitoring and Assessment, 119*(1), 557-569.

Han, J., Kamber, M., & Tung , A. (2001). *"Spatial clustering methods in data mining a survey", in Geographic Data mining and knowledge Discovery* (Vol. 21). Boca Raton, Fla, USA: Taylor and Francis.

Hilgenkamp, K. (2006). *Environmental health: Ecological Perspective. .* Toronto Canada: Jones and Bartlett Publishers.

Hogan, C. (2010). Emily Monosson and Cleavage, C edition. "Abiotic factor". Encyclopedia of Earth. *National Council for Science and the Enviroment*.

Ikamaise , V., Akpan, I., Essiett, A., & Uwah, I. (2013). Concentrations and source apportionment of total suspended particulate in Calabar Air basin. *International Journal of Development and Sustainability, 2*(2), 1203-1213.

Ingrid P.S Araujo, Dayana B Costa, & Rita J.B deMoraes. (2014). Identification and Characterization of particulate matter concentration at construction Jobsites. *Sustainability, 6*, 7666-7688.

IPCC (2007). Four Assessment Report. Intergovernmental panel on climate change secretariat. Geneva, Switerland. http://www.ipcc.ch.

Ji, D., LI, L., Wang, Y., Zhang, J., Cheng, M., Sun, Y., Miao, H. (2014). The heaviest Particulate air-pollution episodes occured in northern China in January 2013: Insights gained from observation. *Atmos. Environ, 92*, 546-556.

Kim, K., Kabir, E., & Kabir, S. (2014). A review on the human health impact of Airborne Particulate Matter. *Environment International*, 136-143.

Kinney, P., Gichuru, M., Volavka-close, N., Ngo, N., Ndiba, P., Law, A., & Sclar, E. (2011). Traffic impacts on PM2.5 air quality in Nairobi, Kenya. *Environ. Sci, Policy, 14*(4), 369-378.

Kumar, S., & Kratoria, D. (2013). Air Pollution and its control measures. *International Journal of Environment Engineering and Management., 4*(5), 445-450.

Kura , B., Verma, S., Ajdari, E., & Iyer, A. (2013). Growing Public Health Concerns from poor urban Air Quality; Strategies for Sustainable urban living. *Computational water, Energy and Environment Engineering. , 2*, 1-9.

Leili, M., Naddafi, K., Nabizadeh, R., Yuneisan, M., & Mesdaghinia, A. (2008). The study of TSP and PM_{10} Concentration and their heavy metal content in central area of Tehran Iran. . *Air Quality Atmospheric Health, 1*, 159-166.

Lennutech. (2004). *Water treatment and Air purification.* Netherlands.: Lennutech Rotterdamsereg. Retrieved from (www.excewater.com/hhp/fihers/waterpurificationhtm)

Miculescu, F., Misculescu, M., Ciocan, L., Ernuteanu, A., Antoniac, I., Pencea, I., & Matei, E. (2011). Comparative studies regarding heavy elements concentration in human cortical bone. *Digest Journal of Nanomaterial and Biostructures, 6*, 1117-1127.

Misra , S., & Mani, D. (2009). Soil pollution New Delhi, India. New Delhi: S.B Nangia Apit publishing corporation.

Moosmuller, H., Chakrabarty, R., & Arnott, W. (2009). Aerosol light absorption and its measurement: A review. *J. Quant. Spectrosc. Radiat., 110*, 844-878.

Nerquaye-Tetteh, E. (2009). Urban Air Quality Monitoring Programme in Accra Environmental Protection Agency, Accra Ghana. *Available: http//www.unep.org/urban environment/PDFs/BAQ09 ghanacasestudy.pdf (Accessed 30th september,2019)*.

Okokon, E., Taimisto, P., Turunen , A., Amoda, O., Fassasi, A., Adeyemi, L., Lanki, T. (2018). Particulate air pollution and noise: Assessing commuter exposure in Africas most populous city. *Journal of Transport and Health., 9*, 150-160. doi:doi.org/10.1016/j.jth.2018.04.003

Okuo, J, Chiedu, I., Anegbe, B., Oyibo, F., & Ojo, W. (2017). Elemental characterization and source identification of fine particulate matter (PM2.5) in an idustrial area of lagos state, Nigeria. *Physical Science International Journal, 2*(2348-0130), 1-11.

Okuo, J., & Okolo, P. (2011). Levels of As, Pb, Cd and Fe in suspended particulate matter (SPM) in ambient air of artisan workshopd in Benin City, Nigeria. *Bayero Journal of pure and applied sciences, 4*(2), 97-99.

Olayinka , O., Adedeyi, O., & Ajibola, F. (2015). Monitoring Gaseous and particulate Air Pollutants near major Highways in Abeokuta. *Nigeria Journal of Applied Sci. Env. manag., 19*(4), 751-758.

Petrovic, M., Kastelan, M., & Horvat, J. (1999). Interactive Sorption of metal ions and humic acids into mineral particles. . *water, Air, Soil pollut., 111*, 41-56.

Phalen, R., & Phalen, R. (2013). *Introduction to Air Pollution Science. A Public Health Perspective* (1st ed.). Jones and Bartlett learning .

Pope, C., & Dockery, D. (2006). Health effects of fine particulates air pollution: lines that connect. critical review. *Journal of Air and Waste Management Association, 56*, 709-742.

Prashant , G., Sengupta, B., & Bowas, D. (2015). Strategies for prevention and control of Air pollution in India. Retrieved october 20, 2019, from http://www.researchgate.net/publication/236179607

Radojevic, M., & Bashkin, V. (2007). *Practical environment chemistry.* London, UK: The Royal Society of Chemistry.

Razos, P., & Christides, A. (2010). An Investigation of Heavy metals in an Industrial Area in Greece. *Internation Journal of Environment Reseacrh , 4*(4), 785-794.

Rogers, D., Sam , G., & Matt, K. (2009). Is soil an appropriate dumping ground for our waste. *Australian Journal of Soil Research*, 35-37.

Safo-Adu, G., Ofosu, F., Carboo, D., & Armah, Y. (2014). Heavy metals and black carbon assessment of PM10 Particulate along Accra-Tema Highway in Ghana. *International Journal of Science and Technology., 3*(NO.8), 467-474.

Sax , N. (2001). Industrial pollution. *Van Nost and Reinhold Ltd, 4th ed*.

Simeonov, L., Kolhubovski, M., & Simeonov, B. (2010). Environmental heavy metal pollution and effects on child mental development. *Dordrecht Netherlands: Springer* , 114-115.

Sioutas, C., Delfino, R., & Singh, M. (2015). Exposure assessment for atmospheric ultrafine particles (UFP) and Implications in epidemiologic research. *Environ. Health Perspect., 113*, 947-955.

Stanek, L., Brown, J., Stanek, J., Gift, J., & Costa, D. (2011). Air pollution toxicology- a brief rewiew of the role of Science in Shaping the current understanding of air pollution health risk. *Toxicology Sciences., 120*(S1), S8-S27.

Taiwo, A., Arowolo, T., Abdullahi, K., & Taiwo, O. (2015). Particulate matter pollution in Nigeria: A review. *Proceeding of the 14th International Conference on Environmental Science and Technology.* Rhodes, Greece.

Talebi, S., & Tavakoli-Ghinani, T. (2008). Levels of PM10 and its chemical composition in the Atmosphere of the city of Istahan. *Iranian Journal of Chemical Engineering, 5*(No.3), 62-67.

Tong, S., Schirnding, Y., & Prapamontol, T. (2000). Environmental lead exposure: a public health problem of global dimensions. *Bulletin of the world Health organization, 78*(9), 1068-1077.

Ukpebor , E., Ukepbor , J., Oviasogie, P., Odiase, J., & Egbeme, M. (2006). Field Comparison of two total suspended particulates (TSP) samplers to assess spatial variation. *International Journal of Environmental studies*.

Ukpebor, J., Ukpebor, E., Kadiri, V., Odiase, J., Okuo, J., & Ogbeifun , D. (2012). Atmospheric Trace metal concentration in suspended particulate matter(SPM) of rural Residential Area in Southern Nigeria Ife . *Journal of Science., 14*(1).

UNEP, U.N. (2013). Urban Air Pollution. *Available: http://www.uncep.org/urban_environment/issues/urban_air.asp (Accessed 29th september 2019)*.

Vincent, E. (2014). Atomospheric concentration of particulate pollutants and its implications for respiratory health hazard management in Port Harcourt Metropolis, Nigeria. *Civil and Environmental Research, 6*(5), 11.

Voet, E., Guinee, B., & Udode, H. (2018). Heavy metals: A problem solved? Dordrecht, Netherlands: Kluwer Academic.

Wieczorek, J., Wieczorek, T., & Bieniaszewski, T. (2004). Cd and Lead in cereal grains and soil from from cropland adjacent to roadways. *Polish Journal of Environment studies, 14*, 535-540.

WHO (2000). Air Quality Guidelines for Europe. WHO Regional publications. European series. No 91, World Health Organization, Copenhagen, Denmark.

World Health organisation (WHO). (2006). Air quality guideline for particulate matter, ozone, nitrogen dioxide and sulphur dioxide. Global update 2005 Summary of risk Assessment. Available at http://www.apps.who.int/iris/handle/10665/69477

World Health Organisation (WHO). (2013). Health effects of particulate matter. Retrieved from http://www.euro.who.int/__data/assets/pdf_file/0006/189051/Health-effects-ofparticulate matter-final-Eng.pdf

World Health Organisation (WHO). (2013). Health topics-Air pollution. Available:http//www.who.int/topics/air_pollution/en/

Yang, J., Kim, J., Jang, J., Lee, G., Kim, S., Shin, D., & Lim, Y. (2013). Exposure and Toxicity Assessment of ultrafine particles from Nearby traffic in urban Air in Seoul, Korea. *Environmental Health and Toxicology, 28*, 1-9.

Yu-Cheng Chen, Chin-Yu Hsu, Sheng-Lun Lin, Guo-Ping Chang-Chien, Mu-Jean Chen, Guor-Cheng Fang, & Hung-Che Chiang. (2015). Characteristics of concentrations and Metals Composition for PM2.5 and PM2.5-10 in Yunlin County, Taiwan during Air Quality Deterioration. *Aerosol and Air Quality Research, 15*, 2571-2583.

Zhou, Z., Dionisio, K., Verissimo, T., Kerr, A., Coul, I., Arku, R., . . . Ezzati, M. (2013). Chemical composition and sources of particle pollution in affluent and poor neighbourhoods of Accra, Ghana. *Environmental Research Letters, 8*, 1-9.

APPENDICES

Appendix I: TSP and $PM_{2.5}$ Concentration (µg/M3) In the Different Sampling Locations For February and March

Weeks	Locations	TSP	PM.2.5
Week 1	1	17202.38	7440.47
Week 2	2	15892.85	6845.23
Week 3	3	17321.48	8630.95
Week 4	4	15416.66	6488.09
February		**16458.34 ± 822.11**	**7351.185 ± 813.43**
Week 1	5	14404.76	5357.14
Week 2	6	14880.95	5238.09
Week 3	7	14166.67	4464.29
Week 4	8	13988.09	4821.43
March		**14360.11 ± 386.90**	**4970.23 ± 408.07**

Appendix II: TSP and $PM_{2.5}$ Concentration (µg/M3) In the Different Sampling Locations for April

Samples	TSP	PM.2.5
Week 1	13630.95	4702.38
Week 2	13095.24	3273.8
Week 3	13750	3630.95
Week 4	13690.47	3690.47
April	**13541.66 ± 301.55**	**3824.4 ± 613.56**

Appendix III: TSP and $PM_{2.5}$ concentration (µg/m3) in the different sampling locations for May and June

Samples		TSP	PM.2.5
Week 1	1	12440.47	3571.42
Week 2	2	11964.28	3035.71
Week 3	3	13392.85	3035.71
Week 4	4	12619.05	2916.67
May		**12604.16 ± 593.99**	**3139.87 ± 293.11**
Week 1	5	11964.25	2976.19
Week 2	6	11011.9	2678.57
Week 3	7	10357.14	2440.47
Week 4	8	9702.38	2321.43
June		**10758.91 ± 965.14**	**2604.16 ± 289.06**

Appendix IV: Concentrations of the heavy metals in PM2.5 (µg/m3) in February and March

Weeks	Locations	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week 1	1	0.45	0.09	0.54	0.19	0.35	0.59	0.12	0.2	0.08
Week 2	2	0.07	0.03	0.58	0.12	0.62	2.07	0.41	0.62	ND
Week 3	3	ND	ND	1.02	0.11	0.35	0.96	0.08	0.29	0.19
Week 4	4	0.82	0.12	Nd	ND	0.45	0.72	0.12	0.47	0.08
February		**0.45**	**0.08**	**0.71**	**0.14**	**0.44**	**1.08**	**0.18**	**0.34**	**0.12**
Week 1	5	0.67	0.22	0.41	0.31	0.37	0.36	0.22	0.36	0.31
Week 2	6	0.37	ND	2.04	0.33	ND	0.99	0.42	0.61	0.12
Week 3	7	0.75	0.05	0.71	0.25	0.45	0.44	0.25	0.81	0.31
Week 4	8	1.46	0.04	0.54	0.37	0.64	0.47	0.62	0.65	nd
March		**0.81**	**0.10**	**0.92**	**0.32**	**0.49**	**0.57**	**0.38**	**0.61**	**0.25**

APPENDIX V: Concentration of heavy metal in PM2.5 (µg/m3) in April

Weeks	**Locations**	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week 1	9	0.79	0.19	1.65	0.12	0.46	0.31	0.32	0.42	0.23
Week 2	10	0.25	0.54	0.94	0.41	0.32	1.09	0.51	0.54	ND
Week 3	11	1.42	0.08	2.03	0.31	ND	0.96	0.12	0.94	0.41
Week 4	12	1.64	0.03	0.61	0.09	0.95	0.75	0.96	1.03	0.32
APRIL		**1.03**	**0.21**	**1.31**	**0.23**	**0.58**	**0.78**	**0.48**	**0.73**	**0.32**

Appendix VI: Concentrations of the heavy metals in PM2.5 (µg/m3) in May and June

Weeks	Locations	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week1	13	0.31	0.21	0.56	0.19	ND	0.62	0.06	ND	0.19
Week2	14	0.49	0.25	2.42	1.54	0.37	0.25	0.06	ND	ND
Week3	15	0.43	0.06	0.99	0.19	0.19	0.31	0.12	0.06	0.12
Week4	16	1.17	0.25	0.76	0.49	0.37	0.19	0.12	ND	ND
May		**0.61**	**0.19**	**1.18**	**0.60**	**0.31**	**0.34**	**0.09**	**0.06**	**0.15**
Week1	17	ND	Nd	ND	ND	ND	0.11	ND	ND	nd
Week2	18	0.37	ND	0.45	ND	ND	0.84	ND	0.05	0.06
Week3	19	ND	Nd	0.43	ND	0.08	0.27	0.12	0.07	nd
Week4	20	0.56	0.04	0.32	0.05	ND	0.09	ND	ND	0.08
June		**0.47**	**0.04**	**0.41**	**0.05**	**0.08**	**0.33**	**0.12**	**0.06**	**0.07**

Appendix VII: Concentrations of the heavy metals in TSP (µg/m3) in February and March

Weeks	Locations	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week 1	1	0.95	0.51	1.56	0.71	1.93	1.57	1.67	1.15	0.11
Week 2	2	0.74	0.35	2.98	0.43	1.25	0.98	0.89	1.33	0.21
Week 3	3	1.11	ND	2.03	1.66	1.44	2.99	0.13	1.40	0.31
Week 4	4	1.98	0.51	0.82	ND	0.97	1.39	0.86	0.91	0.59
February		**1.20**	**0.46**	**1.85**	**0.93**	**1.40**	**1.73**	**0.89**	**1.20**	**0.31**
Week 1	5	1.31	0.52	4.27	0.81	2.29	2.45	1.03	0.78	0.45
Week 2	6	1.42	ND	3.34	0.60	1.81	1.95	0.65	1.21	0.25
Week 3	7	1.33	2.15	3.89	0.71	1.17	2.13	0.66	1.19	0.79
Week 4	8	1.55	1.34	1.22	0.73	0.36	0.88	0.90	0.97	0.67
March		**1.40**	**1.34**	**3.18**	**0.71**	**1.41**	**1.85**	**0.81**	**1.04**	**0.54**

Appendix VIII: Concentrations of the heavy metals in TSP (µg/m3) in April

Weeks	Locations	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week 1	9	0.97	0.67	5.87	0.56	1.98	4.98	0.67	1.64	0.53
Week 2	10	1.64	0.78	2.65	1.86	1.75	2.09	2.86	0.99	0.34
Week 3	11	1.89	1.98	4.76	0.63	2.56	3.16	0.74	1.34	0.95
Week 4	12	1.98	ND	3.87	0.67	0.98	0.87	1.08	1.45	0.79
April		**1.62**	**1.14**	**4.29**	**0.93**	**1.82**	**2.78**	**1.29**	**1.36**	**0.65**

Appendix IX: Concentrations of the heavy metals in TSP (µg/m3) in May and June

Weeks	Locations	Ni	Cu	Fe	Zn	Mn	Pb	Cr	Cd	As
Week 1	1	0.62	nd	5.65	0.31	0.43	0.35	0.45	0.09	0.31
Week 2	2	0.45	0.06	4.78	nd	nd	1.85	0.23	0.11	0.07
Week 3	3	0.05	0.19	2.90	0.37	0.62	0.55	0.19	0.19	nd
Week 4	4	0.03	nd	1.59	0.56	0.56	0.93	0.33	0.12	nd
May		**0.29**	**0.13**	**3.73**	**0.41**	**0.54**	**0.92**	**0.30**	**0.13**	**0.19**
Week 1	5	0.79	ND	2.89	ND	ND	1.05	ND	0.09	nd
Week 2	6	0.45	0.31	0.68	0.42	0.27	nd	0.51	0.12	0.12
Week 3	7	0.73	0.76	1.05	ND	0.12	1.45	0.27	0.21	0.15
Week 4	8	0.25	0.11	0.85	0.15	ND	0.12	0.11	ND	0.12
June		**0.56**	**0.39**	**1.37**	**0.28**	**0.19**	**0.87**	**0.29**	**0.14**	**0.13**

METEOROLOGY PARAMETERS

Appendix X: FEBRUARY (Location 1)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	26.45	89.00	750.80	2.10	130.00	280.48	286.00
10am	27.51	87.00	750.70	5.20	195.00	375.03	571.00
11am	28.35	85.00	750.50	8.40	276.00	485.65	1,002.00
12am	32.15	68.00	749.50	6.50	30.00	575.85	1,258.00
1pm	32.61	67.00	750.80	5.50	250.00	565.25	1,152.00
2pm	31.52	72.00	750.10	5.40	277.00	455.15	985.00
3pm	31.24	75.00	750.10	10.30	301.00	301.45	1,025.00
4pm	30.01	77.00	750.20	4.80	267.00	200.78	625.00
Min	**26.45**	**67.00**	**749.50**	**2.10**	**30.00**	**200.78**	**286.00**
Max	**32.61**	**89.00**	**750.80**	**10.30**	**301.00**	**575.85**	**1,285.00**
Mean	**29.98**	**77.50**	**750.83**	**6.02**	**215.75**	**404.95**	**863.00**

Appendix XI: FEBRUARY (Location 2)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.15	88.00	750.80	9.20	140.00	380.24	295.00
10am	28.21	86.00	750.60	6.10	190.00	475.08	611.00
11am	29.52	79.00	750.30	7.20	286.00	685.65	1,102.00
12am	32.25	65.00	748.50	6.50	235.00	975.85	1,458.00
1pm	32.65	64.00	748.10	5.50	90.00	865.20	1,252.00
2pm	31.61	69.00	749.50	7.50	77.00	450.25	985.00
3pm	31.52	71.00	750.10	6.30	130.00	351.15	1,005.00
4pm	30.21	76.00	750.20	4.90	260.00	250.28	655.00
Min	**27.15**	**64.00**	**748.10**	**4.90**	**77.00**	**250.28**	**295.00**
Max	**32.65**	**88.00**	**750.80**	**9.20**	**286.00**	**975.85**	**1,458.00**
Mean	**30.39**	**74.75**	**749.76**	**6.65**	**176.00**	**554.21**	**920.37**

Appendix XI: FEBRUARY (Location 3)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.45	87.00	749.70	5.10	302.00	280.82	333.00
10am	28.51	85.00	749.60	5.60	158.00	385.03	672.00
11am	29.35	84.00	749.50	5.70	268.00	485.50	1,102.00
12am	33.15	65.00	747.80	8.50	205.00	1,575.15	1,458.00
1pm	33.61	66.00	748.40	6.10	202.00	1,665.25	1,542.00
2pm	32.52	71.00	748.80	4.40	111.00	551.58	1,085.00
3pm	30.24	75.00	749.10	5.30	95.00	371.45	1,125.00
4pm	30.01	76.00	749.20	4.90	260.00	310.78	725.00
Min	**27.45**	**65.00**	**474.80**	**4.40**	**95.00**	**280.82**	**333.00**
Max	**33.61**	**87.00**	**479.70**	**8.50**	**302.00**	**1,665.25**	**1,542.00**
Mean	**30.61**	**76.13**	**749.01**	**5.70**	**200.13**	**703.20**	**1,005.25**

Appendix XII: FEBRUARY (Location 4)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	28.10	86.00	750.50	5.20	145.00	390.25	375.00
10am	29.20	83.00	750.20	4.20	195.00	485.08	681.00
11am	30.20	75.00	750.90	3.20	186.00	695.55	1,202.00
12am	33.00	62.00	748.10	5.50	205.00	1,075.85	1,498.00
1pm	33.40	54.00	747.80	5.70	190.00	1,165.20	1,352.00
2pm	32.40	69.00	748.50	6.20	97.00	850.25	1,085.00
3pm	31.70	71.00	750.10	5.80	120.00	551.15	955.00
4pm	30.40	76.00	750.70	9.50	265.00	350.28	755.00
Min	**28.10**	**54.00**	**747.80**	**3.20**	**97.00**	**350.28**	**375.00**
Max	**33.40**	**86.00**	**750.90**	**9.50**	**265.00**	**1,165.20**	**1,498.00**
Mean	**31.05**	**72.00**	**749.60**	**5.66**	**175.38**	**695.45**	**987.88**

Appendix XIII: MARCH (Location 5)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	26.90	89.00	750.50	4.20	230.00	270.50	296.00
10am	27.80	86.00	750.30	5.20	190.00	395.05	591.00
11am	29.45	83.00	750.00	4.40	76.00	505.95	1,102.00
12am	33.20	60.00	747.80	7.50	30.00	775.85	1,258.00
1pm	33.60	56.00	747.10	6.50	250.00	665.55	1,350.00
2pm	32.50	68.00	748.20	5.40	117.00	555.25	1,005.00
3pm	31.90	72.00	748.50	5.80	305.00	351.45	1,025.00
4pm	30.80	76.00	749.20	4.80	265.00	220.28	645.00
Min	**26.90**	**60.00**	**747.10**	**4.20**	**30.00**	**220.28**	**296.00**
Max	**33.60**	**89.00**	**750.50**	**7.50**	**305.00**	**775.85**	**1,350.00**
Mean	**30.81**	**73.75**	**748.95**	**5.48**	**182.88**	**467.49**	**909.00**

Appendix XIV: MARCH (Location 6)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.20	89.00	750.90	5.00	148.00	350.25	285.00
10am	28.90	85.00	750.40	5.50	180.00	505.28	621.00
11am	30.40	77.00	749.80	7.00	280.00	785.60	1,201.00
12am	32.90	64.00	748.10	6.50	230.00	1,075.15	1,508.00
1pm	33.70	62.00	748.10	5.50	190.00	965.20	1,362.00
2pm	33.90	63.00	748.30	6.50	77.00	650.25	1,385.00
3pm	32.50	70.00	748.20	5.50	130.00	351.15	1,105.00
4pm	31.20	74.00	749.20	4.90	260.00	250.28	755.00
Min	**26.20**	**64.00**	**748.10**	**4.90**	**77.00**	**250.28**	**285.00**
Max	**33.90**	**89.00**	**750.90**	**7.00**	**280.00**	**1,075.15**	**1,385.00**
Mean	**31.24**	**73.00**	**749.13**	**5.80**	**186.88**	**616.65**	**1,027.75**

Appendix XV: MARCH (Location 7)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	28.30	85.00	749.90	2.50	225.00	300.12	433.00
10am	28.90	84.00	748.40	4.60	50.00	405.05	702.00
11am	30.40	80.00	748.50	5.70	268.00	485.50	1,102.00
12am	34.10	63.00	747.00	3.50	185.00	1,875.25	1,868.00
1pm	33.90	61.00	748.60	9.60	215.00	1,665.20	1,542.00
2pm	32.80	70.00	748.10	4.40	15.00	591.65	1,385.00
3pm	31.10	75.00	748.10	5.50	195.00	471.15	1,325.00
4pm	30.20	74.00	748.20	5.90	265.00	410.78	775.00
Min	**28.30**	**61.00**	**747.00**	**2.50**	**15.00**	**300.12**	**433.00**
Max	**34.10**	**85.00**	**749.90**	**9.60**	**268.00**	**1,665.20**	**1,868.00**
Mean	**31.21**	**74.00**	**748.35**	**5.21**	**177.25**	**775.59**	**1,141.50**

Appendix XVI: MARCH (Location 7)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	28.30	81.00	750.10	6.20	95.00	395.15	385.00
10am	28.90	83.00	749.20	4.50	295.00	515.01	701.00
11am	30.80	73.00	749.00	3.20	186.00	695.55	1,202.00
12am	33.70	61.00	747.70	5.80	105.00	1,175.85	1,518.00
1pm	33.80	56.00	747.50	5.90	110.00	1,265.20	1,652.00
2pm	32.80	68.00	748.30	6.50	205.00	880.15	1,185.00
3pm	32.00	70.00	749.10	6.80	320.00	751.25	1,055.00
4pm	30.80	75.00	749.70	5.20	225.00	450.28	795.00
Min	**28.30**	**56.00**	**747.50**	**3.20**	**95.00**	**395.15**	**385.00**
Max	**33.80**	**81.00**	**750.10**	**6.80**	**320.00**	**1,265.20**	**1,652.00**
Mean	**31.42**	**70.88**	**748.83**	**5.51**	**192.63**	**766.06**	**1,061.63**

Appendix XVII: MARCH

LOCATION 8							
Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	28.30	81.00	750.10	6.20	95.00	395.15	385.00
10am	28.90	83.00	749.20	4.50	295.00	515.01	701.00
11am	30.80	73.00	749.00	3.20	186.00	695.55	1,202.00
12am	33.70	61.00	747.70	5.80	105.00	1,175.85	1,518.00
1pm	33.80	56.00	747.50	5.90	110.00	1,265.20	1,652.00
2pm	32.80	68.00	748.30	6.50	205.00	880.15	1,185.00
3pm	32.00	70.00	749.10	6.80	320.00	751.25	1,055.00
4pm	30.80	75.00	749.70	5.20	225.00	450.28	795.00
Min	**28.30**	**56.00**	**747.50**	**3.20**	**95.00**	**395.15**	**385.00**
Max	**33.80**	**81.00**	**750.10**	**6.80**	**320.00**	**1,265.20**	**1,652.00**
Mean	**31.42**	**70.88**	**748.83**	**5.51**	**192.63**	**766.06**	**1,061.63**

Appendix XVIII: APRIL

Location9

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.85	85	749.5	5.2	330	290.81	316
10am	28.7	83	749.5	5.8	195	415.05	611
11am	30.15	81	748	4.5	176	605.95	1202
12am	34.15	56	747.1	7.2	130	995.95	1758
1pm	33.65	58	747.2	9.8	55	865.55	1350
2pm	33.52	64	747.2	5.9	205	755.25	1105
3pm	32.95	70	748.1	6.8	105	551.45	1125
4pm	31.85	74	748.8	4.1	205	210.28	675
Min	**27.85**	**56**	**747.1**	**4.1**	**55**	**210.28**	**316**
Max	**34.15**	**85**	**749.5**	**9.8**	**330**	**995.95**	**1758**
Mean	**31.60875**	**71.375**	**748.175**	**6.1625**	**175.125**	**586.2863**	**1017.75**

Appendix XIX: APRIL

location 10

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.9	86	749.1	2.2	95	390.15	380
10am	28.9	81	749.1	5.7	190	595.25	721
11am	31.8	75	748.3	7	180	885.65	1301
12am	33.8	56	747.5	6.1	130	1375.15	1628
1pm	34.7	52	747.1	5.5	290	1565.2	1762
2pm	33.9	61	747.4	4.5	277	750.25	1525
3pm	33.5	65	748.2	6.5	35	451.25	1205
4pm	32.2	72	748.3	4	160	350.25	855
Min	**26.9**	**52**	**747.1**	**2.2**	**95**	**350.25**	**380**
Max	**34.7**	**86**	**749.1**	**7**	**190**	**1565.2**	**1762**
Mean	**32.00375**	**67.875**	**748.125**	**5.1875**	**181.5**	**795.3938**	**1172.125**

Appendix XX: **APRIL**

LOCATION 11

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.9	80	749.1	4	280	380.62	595
10am	29.6	79	748.1	5.9	250	655.16	795
11am	32.9	72	747.9	6.1	268	515.15	1208
12am	35.5	51	746.5	3.5	185	1885.55	1668
1pm	34.9	52	747.6	5.1	215	1795.12	1649
2pm	32.6	69	748.1	4.7	215	541.95	1485
3pm	31.5	73	748.6	5.7	295	479.25	1385
4pm	31.2	74	748.9	4.9	65	440.56	795
Min	**27.9**	**51**	**746.5**	**3.5**	**65**	**380.62**	**595**
Max	**35.5**	**80**	**749.1**	**6.1**	**280**	**1885.55**	**1668**
Mean	**32.0125**	**69.125**	**748.1**	**4.9875**	**221.625**	**836.67**	**1197.5**

Appendix XXI: APRIL

LOCATION 12

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (μW/m2)
9am	28.9	79	749	6.8	195	405.55	397
10am	29.4	76	748.5	5.5	25	715.21	791
11am	31.9	72	748	1.2	286	605.55	1302
12am	34.1	60	747.3	5.8	125	1575.15	1628
1pm	34.8	56	747.1	5.2	210	1765.2	1872
2pm	33.9	61	748.3	6.5	205	890.65	1385
3pm	32.2	70	748.7	6.8	320	750.15	1055
4pm	30.9	75	749.7	5.8	225	440.28	805
Min	**28.9**	**56**	**747.1**	**1.2**	**25**	**405.55**	**397**
Max	**34.8**	**79**	**749.7**	**6.8**	**320**	**1765.2**	**1872**
Mean	**32.0125**	**68.625**	**748.325**	**5.45**	**198.875**	**893.4675**	**1154.375**

Appendix XXII: MAY (Location 13)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	25.90	87.00	751.90	4.50	230.00	260.45	266.00
10am	26.90	85.00	750.50	5.60	295.00	365.03	371.00
11am	28.70	80.00	750.10	5.80	96.00	395.95	985.00
12am	33.20	65.00	748.50	6.90	30.00	575.85	1,258.00
1pm	32.60	67.00	750.80	5.50	250.00	505.95	1,152.00
2pm	31.60	72.00	750.10	5.40	277.00	455.15	885.00
3pm	31.20	75.00	750.10	5.30	301.00	301.45	1,025.00
4pm	30.10	77.00	750.20	4.80	267.00	200.78	625.00
Min	**25.90**	**65.00**	**748.50**	**4.50**	**30.00**	**200.78**	**266.00**
Max	**33.20**	**87.00**	**751.90**	**6.90**	**301.00**	**575.85**	**1,258.00**
Mean	**30.03**	**76.00**	**750.28**	**5.48**	**218.25**	**382.58**	**820.88**

Appendix XXIII: MAY (Location 14)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.90	83.00	751.70	4.20	210.00	350.64	275.00
10am	27.90	82.00	750.90	9.20	150.00	455.58	311.00
11am	28.90	76.00	750.10	7.60	186.00	685.65	902.00
12am	32.30	65.00	748.50	6.50	135.00	815.25	1,228.00
1pm	32.70	64.00	748.10	5.50	90.00	965.20	1,392.00
2pm	31.70	69.00	749.50	7.50	77.00	450.25	1,005.00
3pm	31.50	71.00	750.10	6.50	130.00	351.15	965.00
4pm	30.20	76.00	750.20	1.50	260.00	250.28	655.00
Min	**27.90**	**64.00**	**748.10**	**1.50**	**77.00**	**250.28**	**275.00**
Max	**32.70**	**83.00**	**751.70**	**9.20**	**260.00**	**965.20**	**1,392.00**
Mean	**30.37**	**73.25**	**749.89**	**6.06**	**154.75**	**540.50**	**841.63**

Appendix XXIV: MAY (Location 15)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.20	86.00	750.80	6.10	152.00	280.82	332.00
10am	28.10	83.00	749.60	5.60	85.00	305.10	572.00
11am	29.10	77.00	748.00	5.80	116.00	385.50	702.00
12am	32.90	62.00	747.90	6.80	215.00	1,275.15	1,258.00
1pm	31.60	68.00	748.20	6.60	262.00	1,165.25	1,142.00
2pm	31.50	71.00	748.80	4.40	111.00	551.58	1,085.00
3pm	30.70	74.00	749.30	5.80	95.00	389.45	625.00
4pm	30.50	76.00	749.40	6.90	260.00	150.58	425.00
Min	**27.20**	**62.00**	**747.90**	**4.40**	**85.00**	**150.58**	**332.00**
Max	**32.90**	**88.00**	**750.80**	**6.90**	**260.00**	**1,275.15**	**1,258.00**
Mean	**30.20**	**74.88**	**749.00**	**6.00**	**162.00**	**562.93**	**767.75**

Appendix XXV: MAY (Location 16)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.30	87.00	750.50	5.90	345.00	290.15	275.00
10am	27.30	83.00	750.20	4.20	195.00	485.08	681.00
11am	30.20	75.00	750.10	3.20	186.00	695.55	902.00
12am	31.10	62.00	749.10	4.50	305.00	975.15	1,198.00
1pm	32.40	54.00	747.80	5.70	190.00	1,165.20	1,352.00
2pm	31.40	69.00	748.50	6.20	97.00	850.25	1,085.00
3pm	30.10	71.00	750.10	5.80	120.00	351.15	455.00
4pm	29.50	76.00	750.70	5.80	165.00	250.28	255.00
Min	**26.30**	**54.00**	**747.80**	**3.20**	**97.00**	**250.28**	**255.00**
Max	**32.40**	**87.00**	**750.70**	**6.20**	**345.00**	**1,165.20**	**1,352.00**
Mean	**29.79**	**72.13**	**749.73**	**5.16**	**200.38**	**620.35**	**775.38**

Appendix XXVI: June (Location 17)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	24.20	89.00	753.90	9.50	330.00	158.15	166.00
10am	26.80	85.00	752.50	5.60	205.00	165.05	375.00
11am	27.10	83.00	751.10	7.80	96.00	345.95	785.00
12am	31.30	69.00	750.50	6.90	30.00	705.85	958.00
1pm	32.60	67.00	749.80	6.50	250.00	935.95	1,152.00
2pm	31.50	72.00	750.10	5.40	277.00	455.15	885.00
3pm	31.20	75.00	750.10	2.30	301.00	301.45	825.00
4pm	30.10	77.00	750.20	4.80	267.00	200.78	625.00
Min	**24.20**	**67.00**	**749.80**	**2.30**	**30.00**	**200.15**	**166.00**
Max	**32.60**	**89.00**	**753.90**	**9.50**	**330.00**	**965.95**	**1,152.00**
Mean	**29.35**	**77.13**	**751.03**	**6.10**	**219.50**	**408.54**	**721.38**

Appendix XXVI: June (Location 18)

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.10	88.00	752.90	8.20	105.00	345.55	205.00
10am	27.20	86.00	751.70	6.50	155.00	455.58	301.00
11am	28.60	75.00	751.30	7.60	18.00	685.05	805.00
12am	32.10	66.00	750.50	6.50	135.00	815.15	798.00
1pm	32.60	64.00	750.10	9.50	90.00	1,095.20	1,055.00
2pm	31.60	69.00	750.20	7.50	75.00	690.55	985.00
3pm	30.50	71.00	751.10	6.50	130.00	351.15	585.00
4pm	30.20	76.00	751.20	5.50	225.00	250.28	555.00
Min	**26.10**	**64.00**	**750.10**	**5.50**	**18.00**	**250.28**	**205.00**
Max	**32.60**	**88.00**	**752.90**	**9.50**	**225.00**	**1,095.20**	**1,055.00**
Mean	**29.86**	**74.38**	**751.13**	**7.23**	**116.63**	**586.06**	**661.13**

Appendix XXVII: **JUNE**

LOCATION 19							
Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	27.10	86.00	752.60	6.10	352.00	370.82	293.00
10am	28.10	84.00	751.10	9.60	185.00	405.10	572.00
11am	28.70	75.00	751.10	5.80	116.00	475.50	702.00
12am	32.90	60.00	749.10	7.80	215.00	1,305.25	1,250.00
1pm	32.60	68.00	749.20	6.60	262.00	1,115.25	1,100.00
2pm	31.50	71.00	749.90	4.40	165.00	671.55	785.00
3pm	30.70	72.00	751.00	10.80	195.00	379.45	525.00
4pm	29.50	76.00	751.30	6.90	265.00	150.58	320.00
Min	**27.10**	**60.00**	**749.10**	**4.40**	**116.00**	**150.58**	**293.00**
Max	**32.90**	**86.00**	**752.60**	**10.80**	**352.00**	**1,365.25**	**1,250.00**
Mean	**30.14**	**74.00**	**750.66**	**7.25**	**219.38**	**609.19**	**693.38**

Appendix XXVIII: JUNE

LOCATION 20

Times (hr.)	Temperature (°C)	Humidity (%)	Pressure (mmHg)	Wind Speed (km/h)	Wind Direction (o)	Solar radiation (W/m2)	Ultra-violet radiation (µW/m2)
9am	26.20	85.00	752.10	5.90	145.00	290.15	275.00
10am	27.20	83.00	751.95	7.50	195.00	485.08	681.00
11am	30.20	75.00	750.90	3.20	346.00	695.55	902.00
12am	32.90	60.00	748.50	4.50	305.00	965.55	998.00
1pm	31.40	63.00	750.10	5.70	190.00	605.25	452.00
2pm	31.40	69.00	749.50	6.20	195.00	580.15	385.00
3pm	30.80	78.00	750.10	10.80	120.00	351.15	285.00
4pm	30.00	80.00	750.70	5.80	165.00	150.28	255.00
Min	**26.20**	**60.00**	**748.50**	**3.20**	**120.00**	**150.28**	**255.00**
Max	**32.90**	**85.00**	**752.10**	**10.80**	**346.00**	**965.55**	**998.00**
Mean	**30.01**	**74.13**	**750.48**	**6.20**	**207.63**	**515.40**	**529.13**