SPATIO-TEMPORAL VARIABILITY OF TRACE METALS IN ATMOSPHERIC FINE PARTICULATE MATTER FROM SELECTED INDUSTRIAL SITES IN OGUN STATE, NIGERIA

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES OF COVENANT UNIVERSITY, OTA, OGUN STATE, NIGERIA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY (Ph.D) DEGREE IN ENVIRONMENTAL CHEMISTRY, IN THE DEPARTMENT OF CHEMISTRY, COLLEGE OF SCIENCE AND TECHNOLOGY, COVENANT UNIVERSITY, OTA.

AUGUST, 2016

ACCEPTANCE

This is to attest that this thesis is accepted in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** in Environmental Chemistry in the Department of Chemistry, College of Science and Technology, Covenant University, Ota.

Professor Samuel Wara ………………………..

Dean, School of Postgraduate Studies Signature & Date

Miss Helen Jevwegaga ………………………..

Secretary, School of Postgraduate Studies Signature & Date

DECLARATION

I, **ANAKE, Winifred Uduak**, (CUGP100233), declare that this research was carried out by me under the supervision of Dr. Godson R. E. E. Ana of the Department of Environmental Health Sciences, University of Ibadan and Dr. Nsikak U. Benson of the Department of Chemistry, Covenant University, Ota. I attest that the thesis has not been presented either wholly or partly for the award of any degree elsewhere. All sources of data and scholarly information used in this thesis are duly acknowledged.

ANAKE, Winifred Uduak **……………………..**

Signature & Date

CERTIFICATION

We certify that the thesis titled “Spatio-temporal Variability of Trace Metals in Atmospheric Fine Particulate Matter from Selected Industrial Sites in Ogun State, Nigeria” is an original work carried out by Mrs. **ANAKE, Winifred Uduak**, (CUGP100233), in the Department of Chemistry, College of Science and Technology, Covenant University, Ota, Ogun State, Nigeria, under the supervision of Dr. Godson R. E. E. Ana and Dr. Nsikak U. Benson . We have examined and found the work acceptable for the award of a degree of Doctor of Philosophy in Environmental Chemistry.

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Supervisor	Signature & Date
Dr. Nsikak U. Benson	**……………………..**
Co-Supervisor	Signature & Date
Dr. Akan B. Williams	**……………………..**
Head of Department	Signature & Date

DEDICATION

To the Almighty God, my saviour, defender and provider. To Him alone be all the glory, praise and adoration.

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Winifred Anake, 2016

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LIST OF ACRONYMS AND ABBREVIATIONS

AGE	Agbara Industrial Estate
APM	Airborne Particulate Matter
AQI	Air Quality Index
AT	Averaging Time
BAM	Beta Attenuation Monitor
BI	Bioavailability Index
CA	Concentration in Air
CAA	Clean Air Act
CMB	Chemical Mass Balance
CUF	Covenant University Farm
EC	Exposure Concentration
ED	Exposure Duration
EF	Exposure Frequency
EFs	Enrichment Factors
ET	Exposure Time
EWC	Ewekoro Community
FA	Factor Analysis
FAAS	Flame Atomic Absorption Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
IARC	International Agency for Research on Cancer
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure and Applied Chemistry
IUR	Inhalation Unit Risk
MDL	Method Detection Limits
MOUDI	Micro-Orifice Uniform Deposit Impactor
NAAQS	National Ambient Air Quality Standards
NESREA	Nigerian Environmental Standards and Regulations Enforcement Agency

NIMET	Nigerian Meteorological Agency
OTE	Ota Industrial Estate
PCA	Principal Component Analysis
PIXE	Proton Induced X-ray Emission Spectrometry
$PM_{2.5}$	Fine Particulate Matter
PMF	Positive Matrix Factorization
PTFE	Polytetrafluorethylene
QA/QC	Quality Assurance/Quality Control
RAGs	Risk Assessment Guidance for Superfund
RfCs	Reference Concentrations
RPD	Relative Percent Difference
SA	Source Apportionment
SEM EDS	Scanning Electron Microscopy (SEM) Energy Dispersive X-Ray Spectroscopy
SPDC	Shell Petroleum Development Corporation
SPSS	Statistical Package for the Social Sciences
PPRTVs	Provisional Peer Reviewed Toxicity Values
TEOM	Tapered-Element Oscillating Microbalance
TSP	Total Suspended Particulate
TXRF	Total Reflection X-Ray Fluorescence
UK	United Kingdom
USA	United States of America
USEPA	United States, Environmental Protection Agency
XRF	X-ray Fluorescence Spectroscopy
WAPCO	West African Portland Cement Plc
WHO	World Health Organization
NRC	National Research Council
SGL	SFURNA Global Limited
µm	Micro metre
mg/l	Milligram per litre
$\mu g/m^3$	Microgram per cubic metre

CHEMICAL SYMBOLS

Ag	Silver
Al	Aluminum
As	Arsenic
Ba	Barium
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenium
Na	Sodium
Ni	Nickel
Pb	Lead
Sb	Antimony
Se	Selenium
Sr	Strontium
Ti	Titanium
V	Vanadium
Zn	Zinc

ABSTRACT

The spatial and temporal variations of fine particulate matter bound trace metals were investigated in three industrial estates namely Ota Industrial Estate (OTE), Ewekoro Community (EWC) and Agbara Industrial Estate (AGE) and one background (Covenant University Farm Ota) in Ogun State. The sampling period was six (6) months covering the wet and dry seasons. One hundred and fifty (150) samples were collected according to standard methods using environtech gravimetric sampler, after which fine particulate matter ($PM_{2.5}$) mass concentration was computed gravimetrically. The total trace metals and chemical sequential extraction of twenty-two (22) trace metals (As, Cr, Pb, Ni, Cd, Mn, Ti, V, Ba, Fe, Al, Mo, Ca, Zn, Cu, Mg, Sr, Se, Ag, K, Na, and Sb) were further analysed by inductively coupled plasma mass spectrometry. Daily mean meteorological parameters for the study period were obtained from Nigerian Meteorological Agency. Cumulative lifetime cancer risk, air quality index and source apportionment of pollutants were also assessed. Spatio-temporal mass distribution of $PM_{2.5}$ in the investigated sites indicated that the average annual $PM_{2.5}$ mass concentrations were fifteen to twenty six (15-26) times and twelve to twenty two (12-22) times higher than the current annual World Health Organisation (WHO) and United States Environmental Protection Agency (US EPA) guideline of 10 and 12 $\mu g/m^3$ respectively. OTE and CUF recorded the highest and lowest $PM_{2.5}$ levels across seasons respectively while distinct seasonal variations trend showed dry > wet. Comparison of the annual average concentrations of Pb, As, Cd, Cr, Ni, Mn, V trace metals to the appropriate standard limit values reveals that out of these 7 trace metals, only V (0.199 - 0.862 μgm^{-3}) was below the existing WHO limit of one (1 $\mu g/m^3$).The meteorological parameter results revealed that relative humidity and rainfall significantly decreased the accumulation of fine particles whereas increased wind speed and temperature, showed a corresponding increase in the concentration of $PM_{2.5}$. Speciation and bioavailability studies identified Cr, V, Cu, Cd and Cr, V Cu, Zn as the most labile metals present in OTE and EWC respectively. The sum of the cumulative lifetime cancer risk of inhalation exposure route was above EPA's acceptable risk range of 1×10^{-6} to 1×10^{-4} for both adults and children with the highest occurrence (9.53×10^{-2}) in Ewekoro community. The absence of 0 to 50 gradations representing the good air quality index category was conspicuously highlighted. Scanning electron microscopy images of fine particles indicate that they are clustered into the following groups: soil dust mineral, soot aggregation, alumino silicate and fly ash particles. Hierarchical agglomerative clustering analysis of fine particles indicated major clustered groups while source identification using principle component analysis identified the origin of this source such as industrial processes, vehicle emissions, re-suspended and crustal dust, biomass burning, solid waste combustion and coal oil combustion. To improve on the present status of air quality, Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) should enforce environmental laws, ensure that all industries adopt standard emission control strategies and encourage the cultivation of green belts.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Investigation of outdoor air pollution has become the prime focus of many researchers in recent years considering the unprecedented deterioration of air quality in remote and urban areas. Unpolluted air is a basic necessity to man and the environment. However, key contributors to the deterioration of air quality include overpopulation, industrialization and transportation. Fine particulate matter otherwise known as $PM_{2.5}$ is a significant indicator of air quality and emissions originate from various sources, both natural (windborne dust, sea spray, volcanic activities and biomass burning) and human-mediated (fuel combustion, industrial processes, non-industrial fugitive sources, and transportation) sources (Loomis, Huang, Wei, & Chen, 2014; US EPA, 2012a). Atmospheric particles can also be classified as primary or secondary particles. Primary particles are emitted directly into the atmosphere while secondary particles result from gas-to-particle conversion of precursor species (Aryal, Kim, Lee, Kamruzzaman, & Beecham, 2013; Belis *et al*., 2014).

Fine particulate matter can be characterized by their physical attributes and chemical compositions. The physical attributes of particles such as the mass concentration usually measured in units of mass per unit volume, or microgram per cubic metre ($\mu g/m^3$) and size distribution measured in aerodynamic diameter influence their transport and deposition (Liu, Zhang, Liu, Zhang, Sun, & Zhang, 2014; WBG, 1998). Aerodynamic diameter can be defined as the equivalent diameter of a spherical particle that has the same setting velocity as that of the collected particles. Particles are grouped into several classes according to their aerodynamic particle diameters or particle sizes such as: Total Suspended Particulate (TSP), which denotes all particles without referring to a specific upper size; PM_{10} refers to all particles smaller than 10 μm in aerodynamic diameter; $PM_{2.5}$ is defined as particles smaller than or equal to 2.5 μm in aerodynamic diameter while $PM_{0.1}$ are particles smaller than about 100 nm in aerodynamic diameter (Chen, Chen, Chang, Chuang, 2013; Liu *et al.*, 2014).

$PM_{2.5}$ chemical composition namely inorganic compounds, elemental carbon (black soot), trace elements, and organic compounds can significantly impact on visibility, human health, atmospheric chemistry, climate change, and agriculture. Among the inorganic compounds are some toxic metals such as arsenic, cadmium, chromium, nickel, vanadium, manganese, lead, iron, cobalt, copper, zinc, titanium, aluminum, antimony, etc. They are of serious concern to man due to their frequent occurrences in the residential and occupational areas and their exposure route is by inhalation (Basha *et al*., 2014). The amount of pollutants in a particular location can be influenced by key meteorological factors and pollutant sources.

Attention has been focused on fine particulate matter ($PM_{2.5}$), as a metric more closely associated with adverse health effects and has been confirmed to be more hazardous than larger size particulate matter as a result of its longer residence time in the atmosphere and ability to act as a carrier of harmful trace metals into the human lungs (AQEG, 2012; Canseco- Lajas, Vargas, & Campos-Trujillo, 2013; Celo & Dabek-Zlotorzynska, 2010; Feng, Dang, Huang & Yang, 2009; Harrison, Giorio, Beddows, & Dall'Osto, 2010; Kim, Kabir, & Kabir, 2015; Pope, & Dockery, 2006).

1.2 Statement of the Problem

The observed air pollution level in industrialized areas is alarming. Gaseous emissions from chimneys, stacks, open burning of solid waste, gales of dust particles from blasting of limestone rocks are conspicuously evident in industrialized areas of Ogun State, ranked among the top most industrialized states in Nigeria. Judging from the nature of raw materials used by these industries, there are strong possibilities of the prevalence of toxic metal bound particles in the environment. The occurrence of atmospheric fine particulate-bound trace metals is primarily due to anthropogenic contributions of which industries are enlisted as one of the major culprits (Etim, 2012; Owoade *et al.*, 2015). Currently, there is dearth of data on industrially emitted fine particulate matter and its associated pollutants in Nigeria. This is primarily attributed to lack of proper emission technique, absence of air quality monitoring stations and lack of availability/access to analytical equipment (Owoade *et al*., 2015; Udeozor and Nzeako, 2010).

In Nigeria, some researchers have investigated the problem of pollution by trace metals. Most of these are short-term studies of total suspended particulates (TSP) (Asubiojo *et al*., 1993; Aziakpono, Ukpebor, & Ukpebor, 2013; Laing & Obioh, 1994; Ukpebor, Ukpebor, & Efebomo, 2004). A few baseline studies have been conducted on ambient concentrations of $PM_{2.5}$ and PM_{10} as well as their elemental composition in some selected locations such as Lagos, Aba, Abuja, Kano, Maiduguri, and Port-Harcourt (Abiye, Obioh, & Ezeh, 2013; Ana & Sridhar, 2009; Ezeh, Obioh, Asubiojo, & Abiye, 2012; Obioh *et al*., 2013; Owoade *et al*., 2006).

1.3 Research Questions

Few recent findings have been reported on $PM_{2.5}$, elemental characterization and source apportionment of fine particulate matter in industrial areas by Orogade *et al.* (2016), Owoade *et al.* (2015, 2013), Oke, Ukpebor, and Ukpebor (2013). Compared with the depth of environmental research conducted in the developed world, there is dearth of data on chemical speciation, $PM_{2.5}$ air quality index, influence of meteorological parameters on $PM_{2.5}$ and health risks assessment associated with $PM_{2.5}$ particulates especially from heavily industrialized areas in Nigeria (Obioh *et al.*, 2013). Therefore, based on the aforementioned gap, this study addresses the following questions:

(i) Are there significant variability in seasonal concentration of $PM_{2.5}$-bound trace metals?

(ii) Do trace metals in air-borne fine particles exist in multi selective speciation phases?

(iii) Are $PM_{2.5}$-bound trace metals associated with health risk?

(iv) Do meteorological factors such as wind speed and relative humidity influence the concentration of fine particulate matter in a location?

(v) Are monitoring locations compliant with $PM_{2.5}$ air quality standards?

(vi) What are the major contributors of $PM_{2.5}$ in the study area?

1.4 Aim and Objectives of the Study

1.4.1 Aim

To determine the spatial and temporal variability of trace metals profile in fine particulate matter from selected industrial sites in Ogun State, Nigeria.

1.4.2 Objectives

The specific objectives of the study were to:

(i) Determine the levels of $PM_{2.5}$ and selected priority trace metals bound to $PM_{2.5}$ in the designated sampling points across seasons,

(ii) Assess the influence of meteorological factors on $PM_{2.5}$ mass distribution,

(iii) Determine the different chemical forms in which the most toxic metals are mainly distributed,

(iv) Assess the health risks of residents in the study area based on inhalation dosimetry method,

(v) Generate $PM_{2.5}$ air quality index spatial map for the study area, and

(vi) Apportion $PM_{2.5}$ and its associated metals to their sources using physicochemical signatures.

1.5 Justification for the Study

$PM_{2.5}$-bound trace metals in the atmosphere are a threat to human health. Although, several laws exist to control industrial pollution, many industries flout the pollution control regulation on account of inefficient enforcement by the regulatory bodies. Air quality can only be improved with a good understanding of the nature of pollution sources.

Therefore, this work assesses the effect of spatial and temporal factors on $PM_{2.5}$-bound trace metals, evaluate the levels of total and bioavailable $PM_{2.5}$ trace metals in the atmosphere and estimate health risk of the pollutant on residents in the study area. The findings from this work will generate a spatial map of the state of $PM_{2.5}$ air quality and identify the pollutant sources in the study area. In addition, the inferences from the data generated from this work will contribute to the on-going development of abatement policies on airborne PM in Nigeria if incorporated into the national database as well as give direction on adequate environmental control and abatement programmes for the Covenant University Community Development Programme.

CHAPTER TWO

LITERATURE REVIEW

2.1 Review of Previous Studies on $PM_{2.5}$ -bound Trace Metals

Over the past decades, measurement of particulate matter in air has concentrated on the determination of TSP concentration, with no preference to size selection. However, recent studies on particle transport and transformation strongly connects several health issues to fine particulates ($PM_{2.5}$). This has triggered extensive research on mass concentrations, chemical and elemental composition of $PM_{2.5,}$ source apportionment of pollutants, etc.

In Nigeria, Owoade *et al.* (2009) investigated the coarse and fine particulate matter fractions from an industrial area in Lagos state, covering the wet and dry seasons. Both fractions were measured with a low-volume Gent Stacked Filter Unit sampler for duration of 4 to 24 hours. The mass concentrations of the samples were determined gravimetrically while the elemental concentrations for 28 elements were determined using the polarized energy dispersive X-ray fluorescence (EDXRF) technique. The coarse fraction had higher mass concentration range of 86 to 8765 $\mu g/m^3$ when compared with 10 to 462 $\mu g/m^3$ for the fine particulate fraction. Six of the elements (Cr, Mn, Fe, Cu, Zn, and Pb) measured in both fractions of the particulates recorded higher concentration in a section of investigated sites indicating serious health impacts on human life.

In a different research, Abiye *et al*. (2013) studied the ambient concentration of $PM_{2.5}$ and PM_{10} airborne particulate matter with their elemental characterization from five urban sites in Abuja, north-central Nigeria. Sampling and characterization of eighteen elements in both fractions was done using “Gent” stacked filter unit sampler equipped with a double stage filter in series and proton-induced X-ray emission (PIXE) spectrometer respectively. The results obtained showed that particle mass concentration of PM_{10} was higher than that of $PM_{2.5,}$ the predominant elements were found in the PM_{10} fraction while their correlation matrix result indicated that strong significant correlation of $r > 0.53$ to 0.90 existed between some metals.

Also, Aziakpono *et al*. (2013) in their study documented the baseline, spatial and temporal variation of $PM_{2.5}$ particulate matter in Isoko land, Delta State, Nigeria. Microdust pro real time dust monitor was used for airborne particulate matter sampling. The obtained result was in the range of 4 – 310 μg/m^3. Their results revealed that the 24 hours national ambient air quality standard limit (NAAQS) for $PM_{2.5}$ threshold in all the sampling sites was exceeded. Also, the dry season exhibited significantly higher levels than the wet season.

Recently, Owoade *et al.* (2015) investigated the chemical composition and source contributors to $PM_{2.5}$ and $PM_{2.5\text{-}10}$ fractions in Ife, Nigeria. Samples were collected with nuclepore polycarbonate filters using a low volume GENT sampler. The mass concentration of the sampled fine PM fraction ranged between 14.4 – 986.5 μg/m^3. These values exceed the permissible daily limit (NAAQS) of 35 μg/m^3 for $PM_{2.5}$. Elemental composition was determined using X-ray fluorescence (XRF). High levels of Mn, Ni, As, Cd and Pb were highlighted. Also, positive matrix factorization (PMF) identified the following four source categories and their contributions to the fine fraction: coking coal (83%), soil (10%), metallurgical industry (6%), and electronic waste processing (1%).

$PM_{2.5}$ studies have also been carried out in other parts of the world. The concentration and sources of $PM_{2.5}$ bound trace metals from Canadian sites were analysed using microwave assisted acid digestion method and inductively coupled plasma mass spectroscopy (ICP-MS). From the findings, anthropogenic activities contributed significantly to ambient $PM_{2.5}$ loadings. Sites closer to industrial manufacturing facilities and high traffic areas had elevated levels of trace metals than sites located in areas with identical land use (Celo, and Dabek-Zlotorzynska, 2010).

Kgabi (2010) carried out a research on the assessment of common methods employed in the sampling of atmospheric particulate matter and analysis of metals in Rustenburg, South Africa. Sampling was conducted with tapered element oscillating microbalance, while the elements associated with the atmospheric particulate matter were analysed using ICP-MS and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS) Their result for the efficiency of the different filters evaluated showed teflon-coated glass fibre > ringed-teflon > quartz filters. The elemental compositions identified from the SEM-EDS on ringed-teflon filters were Si, Fe, Mg, K, Na, C, S, F and O, while for ICP-MS, Fe, Al, Ca, Mg, K, Na, Cr, Ni, Pb, Cu, Zn and Mn were identified. From the results, it was deduced that ICP-MS was an instrument of choice for the analysis of metals.

Lee and Hieu (2011) investigated seasonal variations in the concentrations of fine particulate matter and its associated heavy metals obtained from Ulsan, Korea. The mean concentrations of $PM_{2.5}$ were higher in the spring (23.2 $\mu g/m^3$) than in the summer (18.1 $\mu g/m^3$) and the lower $PM_{2.5}$ levels in summer were attributed to increase in rainfall. Fe, Zn, Cd, Mn, Pb, Cu, Cr and Ni metals were analysed using ICP-MS. Metal results also recorded elevated levels in spring than in summer and this seasonal differences were attributed to differences in weather condition mainly the wind direction. More so, the principal component analysis for the $PM_{2.5}$-bound metals apportioned industries and road dust as major sources of $PM_{2.5}$ and toxic heavy metals at the sampling site.

Also, Qiao *et al*. (2013) investigated twelve hours $PM_{2.5}$ samples collected with air particulate sampler in Guiyang, China. Elemental analysis done with Kevex energy dispersive X-ray spectrometer (XRF) showed significant levels of Ti (30±22 ng/m^3), Mn (250±400 ng/m^3), Fe (340±280 ng/m^3), Zn (290±330 ng/m^3), and Pb (130±130 ng/m^3) and was concluded from obtained results that local anthropogenic sources of heavy metals resulted in their temporal variability.

$PM_{2.5}$ *in situ* measurements of particles using a medium volume air sampler (offline) for a period of one year were conducted by Pipalatkar, Khaparde, Gajghate, and Ba (2014). The morphology and elemental composition analyses were performed by SEM-EDS, respectively. The average mass concentrations of $PM_{2.5}$ were 97.2 and 121.2 µg/m^3 respectively and were substantially higher than the NAAQS, WHO and US EPA standards. The highest mass concentrations of $PM_{2.5}$ followed the trend winter > post-monsoon > summer > monsoon period. SEM and EDS analysis of $PM_{2.5}$ indicated the presence of soot, tarballs, and fluorine - carbon rich particles. The observed variation in the morphology and elemental composition of the particles over the seasons was due to atmospheric processing.

Chen *et al*. (2015) investigated the air quality and impacts of the new ambient air quality standard of 2012 in Beijing, China. Results obtained from the computation of air quality index which includes monitoring of $PM_{2.5}$, revealed that $PM_{2.5}$ was the major contributor to the air quality index (AQI) when compared with the five other pollutants (ground-level ozone, carbon monoxide, sulphur oxides, nitrogen oxides, and lead). Also, spatial analysis of air quality indicated that the national standard was only attained by a background station, while urban and suburban stations exceeded the national standard.

Recently, Khan *et al*. (2016) conducted analysis on fine particulate matter, source apportionment, and health risk assessment in Southeast Asia (SEA). $PM_{2.5}$ samples were collected at different seasons using a high-volume air sampler on 24-hour basis. Results obtained showed that the World Health Organization (WHO) $PM_{2.5}$ guideline and US EPA national ambient air quality standard (NAAQS) were exceeded by a proportion of 48% and 19% respectively. Instrumental analysis was conducted using ICP-MS and As, Pb, Cd, Ni, Mn, V, and Cr trace metals were identified. Five potential sources were identified using positive matrix factorization (PMF) 5.0. The carcinogenic heavy metal of concern to health was As. The finding concluded that the associated lifetime cancer risk as a function of the exposure of hazardous $PM_{2.5}$-bound metals was 3-4 per one million people at the study site.

2.2 Fine Particulate Matter ($PM_{2.5}$)

In principle, fine particulate matter otherwise known as particulate matter 2.5 ($PM_{2.5}$), refers to particles that are 2.5 micrometers (μm) in diameter or less. Fine particles are much smaller in size than a human hair. To provide some perspective, the average strand of a human hair is about

70 μm in diameter and a grain of sand is about 90 μm in diameter (Figure 2.1). Given their minute sizes of 2.5 micrometers, this enables it to be easily inhaled into human lungs and respiratory tracts, increasing the potential for health risks. Fine particles in the air comprise of directly emitted elemental carbon, organic carbon, sulphate, nitrate, and other inorganic particles such as metals, crustal material and sea salt. Their atmospheric lifetime is in the order of days to weeks and it is capable of traveling hundreds to thousands of kilometers (Figueroa, Rodríguez-Sierra, & Jiménez-Veleza, 2006; Yu, Zhu, Xie, Yan, Zhu, & Zheng, 2015). Fine particles are also largely water soluble and hygroscopic, with the exception of carbon and some organic compounds, which makes them bioavailable (WHO, 2000).

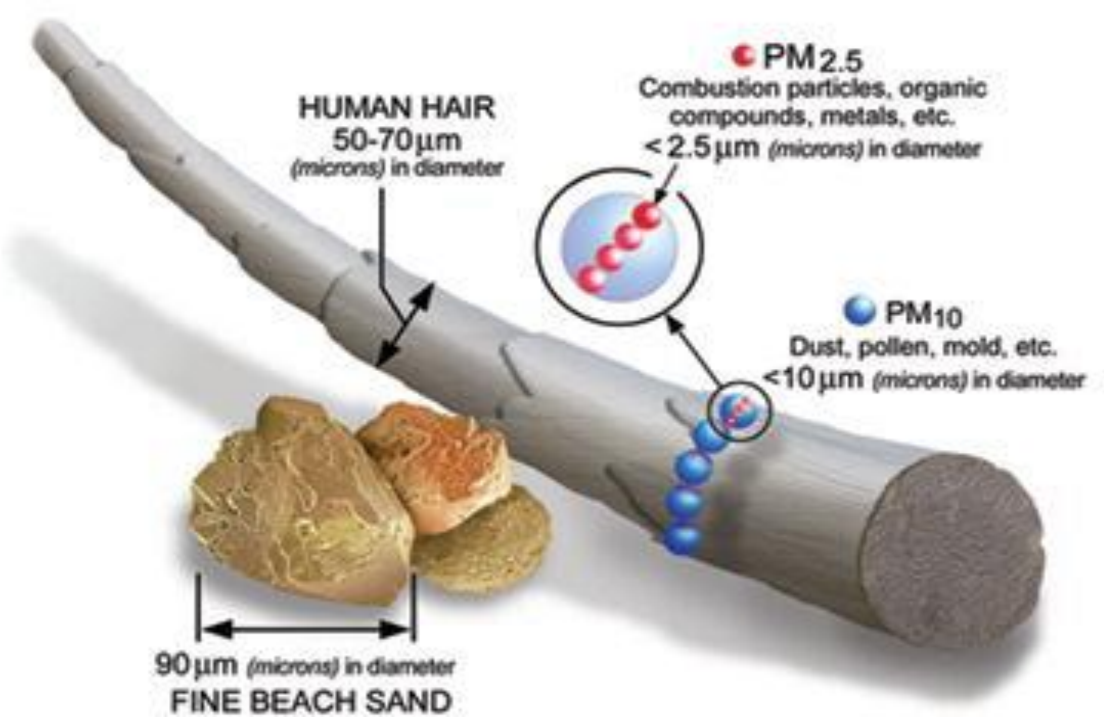

Figure 2.1: Comparison of a $PM_{2.5}$ particle to the diameter of a human hair, a particle of fine beach sand, or a PM_{10} particle (US EPA, 2012a).

2.2.1 Sources of $PM_{2.5}$

Fine particles originate from diverse sources, among which anthropogenic activities such as industrial production, vehicular emissions, etc. have been identified. Atmospheric particulates can be classified into two according to their sources namely primary and secondary sources. Primary sources of particles are directly emitted into the air while secondary sources of $PM_{2.5}$ can be formed from the chemical reactions of gases such as sulphur dioxide (SO_2), volatile organic carbons, nitrogen oxides (NO_x) and ammonia (Aryal *et al*., 2013; Belis *et al*., 2014).

Both sources can be further classified into natural and anthropogenic sources:

(i) **Natural Sources**: The natural sources of $PM_{2.5}$ include sea spray, dust storm, volcanoes, forest and wild fires, etc. Different types of mechanical processes accelerate the generation of fine particles containing crustal metals. Examples of these mechanical processes are mining, grinding, mineral processing, and dust re-suspension.

(ii) **Anthropogenic Sources**: These include, gas flaring, burning of fossil fuels in vehicles, power plants, coal and wood combustion, construction and demolition and high-temperature industrial activities.

Table 2.1 Diverse sources of trace metals emission

Emission Source	Characteristic Trace Metals Emitted
Road Transportation	Pb, Ba, Mn, Zn, V, Ni, Sb, As, Zn, Fe, Al
Dust Storms	Al, K, Ca, Ti, Si, Fe, Zn
Re suspended Soil	Si, V, Cr, Ca, Ti, Sr, Al, Mn, Se
Refuse Incineration	Zn, Sb, Cu, Cd, K, Pb
Wood Smoke	Fe, K, Na, Ca, Cu, Zn,
Mineral Dust	Al, Si, Fe, K, Ca and Mg
Industrial Sources	Cu, As, Pb, Sb, Cd, Zn, Cr, Fe, Ni, Na, Mn, V,As
Construction	Al, K, Cd, Cr
Sea-spray	Na, Cl, Mg, K and S

Source: (Belis *et al*., 2014; Huang *et al*., 2013)

2.3 Effect of PM $_{2.5}$ Exposure

2.3.1 Human Health Effects

Fine particulate matter are easily deposited in the human respiratory tract once inhaled due to its minute sizes, morphology, particle density and a person's breathing pattern. The effect of $PM_{2.5}$ exposure on the human organism is to a large extent dependent on different individual's genetic factors, the nature of chemicals associated with the fine particulates, as well as the duration and intensity of exposure. Soluble components of fine particulate matter are capable of travelling deeply into alveolar regions of the lungs, while the insoluble portions adhere to the surface and are difficult to remove, thereby affecting the lung's ventilation function (Ren, Li, Yu, Liu, & Ma, 2016; Seaton, Macnee, Donaldson, & Godden, 1995).

This can result in ailments such as coughing, difficulty in breathing, low pulmonary function, irregular heartbeat, heart attacks, aggravated asthma, chronic bronchitis, skin disorder and premature death (US EPA, 2012b).

Moreover, fine particles are carriers of potentially harmful and loosely bound metals such as cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), iron (Fe), zinc (Zn), manganese (Mn), etc. If present in elevated concentrations in ambient air, these metals can pose a significant risk to human health (Khan *et al.*, 2016). Particulates in the blood damage its ability to transport oxygen via haemoglobin. This process can cause serious consequences, such as respiratory disease aggravation and congestive heart failure. It is often irreversible and can lead to several chronic upper respiratory diseases, as well as an increased probability of lung cancer and cardio-respiratory mortality (Neuberger, Rabczenkob, & Moshammera, 2007).

Certain sensitive groups of people such as children, older adults (aged 65 or greater) and persons with pre-existing heart and lung disease when exposed to high $PM_{2.5}$ levels are susceptible to acute pulmonary and cardiovascular strain and even death due to aggravated heart or lung disease. Children are considered to be a high risk population due to the fact that they naturally breathe more deeply as a result of their higher basal metabolisms compared to adults, thus, exposing them to greater concentrations of $PM_{2.5}$ (Saadeh & Klaunig, 2014).

Clinical, epidemiological, and toxicological sources are used to estimate the mortality and morbidity effects of short and long term exposure to $PM_{2.5}$ concentration levels. Several researches indicate that there is a positive relationship between $PM_{2.5}$ and cardiovascular and respiratory disease (Krewski *et al*., 2009; Ren *et al*., 2016).

According to the World Health Organization (WHO), fine particulate matter ($PM_{2.5}$) has been estimated to contribute approximately 800,000 premature deaths yearly, ranking $PM_{2.5}$ as the 13th leading cause of mortality in the world (Anderson, Thundiyil, & Stolbach, 2012).

2.3.2 Climatic and Environmental Effects

High concentrations of $PM_{2.5}$ in the atmosphere can affect the radiative balance of the earth-atmospheric system by blocking incoming solar energy leading to a reduction in surface-level sunlight (Ren-Jian, Kin-Fai, & Zhen-Xing, 2012; Singh, Rastogi, Sharma, & Singh 2015). These can result in atmospheric haze, reduced visibility, changes in temperature and precipitation patterns, reduced crop yield and insufficient light as well as adverse effect on transport safety, and property values. These fine particles also have a great affinity for water thus, contributing to acid rain (US EPA, 2012a).

Furthermore, trace metal present in particulates, when deposited on soil, interferes with the soil process that makes nutrients available to plants (Oka, Thomas, & Lavkulich, 2014). In addition, fine particulate deposition on materials and building overtime can result in discolouration, frequent maintenance cost and decline of aesthetic value.

2.4 Factors Influencing the Dispersion and Accumulation of Particulate Matter

The dispersion and accumulation of particulate matter are predominantly influenced by the emission sources, meteorological parameters and local topography. Fine particles by reason of their minute sizes are easily transported by wind and weather to other distant locations from the emission sources. Pollutants such as nitrates, sulphates, trace metals, etc. are conveyed to distant locations from their origin there by causing significant background accumulation (Csavinaa *et al.*, 2012; Moustafa, Mohamed, Ahmed, & Nazmy, 2015).

2.4.1 Meteorological Effects on PM Concentrations

The local and regional meteorology of an environment contribute significantly to the quality of air in that vicinity. Thus, large diffusion, dilution and accumulation of atmospheric fine particles pollution are significantly influenced by meteorological parameters such as rainfall, relative humidity, temperature, atmospheric pressure, solar radiation, wind speed and direction (Liu, & Cui, 2014; Yang, Ye, Jerry, & Jiming, 2011).

Many studies have indicated that the dilution of atmospheric pollutants is a function of high wind speed while low wind speed favours accumulation of pollutants. Wind speed can, therefore, greatly impact on the levels of fine particles due to changes in dispersion and transport, dry deposition and marine particle formation (Megaritis *et al*., 2014). More so, wind direction has been associated with pollutants dispersion (Tecer, Süren, Alagha, Karaca, & Tuncel, 2008). Wind speed and direction can aid in the apportionment of fine particles concentration to their respective sources (Giri, Krishna, & Adhikary, 2008). Cloudiness increases the accumulation of fine particles, while radiation sets up photochemical reactions with other pollutants (Giri *et al*., 2008). However, temperature affects ambient chemical reactions and stagnant air masses are formed during low temperatures events, resulting in high particle level and vice versa (Wu *et al*., 2013).

Also, high and low relative humidity conditions have different effect on $PM_{2.5}$ levels. High relative humidity influences particles to settle down on the ground, causing low accumulation of fine particles and the reverse applies for low relative humidity. Relative humidity also encourages the formation of secondary pollutant (Giri *et al.*, 2008). Furthermore, rainy weather causes wet deposition of particles which results in the removal of $PM_{2.5}$ in the atmosphere; hence the rate of precipitation has a significant impact on fine particle concentrations (Megaritis *et al.*, 2014). Increase in atmospheric pressure causes air to sink on a large scale and trap pollutants and moisture near the surface leading to increase in fine particles. It is worth noting that on peculiar situations higher $PM_{2.5}$ levels can also be observed in low pressure when the winds associated with the storm passage stirs up dust particles (Hawkins & Holland, 2010).

Previous findings identified that variation between pollutant concentrations and some meteorological parameters is strongly influenced by different seasons. In China, according to Wu, Wang, and Ma (2012), the lower $PM_{2.5}$ exposure levels in summer were attributed to high temperature and wind speed. Hawkins and Holland (2010) examined the local meteorological data and fine particulate levels for Carlisle, Pennsylvania. The results of the analysis showed higher $PM_{2.5}$ concentrations in the summer, followed by the winter season while the spring and fall had relatively low concentrations. Wind speed was identified as the dominant meteorological variable controlling the seasonality of this region. Temperature and relative humidity were lower for high $PM_{2.5}$ concentration days in the fall. The local weather conditions on days with elevated fine particulate matter concentrations were observed to be warmer, more humid, less windy, higher pressure, and with low precipitation.

Furthermore, Owoade, Olise, Ogundele, Fawole, and Olaniyi (2012) investigated the correlation between $PM_{2.5}$ levels and meteorological variables in Ile-Ife, Nigeria. The result of the study showed elevated concentration of $PM_{2.5}$ mass concentration in the dry season as a result of atmospheric haze than in the wet season. The major outcome of their findings revealed that meteorological parameters such as rainfall, global radiation, air temperature and relative humidity contributed significantly to the accumulation of $PM_{2.5}$ in the investigated site.

2.4.2 Topography Effects on PM Concentrations

Topography refers to the representation of surface features such as mountains, hills, rivers, and valleys. Fine particle transport and diffusion in a specific location can be influenced by topographical features in that locality. For example, an urban area located around a mountain range can create significant pollution problems by increasing atmospheric stability which brings about high fine particle concentrations in the nearby valleys due to cold air drainage into those valleys. Moreover, horizontal and vertical airflow can be conducive to pollutant dispersion, but a mountain range becomes a natural barrier (Hawkins and Holland, 2010).

2.5 PM$_{2.5}$ Regulations

Ambient air refers to the natural state of air in the outdoor environment or the air we breathe outside. When this natural air is contaminated by any chemical, physical or biological agent, such changes affect people in different ways. In order to address the health effects of particulate matter, various governments and groups focusing on global health issues such as US EPA, WHO, etc., have both created regulations for the ambient concentration of particulates (WHO, 2006; US EPA, 2012a).

In the United States, the Environmental Protection Agency (EPA) is saddled with the responsibility of setting standards known as National Ambient Air Quality Standards (NAAQS) for particulate matter covering both human health and welfare. NAAQS has been classified into two namely the primary and secondary standards. Primary standards is concerned with public health protection, most especially that of the "sensitive" populations. These include the older people, children and persons with respiratory diseases. Also, the threshold limit set by secondary standards is to ensure protection of animals, crops, vegetation, buildings as well as avoid decreased visibility.

The current NAAQS for PM$_{2.5}$ is 12 μg/m^3 as an annual average and 35 μg/m^3 as daily average (Robert, 2013; US EPA, 2012a). In addition, the World Health Organization (WHO) air quality guidelines recommend that the PM$_{2.5}$ level must not exceed 10 μg/m^3 annual average and 25

$\mu g/m^3$ daily average (WHO, 2006). As shown in Figure 2.2, most of the world's major cities routinely exceed World Health Organization (WHO) air pollution guidelines.

In Nigeria, the agency responsible for environmental laws, guidelines, policies, regulations and enforcement is the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) (NESREA, 2013).

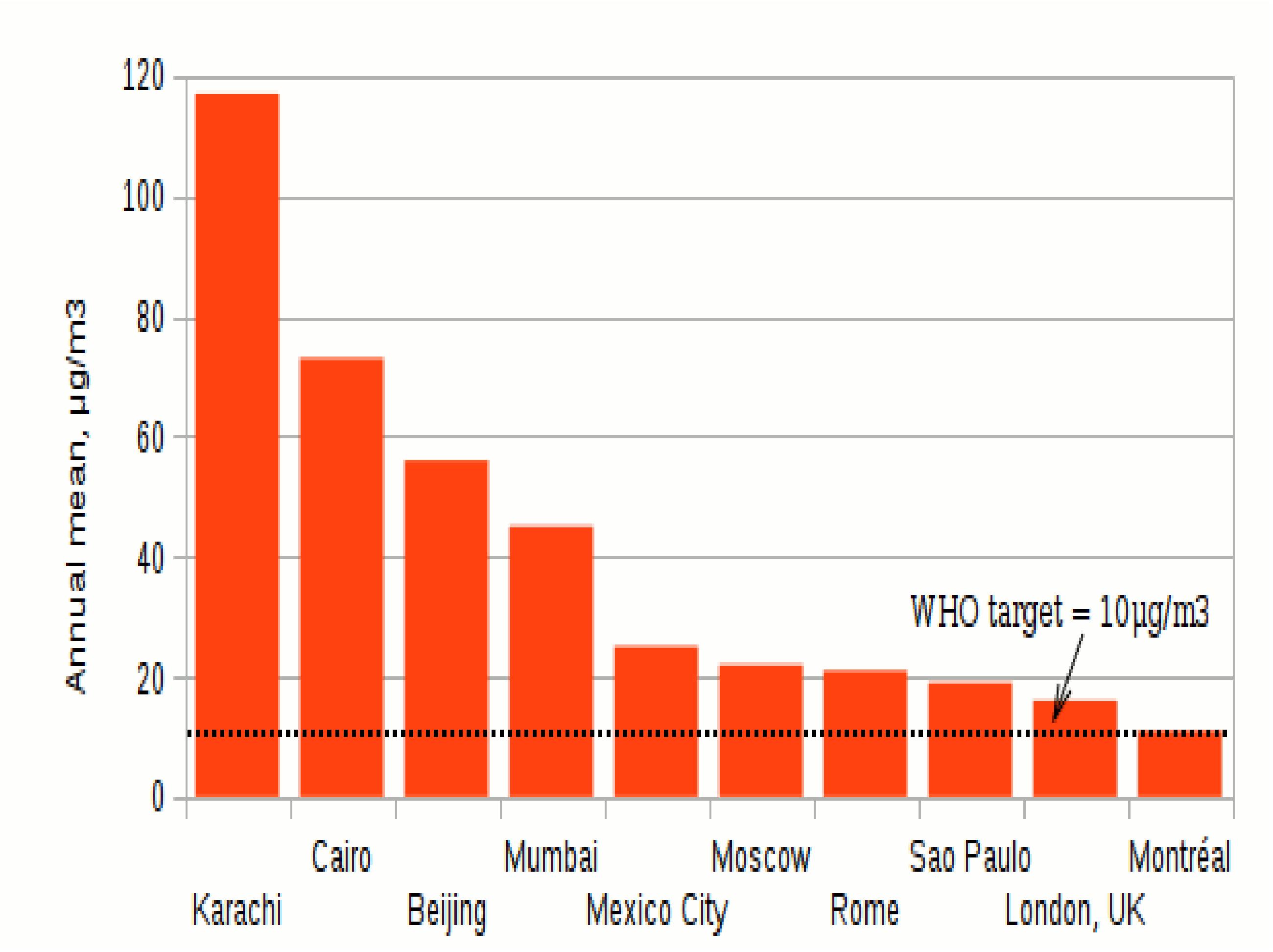

Figure 2.2: World health organization ambient air pollution of fine particulate matter concentrations $PM_{2.5}$ in cities (WHO, 2014)

2.6 $PM_{2.5}$ Monitoring Equipment

A fundamental concept in the measurement of mass concentrations of PM in ambient air employs both integrated and continuous methods. The integrated method incorporates time-weighted averages of particulate matter mass. This involves the use of filter-based gravimetric samplers that adsorbs the particulates onto a filter, and is subsequently weighed in a laboratory. Some examples of the gravimetric samplers are high volume sampler, dichotomous sampler, partisol air sampler, micro-orifice uniform deposit impactor (MOUDI) and stacked filter samplers (Watson *et al*., 1998).

Continuous method measures real-time monitoring of PM mass on a minute-by-minute cycle through the use of direct reading instruments that gives the actual result of particle concentrations as they are being measured. Several state-of-the-art technologies available for automated continuous monitoring of particulate matter include dust track aerosol monitor, beta attenuation monitor (BAM), piezoelectric microbalance, and tapered-element oscillating microbalance (TEOM) (Baron & Willeke, 2001; Watson *et al*., 1998). Gravimetric samplers are used to estimate time-weighted average levels of $PM_{2.5}$ in different settings. However, they generally have long averaging times to collect enough mass unlike real-time $PM_{2.5}$ samplers (Zhu *et al*., 2011). Continuous automated real-time sampling has the ability to measure 10-second average concentrations and can identify transient elevations caused by air pollution episodes or meteorological changes.

2.7 Filter Media

Sample collection of atmospheric particulate matter (PM) can be carried out by collecting air through a variety of filter media. The choice of filters for particle sampling depends on the sampler type, characteristics of the filter and most importantly the analytical method used. In addition, other factors considered in the choice of a filter media in general include high particle collection efficiency, low blank values, low flow resistance, loading capacity, mechanical stability, chemical stability, artifact formation, cost, availability and compatibility with analytical techniques. Filters with very high and variable blank levels are not suitable for quantification of particle deposits (Chow, 1995; Kgabi, 2010).

Atmospheric particulates can be collected using Teflon membrane, Teflon-coated glass fibre, glass fibre, quartz fibre, nylon membrane, cellulose fibre, etched polycarbonate membrane, etc. Of all the aforementioned filters, none is suitable for all type of chemical analyses; as such different types of filters may be required based on the desired chemical characterization.

However, the most suitable type of filters for $PM_{2.5}$ sample collection includes polytetrafluoroethylene (PTFE), polytetrafluoroethylene-bonded glass fibre, glass fibre, and quartz filters. This is so because of the determination of mass concentration and several other chemical components associated with $PM_{2.5}$, such as elemental carbon, water soluble ions, organic carbon, volatile organic carbon, polycyclic aromatic hydrocarbons, etc. (Kgabi, 2010; Perrino, Canepari, & Catrambone, 2013).

PTFE filters are suitable for gravimetric and elemental determination by most analytical instruments. They are used to a large extent for gravimetric analysis because they are highly insensitive to relative humidity. In addition, they show better performances when used for elemental analysis and they have the lowest blank for metals. Usually, filter blanks are analysed along with the sampled filters when carrying out chemical analysis in order to correct interferences and contaminants introduced into the sample by the filter media (Chow, 1995; Kgabi, 2010).

2.8 PM$_{2.5}$ -Bound Trace Metals

Trace metal refers to any metallic chemical element such as nickel, arsenic, lead, chromium, beryllium, cobalt, copper, iron, and zinc that has a relatively high density and is toxic at very low levels in the environment. They can be found naturally in rocks and soil and are present in diverse forms such as elemental, ions dissolved in water and vapours. Health risks resulting from exposure to trace metals include reproductive toxicity, cancer, genetic damage, neurotoxicity, etc. (Anake, Benson, Akinsiku, Ehi-Eromosele, & Adeniyi, 2014; US EPA, 1999a; Yaman, 2012).

Trace metals enter the environment through a variety of ways, either as a point or diffuse source, natural or anthropogenic source, gaseous or particulate form. Toxic trace metals including lead (Pb), mercury (Hg), cadmium (Cd), copper (Cu) and zinc (Zn) have all been produced as by-products of various industrial processes including technological processes related to coal, oil, cement production, municipal waste, metal smelting, wood and fossil fuels combustion and by other non-industrial sources such as the release of lead as toxic alkyl-lead compounds from petrol engines.

Most metal-containing compounds associated with particulates are less prone to chemical transformations and remain in their emitted form due to their non-volatile nature. Once introduced into the atmosphere, they travel great distances from their original source, transferring contaminants to ecosystems far and wide. The dispersion of trace metals after emission is very much related to meteorological conditions, particularly wind velocity and precipitation (Carbone *et al*., 2015).

Fine particles are made up of variable concentrations of many potentially toxic trace metals, such as arsenic (As) cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn). The amount and type of water soluble metals present on the fine particles have the capacity to support electron exchange and catalyse free radical production. The generation of free radicals can result in lung tissue damage by catalyzing oxidant formation, alteration in the pulmonary defence system, adverse respiratory health effects, oxidative stress as well as promoting the release of inflammatory mediators and cytotoxicity (Figueroa *et al*., 2006; Islam *et al*., 2015).

Generally, metallic components of atmospheric particulate matter with high solubility are more readily bio-activated as such can be potentially more harmful for humans. A number of factors influence the adverse health effects of atmospheric trace metal particulates on human. These include, the shape and size of particles, bonding and solubility of metallic components, the overall human exposure and the general well being of a person (Øvrevik, Refsnes, Låg, Holme, & Schwarze, 2015). In addition to the total amount of specific metals present in particulate matter, water and acid solubility may play a major role in the bioavailability, and potential toxicity of each metal. The solubility of $PM_{2.5}$-bound metal depends on its chemical form, the particle size and the pH of the sample. Therefore, in order to evaluate the risk posed by metal toxicity, it is important to determine bio-available levels instead of total metal contents (Mukhtar & Limbeck, 2013).

2.9 Chemical Speciation of Fine Particulates

Chemical speciation is an important analytical tool which offers a way for the elucidation of the chemical form(s) and the quantitative estimation of a specific element in toxicological and biochemical investigations (Benson, Anake, & Olanrewaju, 2013). According to International Union of Pure and Applied Chemistry (IUPAC), speciation of an element refers to the partitioning of an element amongst distinct chemical species. Chemical species here imply the specific form(s) of an element, with respect to oxidation or electronic state, molecular structure and isotopic composition. Also, speciation analysis outlines the analytical activity which identifies and measures the amount of individual chemical species in a sample (Adamu, Luter, Mohammed, & Umar, 2013; Templeton *et al.,* 2000)

Chemical speciation is essential for the determination of the precise relationships between particle levels and measures of public health. It also facilitates understanding of toxicity, bioavailability, environmental fate and transport, particulate matter temporal and spatial variations, source/receptor relationships, and the effectiveness of emissions reduction strategies (Jeanne, Mitchell, Chris, & Jessica, 2010). The different chemical forms of a particular element and associated patterns of toxicity are best understood through the use of speciation of elements to assess the bioavailability and mobility of metals in environmental and bio-physicochemical systems. It is of utmost importance to quantify individual metallic forms since bioavailability, solubility, and metal cycles is a function of physical-chemical speciation, including how the metals are distributed within the various particulate matter matrix components (Templeton *et al.*, 2000).

Chemical sequential extraction methods have been observed to be the most versatile analytical techniques used for chemical speciation of trace metals in particulate samples. It provides elaborate information on the source, mode of occurrence, biological and physicochemical availability, mobilization, fate and transport of trace metals in the environment (Tessier, Campbell, & Bison, 1979; Betha *et al.,* 2013). According to several literatures, sequential extraction procedure has not been standardized. Individual researchers employ different developed schemes such as sequential extraction procedure developed by Tessier (Tessier *et al* 1979), the Standards, Measurements and Testing Programme of the Commission of European Communities, as well as other modified methods of individual researchers such as Fernández-Espinosa *et al.* (2002) and Jamali *et al*. (2009) scheme.

Different chemical speciation fractions can be obtained. These include soluble and exchangeable fractions, carbonates, oxides and reducible metals, organic matter, oxidisable and sulphidic metals and residual metals. Metals present in soluble and exchangeable fractions are easily adsorbed on particle surfaces and released into aqueous solutions. This fraction of the trace metals is readily bioavailable once inhaled, to the respiratory system, posing the greatest risk to human health. Those present in carbonates, oxides and reducible fractions are susceptible to pH changes and redox conditions and can be a threat to human health under acidic aquatic conditions. Organic matter, oxidisable and sulphidic metals reflect water-insoluble humic-like materials and sulphides, which would be released if conditions became oxidizing. Those present in the residual fraction usually have a stronger association with the crystalline structures of the minerals, and can only be extracted from the sample matrix under hard acid conditions. They are the most difficult to separate from the samples and therefore have the least negative impact on the environment (Adekunle, Ashaolu, & Obinka, 2015; Tahri *et al.*, 2012; Betha *et al*., 2013).

Extraction methods have been developed and applied to chemical fractionation of particle bound metals by different researchers. Feng *et al*. (2009) reported a four-step fractionation scheme applied in the quantification of $PM_{2.5}$ associated trace metals in Guangzhou, South China for twelve trace metals. The analysis of the extracts by ICP-MS (Agilent 7500A Series) indicates about 91% of cadmium, 85% of lead and 74% of arsenic present in the bioavailable forms implying significant health risks to the people residing in Guangzhou South China.

Tahri *et al*. (2012) also investigated a five-stage extraction procedure and analysis using atomic emission spectroscopy (AAS), total reflection X-ray fluorescence (TXRF) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) in two cities namely Meknes and Kenitra, Morocco. The results indicated that, in both study area, majority of the trace metals were partitioned in the residual phase (F5).

In another research, Betha *et al*. (2013) carried out a four step sequential extraction procedure for chemical speciation of twelve $PM_{2.5}$ toxic metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn) using ICP-MS from Indonesian peat fires. It was realized that Cr, Mn, Fe, Ni and Cd, were found in the exchangeable form while two carcinogenic metals Cd and Ni significantly exceeded the WHO guideline values.

2.10 Instrumental Techniques for Chemical Particle Characterization

These methods generally provide data on the elemental composition of particulate matter. There are several conventional analytical techniques for metal analysis, such as X-ray fluorescence spectroscopy (XRF), proton-induced X-ray emission spectrometry (PIXE), instrumental neutron activation analysis (INAA), flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), ion chromatography (IC), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), scanning electron microscopy coupled with energy dispersive spectrometry or X-ray (SEM-EDS/EDX), etc.

XRF and PIXE are the most commonly applied methods because they are non-destructive and are relatively inexpensive. FAAS, GFAAS, ICP-AES, and ICP-MS are very appropriate for quantitative determination after extraction of particles following suitable digestion procedures and IC is used for soluble metals. The above analytical techniques are unique in terms of their sensitivity, specific conditions for sample preparation and costs of analyses (US EPA, 1999b).

2.10.1 Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX)

Scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) is a combined analytical method for high resolution surface imaging and quantitative identification of elements present in the sample (Singh, Saini, & Taneja, 2014a). It is a non-destructive technique, which allows the same sample material to be analysed repeatedly as well as subsequent analysis by some other instrument. Also, a very small sample size such as 1 µm or less can be analysed.

SEM-EDX instrumentation consists primarily of electron source, electron lenses, sample stage, solid-state detector, semiconductor, and display monitor. SEM uses optoelectronic system to focus electrons generated by an electronic gun onto a small spot on the sample surface. The SEM electron beam penetrates the sample and generate different electron displacements, the various type of displacement emits its own unique electrons or X-rays such as secondary electrons, back scatter and signature X-ray. This unique electrons or X-rays are then separated and analysed to give the samples image and elemental map. The signals are detected from the surface of the samples using the scan coil. The SEM works by collecting secondary electrons to form an image. Due to its high resolution, the maximum magnification can reach over 100,000 times, and covers a large depth of field. Primarily, it functions by observing the sample surface and cross section micro structure (Pachauri, Singla, Aparna, Anita, & Kumari, 2013; Singh *et al.*, 2014a).

On coupling the scanning electron microscopy with an energy dispersive X-ray, it can also be used to provide qualitative or semi-qualitative information on the elements present in the sample. In order to achieve these, the EDX detector collects and separates the characteristic X-rays emitted from the sample during bombardment by SEM's electron beam. This bombardment by SEM's electron beam ejects electrons from the atoms on the surface of the sample creating a vacant space in a lower electron shell. This results in the movement of electrons from a higher electron shell to fill the vacant space in the lower electron shell; this is accompanied by emission of X-ray to balance the energy difference between the two electrons' states.

The X-ray energy is characteristic of the element from which it was emitted because each element has its unique electromagnetic radiation, hence the emitted electromagnetic radiation are used to characterize the molecular make-up of the investigated sample.

The photons of electromagnetic radiation are identified by the EDX detector (lithium-drifted silicon). A charge-sensitive preamplifier transforms the created charge pulse into a voltage pulse and the signal is forwarded to a multichannel analyzer where the pulses are sorted by voltage. These voltage measurements generate energy that is unique to each incident X-ray and communicate to a computer for display and data assessment. The spectrum of X-ray energy versus counts is used by analyst to detect the elemental composition of the sample. Only elements occurring within four (4) to ninety two (92) atomic numbers can be detected.

SEM-EDX provides useful information on the morphology (structure), semi quantitative elemental composition and density of particles as well as a better insight on the origin of particles (anthropogenic or natural processes), formation and influence on climate and human health (Galvez *et al.,* 2013; Pachauri *et al.,* 2013). Several applications of SEM-EDX to access information on the physical (morphology) and chemical composition of $PM_{2.5}$ particles in environmental studies have been reported in the literature (Margiotta, Lettino, Speranza, & Summa, 2015; Mummullage *et al*., 2016; Singh 2014b).

2.10.2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively coupled plasma-mass spectrometry (ICP-MS) is the most preferred analytical instrument for the determination of trace metals in environmental samples. It measures the emission from an excitation source, such as high temperature plasma passing through an atomizer. This plasma is gaseous mixture of atoms, cations, and electrons, fed through an induced magnetic field, which causes coupling of the ions in the mixture with the magnetic field. This eventually results in atoms and ions undergoing severe resistive heating. The advantages of ICP-MS over other elemental analysis techniques include ability to carry out simultaneous multi-element analysis, conducting analysis for both micro-levels and high-levels of substances with less matrix interferences as a result of the high-temperature of the ICP source, higher rate of sample analysis and results output than GFAAS, better sensitivity compared to ICP-AES and the ability to obtain isotopic information. The only limitation of ICP-MS is the high cost of procurement and maintenance of the instrument (Bazilio & Weinrich, 2012; Kenkel, 2003).

2.10.2.1 ICP-MS instrumentation

ICP-MS instrumentation process can be further classified into the following stages:

a) Sample introduction

Samples for ICP-MS analysis are usually prepared in a liquid form, but are injected in either a gaseous or an aerosol form into the torch. The sample is pumped from its container with a peristaltic pump to a nebulizer. The nebulizer converts the sample solution into fine droplet that flows with the argon to the torch.

(b) Torch

The ICP torch is made up of a copper induction coil entwine with a concentric quartz tube, which functions as the conduit for the plasma through the magnetic field. The quartz tube consists of three concentric tubes in one, namely the plasma (center tube), coolant gases and flowing auxiliary tubes.

The plasma is made up of a rushing stream of argon gas, partially ionized with the use of an in-line electrical discharge device prior to reaching the magnetic field. A radio frequency generator and an induction coil induce the magnetic field through the passage of an alternating radio frequency current through the coil. This results in extreme resistive heating by atoms and ions. Once appropriate amount of argon gas is made available, the plasma will attend equilibrium and maintains a constant temperature of about 6,000 °C until the entire analysis is complete. The ICP torch has the appearance of a flame as the plasma surfaces from the magnetic field. The aerosol generated through nebulization goes into the high temperature plasma, after which it is dried into solid and later converted into gaseous form by heating; a process known as atomization. These atoms absorb energy as they move along the plasma, until they release an electron, referred to as ionization. Ionization takes place in a chemically inert environment, thereby preventing the formation of oxides. This gives plasma an edge over other ionization methods (Bazilio & Weinrich, 2012; Kenkel, 2003).

(c) Interface

The sample from the ICP section of the instrument is introduced to the mass spectrometry (MS) through the interface. This interface region consists of two metallic cones, called the sampler and a skimmer cone. After ionization, the sample matrix passes through the sampler cone, made up of water cooled cone with a small orifice which enables the hot plasma gas to enter a depressurizing chamber where rapid cooling and expansion of gas takes place. A fraction of this gas passes through a skimmer cone, and into a chamber which is maintained at the same vacuum with that of the mass spectrometry. These extracted ions are carried by ion optics into the vacuum chamber (Batsala, Chandu, Sakala, Nama, & Domatoti, 2012).

(d) Optical path for the ICP instrument

The plasma is viewed horizontally by an optical channel. Light from the plasma is focused through a lens and passed through an entrance slit into the spectrometer. There are two types of spectrometers used in ICP-MS analysis:

(i) **Sequential Optical Path**: The sequential optical path employs a monochromatic and the emissions are measured one wavelength per time by rotating the dispersing element while the individual lines emerge from the exit slit. A phototube does measurement for all emission lines. The benefits of this option are that all wavelengths of measured elements can be utilized, and with careful wavelength selection, spectral interferences can be avoided. The disadvantage is that it is a slower process.

(ii) **Simultaneous Optical Path**: The simultaneous direct reading polychromatic design uses several exit slits and photo tubes for measuring a number of lines simultaneously. Specific wavelengths to be measured are programmed by the manufacturer. This option is a fast process, because all intended wavelengths are measured simultaneously. This is beneficial especially for samples with known matrices since it can be preset to the optimum wavelengths. However, there could be possibility of spectral interferences and it is quite expensive to change the wavelength (Kenkel, 2003)

(e) Mass Spectrometry

A source of charged monoatomic ions from the ICP source is fed into the mass spectrometer for analysis through the mass analyzer. Signal intensity generated due to the analyte ion is proportional to the concentration of the analyte in the sample. It is conventional to observe more than one analyte ion for a specific element leading to the appearance of multiple signals for the analysed element. This is so, because of the occurrence of many naturally occurring isotope. To resolve this, since almost all elements have an isotope mass that is different from any other element, the signal associated with the spectral interference is usually ignored in favour of the one generated by a single element (Batsala *et al*., 2012; Bazilio & Weinrich, 2012; Kenkel., 2003).

2.11 The Air Quality Index (AQI) for Fine Particle Pollution ($PM_{2.5}$)

Air quality index (AQI) is defined by the concentration of specific pollutants in air. It is also known as a single number for reporting the quality of air with respect to its effects on the human health (Bishoi, Prakash, & Jain, 2009). AQI is a colour-coded tool for notifying the public how clean or polluted the air is, and ways to reduce their daily exposure to pollution. The AQI focuses on health effects that can happen within a few hours or days after breathing polluted air (US EPA, 2014). Several countries such as the United States of America (USA), the United Kingdom (UK), China, Canada, Belgium, France, Malaysia, Thailand, Indonesia and Taiwan, amongst others use AQI to communicate air quality status.

2.11.1 Types of Air Quality Index System

Two most current air quality index systems are the United Kingdom (UK) and the United States Environmental Protection Agency (US EPA) index system. The UK index system has a 1-10 index scale, which are further grouped into 4 bands: low (1-3), moderate (4-6), high (7-9) and very high (10). The individual bands have different interpretation for the groups at risk and the general population (Cairncross, John, & Zunckel, 2007).

The USEPA AQI is scaled from 0 to 500 for ambient concentration, where an AQI value of 50 represents good air quality, while an AQI value of over 300 represents hazardous air quality. An

AQI value of 100 corresponds to the NAAQS set by the EPA to protect public health. The index value of 100 is set at the level of the current 24-hour $PM_{2.5}$ standard, which is 35 $\mu g/m^3$. Therefore, AQI values below 100 are said to be satisfactory. When AQI values are above 100, air quality is considered as unhealthy - at first for certain sensitive groups of people, then for everyone as AQI values rise (US EPA, 2014). The index values, descriptors and colours associated with the US EPA AQI system are as shown on Table 2.2.

Table 2.2: US EPA AQI colour and health implications

AQI Values	Levels of Health Concern	Colour
0-50	Good	Green
51-100	Moderate	Yellow
101-150	Unhealthy for Sensitive Groups	Orange
151-200	Unhealthy	Red
201-300	Very Unhealthy	Purple
301-500	Hazardous	Maroon

Source: US EPA, 2014

Each category corresponds to a different level of health concern. Considering the fine particle pollutant, the six levels of health concern, their implication and actions to take in protecting human health from particle pollution are:

(i) "Good" AQI is 0 – 50: Air quality is considered satisfactory, and air pollution poses little or no risk, No action required.

(ii) "Moderate" AQI is 51 – 100: Air quality is acceptable; however, the unusually sensitive people may consider reducing prolonged or heavy exertion.

(iii) "Unhealthy for Sensitive Groups" AQI is 101 – 150: implies that this AQI range may not affect the general public, but could affect persons with heart and lung disease, older adults and children.

(iv) "Unhealthy" AQI is 151 – 200: Everyone may begin to experience some adverse health effects, and members of the sensitive groups may experience more serious effects.

(v) "Very Unhealthy" AQI is 201 – 300: This implies that everyone may experience more serious health effects.

(vi) "Hazardous" AQI greater than 300: This would trigger health warnings of emergency conditions. The entire population is more likely to be affected (US EPA, 2014).

2.12 Human Health Risk Assessment

Human health risk assessment refers to the characterization of the potential adverse health effects on humans due to exposures to hazardous or toxic chemical pollutants in the environment. Some of the adverse health effects include: cancer, developmental disorders, birth defects, etc. (Zheng *et al*., 2016). Risk assessment is employed to examine the human health impacts as a function of exposure to contaminants through multiple exposure pathways such as inhalation, ingestion, and dermal contact (US EPA, 2012b).

Several hazardous air pollutants for example benzene, nitrosamine, trace metals (arsenic, cadmium, nickel, beryllium, chromium, etc.) have been classified as human or animal carcinogens by IARC and US EPA. This is so based on the overwhelming evidences of results from cohort studies pointing to an increase in cancer risk after inhaling air with relative levels of these pollutants. Two major factors, oxidation states and chemical structures determine the carcinogenic capability of these metals (Mulware, 2013). Carcinogenic hazardous air pollutants do not have effective threshold which makes a receptor susceptible to the risk of developing cancer even at low doses. On the contrary, non-carcinogenic hazardous air pollutants have a threshold signifying a dose level below which no health risk can occur (Koki, Bayero, Umar, & Yusuf, 2015). Chronic human health toxicity values, such as cancer inhalation unit risk (IUR) and reference concentrations (RfCs) estimates for cancer and non-cancer chemicals respectively for the inhalation exposure pathway assessment can be obtained from Integrated Risk Information System (IRIS) website (IRIS, 2015).

The process of health risk caused by $PM_{2.5}$ bound metals occurs through inhalation of these particles during breathing. Once inhaled the particles are deposited on the human respiratory system, where it easily gets in contact with the gastric juice in the gastrointestinal tract, releasing the bio-available trace metal fractions which subsequently get absorbed into the human physiological systems inducing adverse toxic effects (Mukhtar and Limbeck, 2013). Different studies have assessed toxic health risk of hazardous and toxic pollutants in inhalable particles, including trace metals (Hu, Waller, Lyapustin, Wang, Liu, 2013; Li *et al*., 2013; Xu, Hao, & Xie, 2014; Zheng *et al.,* 2016) polycyclic aromatic hydrocarbons (Kaushik, Sangwan, & Haritash, 2012) and nitrosamines (Farren *et al*., 2015).

2.12.1 Steps in Risk Assessment

According to NRC (1983), US EPA (2009) and IEc (2009), risk assessment can be further classified into four steps (Figure 2.3), as follows:

(i) **Hazard Identification**

Hazard identification involves carrying out analysis on the contaminants to determine whether exposure to the contaminant can cause an increase in specific adverse health effects (e.g., cancer, birth defects) in humans. When considering chemical pollutants, the process examines the available scientific data for each monitored chemical contaminant in order to identify the potential hazards (carcinogenic and non-carcinogenic) posed by these chemical pollutants.

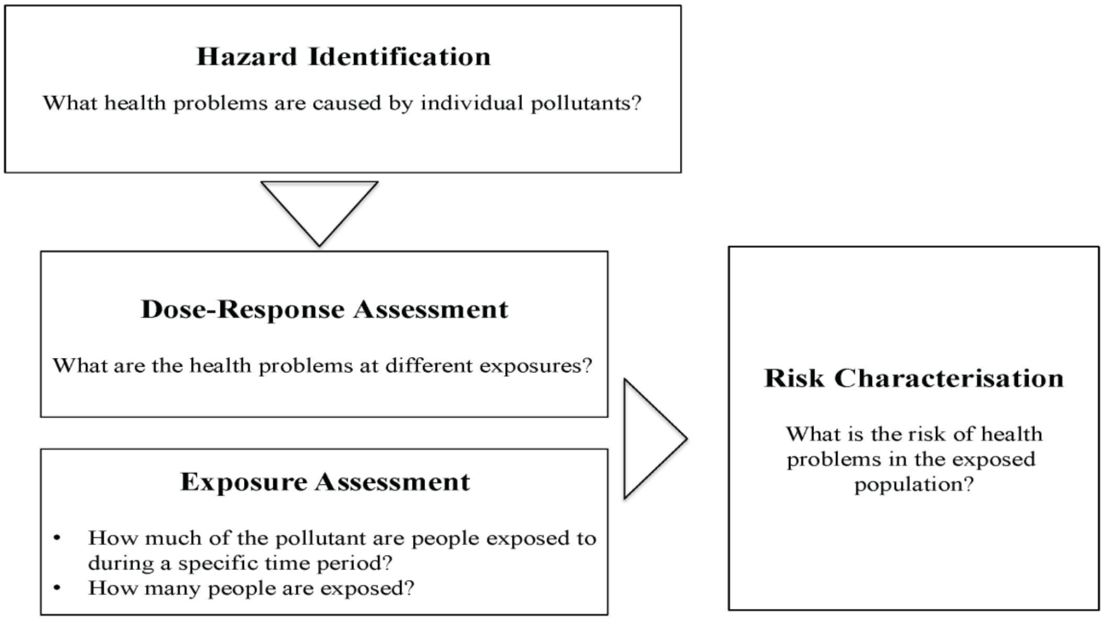

Figure 2.3: The 4 step risk assessment process (Adopted from US EPA, 2015a)

(ii) **Concentration-Response Assessment**

A concentration-response assessment describes how the adverse health effect that rises from exposure to toxic chemical contaminants is related to the amount and degree of exposure. In order to estimate the cancer risk from inhaled chemical contaminants such as trace metals, selected inhalation toxicity values for each of the contaminant of potential concern (COPC) such as RfCs for analyzing non-cancer risks and IURs for cancer risk analysis are employed.

(iii) **Exposure Assessment**

This refers to the process of quantifying and estimating the intensity, frequency, and duration of individuals' exposure to toxic chemical contaminants in the environment.

(iv) **Risk Characterization**

This is the final step of risk assessment. It examines the magnitude of toxic chemical contaminants, taking into account the amount of exposure and the extent of the effect on humans.

2.13 Source Apportionment (SA)

Source apportionment is the practice of identifying and apportioning pollutants to their sources (Belis *et al*., 2014). According to Environment & Climate Change Canada (2013) and Belis *et al*. (2014), the objectives of source apportionment studies amongst others include:

(i) relating emissions to the characteristics of targeted aerosols at a specific receptor site,

(ii) evaluating the effectiveness of control strategies over time,

(iii) improving emission inventories by determining major sources of air pollutants such as particulate matter and other contaminants,

(iv) strengthening environmental management, particularly at regional and local levels,

(v) providing data to support the reduction of emissions via integrated strategies, and

(vi) development and implementation of policies protecting human health and the environment.

2.13.1 Ways of Performing Source Apportionment

Source apportionment can be performed in two ways namely dispersion modeling and receptor modeling:

(i) Dispersion Model

This is a series of equations that mathematically describe the behaviour of pollutants in the air. Based on knowledge of emissions and other factors like meteorological variables, pollutant concentration can be predicted through the use of physics, mathematical, and chemical calculations at some distance from the source.

(ii) Receptor Model

Receptor model identifies and quantifies the sources of atmospheric particles and the contributions of these sources through the information obtained from pollutant concentrations (BCAQ, 2013; US EPA, 2015b).

Among both models, receptor modeling is the most commonly used source apportionment technique. Several receptor models such as enrichment factors (EFs), factor analysis, chemical mass balance (CMB), principal component analysis (PCA), cluster analysis, fourier transform time series amongst other multivariate data analysis methods have been used for source apportionment of pollutants at a receptor location (Belis *et al.*, 2014, Pipalatkar *et al.*, 2014). The most widespread receptor methodologies used in SA studies include, the principal components analysis (PCA), positive matrix factorization (PMF) and chemical mass balance (CMB) (Pipalatkar *et al.*, 2014). Further discussion will only be done on receptor models applicable in the study; these are cluster analysis, principal component analysis (PCA) and factor analysis.

2.13.2 Cluster Analysis

Cluster analysis aims at identifying groups, or clusters, of similar objects characterized by a multivariate feature set in a large class of data-analysis techniques. Hierarchical cluster analysis (HACA) is the most commonly used method in cluster analysis. HACA uses the original data matrix, by constructing an appropriate matrix of similarity measures among objects and the most similar pair of objects is combined to produce a new "clustered" object, and the process is continuous and considered complete when all objects have at least a single cluster. A more widely used similarity measure for cluster analysis is the Euclidean distance metric. The information is usually displayed as a two-dimensional linkage diagram known as a dendrogram. The dendrogram reduces the original data matrix to a two-dimensional graph that illustrates, the presence of distinct groups of samples, with each group containing objects. The power of hierarchical clustering methods to reduce systematically, complex multidimensional data to a two-dimensional representation makes clustering techniques popular, and widely employed (Adams, 2004).

2.13.3 Principal Component Analysis (PCA)

Principal component analysis is used primarily for data reduction and information extraction. It is among the most preferred multivariate statistical techniques employed for the extraction of linear relationship among set of variable and providing information on the relevant parameters with minimum loss of original information. PCA characterizes patterns within large sets of data through a rotated coordinate system that explains variability to a large extent by the first few dimensions that the eigenvectors of the variance covariance matrix are computed, to obtain the principal component score (Chen *et al*., 2013). The scores of the original variables, otherwise known as principal component loadings (PC loadings), are applied to show the relationship between the variable and the principal component. This reduces the raw data matrix to two or three principal component loadings that account for the majority of the variance. The ability to perform chemical interpretation of eigenvectors is the underlying reason for the success of PCA (Adams, 2004; Chen *et al*, 2013**)**.

2.13.4 Factor Analysis

The PCA process can be extended further to factor analysis. Factor analysis attempts to identify and interpret the nature of the exact causal forces of the various parameters describing a system, resulting in the state of the system as it is observed. It is a multivariate statistical technique that communicates source apportionment information on a measurement site (Belis *et al*., 2014; Martinez *et al*., 2012).

The aforementioned multivariate statistical techniques are computed easily with the abundance of available statistical and mathematical software namely; the statistical package for the social sciences (SPSS) (Chen *et al*., 2013; Li *et al*., 2013), Xlstat (Basha, Yasovardhan, Satyanarayana, Reddy, & Aerattukkara, 2014; Mustaffa, Latif, Ali, & Khan, 2014; Dominick, Juahira, Latifc, Zaind, & Aris, 2012), minitab (Murillo *et al*., 2013), and statistica (Shah, Shaheen, & Nazir, 2012).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the Study Area

The study area for this research was Ogun State, one of the most industrialized States in Nigeria with a population of about 3,751,140 (NPC, 2006; OGS, 2016). The sampling locations were selected based on ease of access, lack of local source of contamination, operator's safety, security of equipment and the existing anthropogenic activities responsible for air pollution. The study location comprised of three industrial areas and a background: Ota Industrial Estate (OTE), Ewekoro Community (EWC), Agbara Industrial Estate (AGE) and one background location which was Covenant University Farm (CUF). Three sampling sites were further mapped out from each study location. The abbreviations for the different sampling sites are as follows OTE (OA, OB, and OC), EWC (EA, EB, and EC), AGE (AA, AB, and AC) and CUF (CA, CB, and CC) as shown in the map in Figure 3.1. A hand-held Garmin-GPSMAP 76S-type global positioning system was used to identify the sampling locations. The coordinates and major activities in these locations can be seen on Table 3.1.

Ewekoro is domiciled in Ewekoro Local Government Area (LGA). It is a major town along Sango-Ifo, Abeokuta expressway of Ogun State, with Papalanto in the west, Abeokuta in the East and numerous villages along the northern and southern axis. This community is well known for its rich deposits of limestone. The major industries found here are the Lafarge Cement WAPCO Nigeria Plc, Portland Paint and Products PLC and Dulphin Steel Industry. The three sampling sites in Ewekoro were located at Iyana Egbado Ajegunle (site EA), Ewekoro village close to Lafarge Cement Plant 1 (site EB) and Ajobiewe village (site EC).

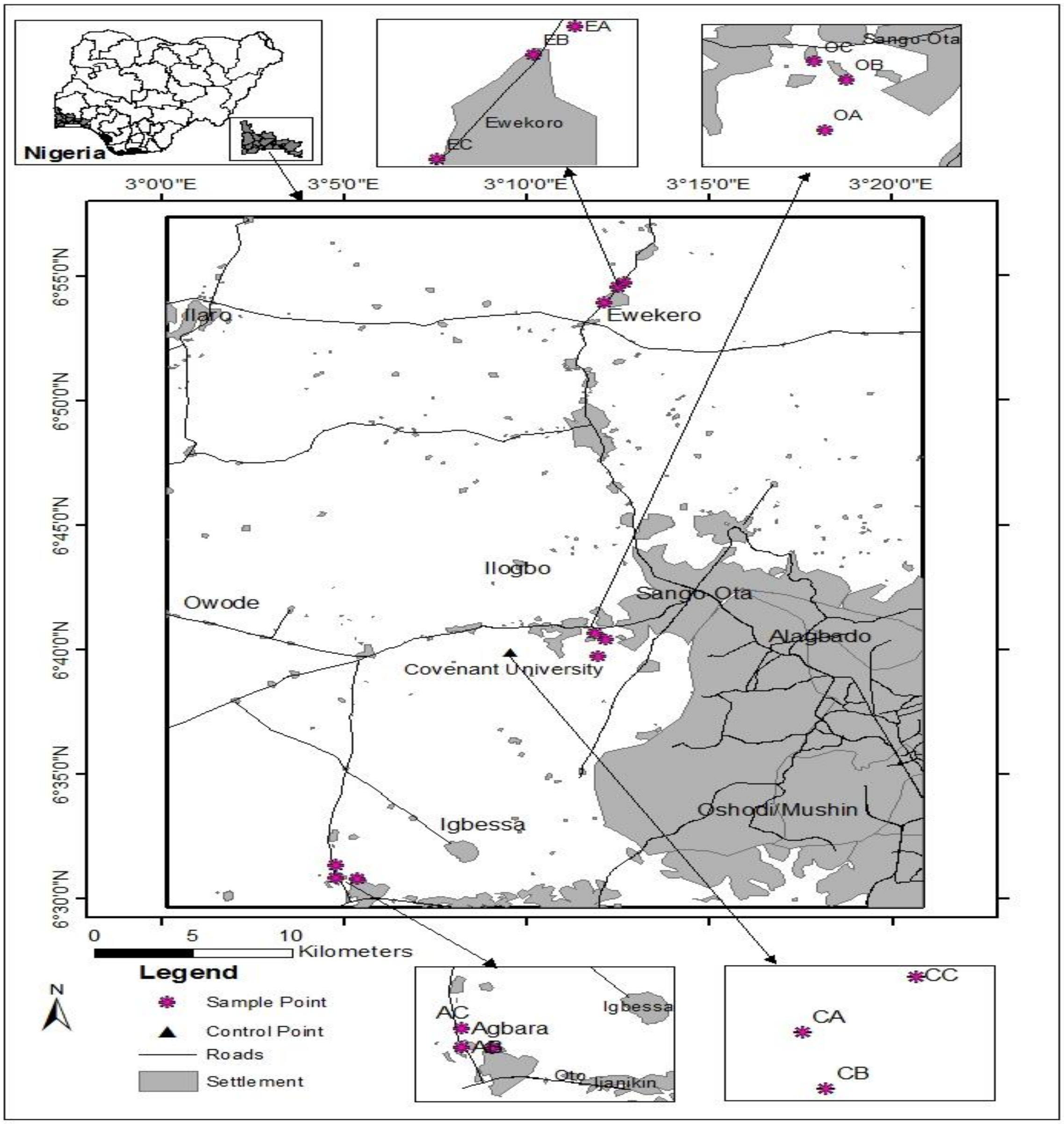

Figure 3.1: Sampling sites of $PM_{2.5}$. Insert: Map of Nigeria showing the location of the study areas.

Table 3.1: Description of sampling site, number of samples and major local emission sources

Location	Site classification	Coordinates	No. of samples	Sampling period		Study site activities
				Wet season	Dry season	
Ota Industrial Estate	OA	31N 0522050 UTM 0736371	36	July, Sept., Oct. 2014	Nov. 2014 – Jan. 2015	Recycling of metal scraps, schools, churches, residential houses, manufacturing of plastics, zinc, chemical products, detergent, steel mill, vehicular traffic, commercial shops, etc.
	OB	31N 0522403 UTM 0737629				
	OC	31N 0521866 UTM 0738087				
Ewekoro Commnunity	EA	31N 0523383 UTM 0763957	36	July, Sept., Oct. 2014	Nov. 2014 – Jan. 2015	Cement and paint manufacturing, recycling of scraps, constructions, railway line, schools, tipper park, farming, vehicular traffic.
	EB	31N 0523068 UTM 0763651				
	EC	31N 0522334 UTM 0762491				
Agbara Industrial Estate	AA	31N 0509888 UTM 0719892	28	Oct. 2014	Nov. 2014 – Jan. 2015	Food, drugs, beverage industries, gas plants, wood mills, hospitals, schools, churches, vehicular traffic, residential houses, constructions solid waste combustion, mechanic-workshops, etc.
	AB	31N 0508845 UTM 0719916				
	AC	31N 0508802 UTM 0720895				
Covenant University Farm, Ota	CA	31N 0517520 UTM 0736588	36	July, Sept., Oct. 2014	Nov. 2014 – Jan. 2015	Farming, welding of farm tools and a farm house.
	CB	31N 0517526 UTM 0736567				
	CC	31N 0517549 UTM 0736609				

Ota and Agbara industrial estates are located in Ado-Odo/Ota local government area which borders on metropolitan Lagos. Ota industrial estate is situated in Ota, the capital of Ado-Odo/Ota local government area. Residential estates are also found within the Ota industrial estate. Site OA, in Ota industrial estate is located close to SFURNA Global Limited, involved in melting of aluminum and heavy recycling of metal scraps and used batteries. Other industries within the vicinity include Plenco Limited (manufacturing of plastic), Sand and Sun industries (recycling of metal scraps), and Aarit Steel (zinc manufacturing). Site OB is located in the Baptist Church compound which acts as a boundary between the industrial and residential area. Other Industries within this vicinity are Tower, Kolorkote Nigeria Limited, LEXCEL Limited, Vego Nigeria Limited, West African Building Materials, MINL Nigeria Limited, Human Nigeria Limited (steel and galvanized pipes). The OC sampling site lies along an unpaved street between Nycil and Sonnex Industries at the back of Daraju Industry. Other surrounding companies are Federated Steel Mill Limited and a Gas Plant Company.

Agbara industrial estate is located in Agbara, Ogun State. It is a highly industrialized area sandwiched between Ogun State and Lagos State. It is a home to a number of manufacturing industries including Glaxo Smith Kline Nigeria Plc., Nestle Nigeria Plc., P&G Nigeria, Shell Petroleum Development Corporation (SPDC), Unilever Nigeria Plc., etc. Also, two residential estates, Agbara Estate Phase II and Opic Estate are located in Agbara Industrial Estate. Table 3.1 shows the description of the three sites. Site AA, is located in a private facility at the centre of Agbara Estate Phase II, a residential estate which houses over 150 residential buildings. Site AB is located outside the premises of Unilever Nigeria Plc., involved in the production of savouries, toothpastes detergents, etc. Site AC is located at Living Faith facility in Opic estate, a residential estate within Agbara. Opic estate houses over 100 residential buildings.

Covenant University Farm is located in Ota. It is selected to represent a background location for comparative purposes being a farming environment with no nearby point source. It houses a farm building where small scale fabrication and repair of farm tools are done. Site CA, is located around the farm house, while CB and CC are positioned inside the farm.

It is worth noting that the predominant land-use of the various study areas are considered while selecting the sampling locations. since all the industrial areas are surrounded also by residential and commercial areas, with heavy vehicular traffic, and unpaved roads.

3.2 Sampling of $PM_{2.5}$

3.2.1 Filter Preparation

Before and after sampling, the filters were equilibrated in a desiccator for 48 hours to eliminate the effect of humidity and also obtain accurate PM measurements. After which, 47 mm diameter polytetrafluoroethylene (PTFE) Teflon filters and 46 mm Whatman GF/C glass fibre filter papers were weighed thrice using four-digit balance (Mettler Toledo Me 204).

3.2.2 Equipment Preparation and Set up

The ambient $PM_{2.5}$ samples were collected according to standard methods with Environtech gravimetric sampler, model SLE-FPS105 using $PM_{2.5}$ inlet (US EPA, 1999b). The preweighed, coded and conditioned filters were placed in the filter holder and screwed properly before turning on the sampler. Large volumes of air were pulled through a filter-based high volume vacuum device where the particulates were collected on conditioned filters which were placed in the sampler. The flow rate and time were recorded before and after sampling for duration of 4 hours on each site. After sampling, the $PM_{2.5}$ filter papers were removed with forceps, stored in a petri dish, conditioned, weighed, and stored in the refrigerator at 4^{o} C to prevent thermal degradation and evaporation of volatile components prior to further analysis. Field and laboratory blank samples were collected in order to reduce gravimetric bias that may result from filter handling, before, during and after sampling. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. The monitoring and sampling period were spread for six (6) months namely July, September and October 2014 in wet season and November, December and January 2014/2015 in the dry season with a total of 136 sampled filters and 24 quality control samples. It is important to note that sampling could not be done at the AGE site for the months of July and September 2014 during the wet season due to serious resistance by the security arm of one of the industries in collaboration with the estate security.

3.3 Determination of $PM_{2.5}$ Mass Concentration

The particle mass concentrations were determined using the gravimetric method of analysis. This was done by subtracting the initial average mass of the blank filter from the final average mass of sampled filter. Filters were repeatedly weighed using an electric micro-weighing balance (Mettler Toledo Me 204) 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 (CEPA, 2002; US EPA, 1999b). The mass concentration of $PM_{2.5}$ in the ambient air was then determined by the following equation:

$$M_{2.5} = \left(M_f - M_i\right) \times 10^6 \qquad (3.1)$$

where:

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

M_f = final mass of conditioned filter after sample collection (g)

M_i = initial mass of conditioned filter before sample collection (g)

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

Therefore,

$$PM_{2.5} = \frac{M_{2.5}}{V} \qquad (3.2)$$

$PM_{2.5}$ = mass concentration of $PM_{2.5}$ particulate (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 16.7 (L/min)

t = duration of sampling period in minutes

10^{-3} = Unit conversion factor for litres (L) into cubic metre (m^3)

3.4 Meteorological Data Analysis

Nigeria belongs to the tropical climate and has two distinct seasons, namely wet and dry seasons. This study kicked off in the wet season, which was observed for the months of July, September and October. During this period, the weather was characterized by moderate to heavy rainfall and highly humid conditions. Dry season spanned from November to January, with the following weather conditions: clear sky, moderate to high solar radiation, moderate to high air temperature and no precipitation. In addition, a short harmattan period was observed from late December to mid-January. Very dry and dusty weather along with low humidity was experienced during this period which was attributed to the contribution of wind borne dust due to the North-east trade winds from the Sahara desert. Daily mean meteorological parameters such as atmospheric temperature, wind speed, wind direction, relative humidity and precipitation for July, September and October 2014 in wet season and November, December and January 2014/2015 for dry season were monitored at Nigerian Meteorological Agency (NIMET), Abeokuta station, Ogun State. The average values for the obtained data were calculated for the sampled days.

3.5 Extraction of Filter Samples for Total Trace Metals using Acid Digestion Method

Filter samples were shredded into tiny pieces with stainless steel scissors in a labeled centrifuge tube and poured into the microwave Teflon vessel. The 10.0 mL of the extraction solution, 7 mL HNO_3 (69%) and 3 mL HCl (70%) was added with the aid of a micro eppendoff dispensing pipette, to each of the centrifuge tubes. The vessel caps and pressure release valves were properly tightened on the vessels and placed in their respective numbered positions (1 to 24) in the carousel. The carousel containing vessel was positioned in the CEM MARS 6 microwave reaction system, one touch technology and the instrument turned on, operating conditions such as extraction method, load samples, and sample type (filter membrane) was chosen and start button was pressed to commence the extraction process. A 20 minute extraction time was displayed by the instrument. The same extraction procedure was performed on blank filters. A final extraction volume of 8 mL was filtered with Whatman No. 41 into a polyethylene bottle and the final volume made up to 13 mL and kept at $4^{o}C$ in the refrigerator prior to ICP-MS analysis according to US EPA method IO-3.5 (US EPA, 1999b).

3.6 Determination of Chemical Speciation

The modified Tessier derived procedure by Fernandez-Espinosa, Rodríguez, and Álvarez (2004) and Smichowski, Polla, Gomez, Fernandez Espinosa, and Lopez (2008) was followed. This procedure used a combination of mechanical shaker and microwave oven was followed to fractionate the $PM_{2.5}$-bound trace metals into four fractions. These fractions were soluble and exchangeable metals (F1), acid soluble carbonates, Mn, Fe oxides and reducible metals (F2), metals bound to organic matter, oxidisable and sulphidic metals (F3) and residual metals (F4). Table 3.2 outlines the multistep procedure adopted for this work.

Table 3.2: Chemical speciation reagents and extraction conditions

Metallic fraction	Reagent	Experimental conditions
F1: Soluble and exchangeable metals	15 mL H_2O (pH=7.4)	Shaker agitation, 3 hrs at RT[a]
F2: Carbonates, oxides & reducible metals	10 mL $NH_2OH.HCl$ (0.25 M) at pH=2.0	Shaker, 2hrs at RT
F3: Bound organic matter, oxidizable and sulphidic metals	a) 7.5 mL H_2O_2, 30% b) + 7.5 mL H_2O_2, 30% c)+15 mL NH_4AcO [2.5 M] at pH=3.0	Shaker at $\Delta T(95\ ^oC)$[b] Shaker at $\Delta T(95\ ^oC)$[b] Shaker, 90 min. at RT
F4: Residual metals	10 mL (HNO_3: HCl: HF) (ratio = 2: 6:2) + boric acid	20 min at MW oven

[a]RT= room temperature; [b]ΔT= applied heat; MW= microwave (Fernandez-Espinosa *et al*., 2004; Smichowski *et al*., 2008).

The following procedures were used to fractionate the $PM_{2.5}$-bound trace metals into four fractions, were as follows:

1. Fraction 1: The strips of each sample were extracted with 15 mL of ultra-pure water in 50 mL polypropylene centrifugal tubes and adjusted to pH 7.4 by adding NH_4OH, followed with continuous agitation at room temperature in a mechanical shaker (ZWY-11OX 30, Zhicheng) at 55 rpm for three hours. The extracted solutions were separated from the filters by centrifugation (HC-3514, Zonkia) at 5000 rpm for 3 min. Extracts were carefully filtered and aliquot of 10 mL of the supernatant was drawn with a micropipette

and placed in a preconditioned 15 mL polyethylene.

2. Fraction 2: The residue from F1 fraction was treated with 15 mL of 0.25 M hydroxylamine hydrochloride acidified to pH 2 with HCl in the 50 mL polypropylene centrifugal tubes. The closed polypropylene tube was set for continuous agitation at room temperature in a mechanical shaker at 110 rpm for two and a half hours. The samples were subsequently centrifuged for 3 minutes at 5000 rpm. Extracts were carefully filtered and aliquot of 10 mL of the supernatant was drawn with a micropipette and placed in a preconditioned 15 mL polyethylene tube. The F2 filter residue obtained was used for the next extraction.
3. Fraction 3: The F2 fraction residue was further extracted with 7.5 mL of 30% H_2O_2. The closed polypropylene tube was set for continuous agitation at 95^o C in a mechanical shaker at 55 rpm for 90 min. This step was repeated twice. After which, 15 mL of 2.5 M NH_4AcO acidified at pH 3 was added and the procedure repeated at room temperature before centrifuging the extract for 3 minutes at 5000 rpm. Extracts were carefully filtered and aliquot of 10 mL of the supernatant was drawn with a micropipette and placed in a preconditioned 15 mL polyethylene tube. The F3 filter residue obtained was used for the next extraction.
4. Fraction 4: The F3 residue was extracted with 10 mL of 1:2:1 mixture of 65% HNO_3 (2 mL), 37% HCl (6 mL) and 40% HF (2 mL) in a microwave Teflon vessel. The oven was operated according to the same programme that was used for total trace metal determination as described in section 3.5. After cooling, 170 mg of boric acid was added to remove any residual HF. Extracts were carefully filtered and aliquot of 8 mL of the supernatant was taken with a micropipette and placed in a preconditioned 15 mL

polyethylene tube. The above four-steps chemical extraction procedure were repeated on blank filters and all the extracts obtained were preserved at 4° C in the refrigerator before analysis with ICP-MS.

3.7 Determination of Bioavailability Index (BI)

The first two fractions (F1 and F2) were labile fractions and completely bioavailable (Betha *et al.*, 2013; Tahri *et al.,* 2012). The bioavailability index (BI) was calculated using equation (3.3) below:

$$BI = \frac{F1 + F2}{\sum_{i=1}^{4} F_i} \tag{3.3}$$

3.8 Analysis of Trace Metals using Inductively Coupled Plasma Mass Spectrometry

All solution samples were analysed for 22 trace metals, namely, As, Cr, Pb, Ni, Cd, Mn, Ti, V, Ba, Fe, Al, Mo, Ca, Zn, Cu, Mg, Sr, Se, Ag, K, Na, and Sb, using ICP-MS (Agilent 7500ce Series), equipped with an octopole collision cell following the operating conditions as listed in Table 3.3.

Calibration of the ICP-MS instrument was performed with multi-element calibration standards from 10 to 1000 mg/L. During the measurement, ^{6}Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{71}Lu and ^{209}Bi at 100 mg/L were used as the internal standards to monitor possible instrumental drifting and to compensate for the matrix effect. During the acid digestion and sequential extraction procedures, each of the samples were analysed in triplicates in order to evaluate the precision of the analyses. Blank filters and field blanks were analyzed simultaneously and the sample results were corrected by the average of blank concentrations. Also, recovery, reproducibility or precision test and the detection limit of trace elements were determined following US EPA method IO-3.5 (Fernández-Espinosa *et al.*, 2002; US EPA, 1999b; Ventura, Amaral, Wanderley, Godoy, & Gioda, 2014).

Table 3.3 Operating conditions of the Agilent 7500ce ICP-MS instrument

RF power	1410 W
Plasma gas flow rate	15 l/min
Auxiliary gas flow rate	1.0 l/min
Carrier gas flow rate	0.90 l/min
Makeup gas flow rate	0.17 ml/min
Nebuliser	Microflow
Nebuliser Pump	0.10 rps
Torch injector internal diameter	2.5 mm
Sample depth	8.1 mm
Interface	Ni skimmer cone
CeO+/Ce+	1.12%
Gas/flow rate	18 l/min
Octopole bias	-6.0 V
Quadrupole bias	-3.0 V
Integration time varied over mass range	0.3s
No of replicates per sample	3
Internal standards	^{6}Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{71}Lu and ^{209}Bi

3.9 Cancer Risks Assessment

The cumulative lifetime cancer risk for a receptor exposed to the target trace metal species via the inhalation pathway was assessed using the inhalation dosimetry methodology outlined in EPA's Risk Assessment Guidance for Superfund (RAGS). The concentration of the target metal in air (µg/m^3) was used as the exposure metric, instead of the intake of contaminants in air based on inhalation rate and body weight (mg kg^{-1} day^{-1}) (US EPA, 2009). Initially, the exposure concentration (EC), which is a time weighted average concentration, was calculated for each individual contaminant according to equation 3.4:

$$EC = \frac{CA \times ET \times EF \times ED}{AT} \qquad (3.4)$$

where:

EC ($\mu g/m^3$) = Exposure Concentration.

CA ($\mu g/m^3$) = Concentration of the metal in the air to which the person is exposed.

ET (hours/day) = Exposure time. Duration of an individual exposure in a day;

EF (days/year) = Exposure frequency (days/year). Evaluates the frequency of an individual exposure for a year. When the exposure period is less than a year, exposure frequency is expressed in days/week;

ED (years) = Exposure duration (years). Describes how long an individual is likely to be exposed during their lifetime. When the exposure period is less than a year, exposure duration is expressed in weeks; and

AT (hours) = Averaging time. For carcinogens, exposure is averaged over the course of a lifetime; AT (lifetime in years x 365 days/year x 24 hours/day) = averaging time

The cumulative lifetime cancer risk is then calculated using equation 3.5 (IEc, 2009):

$$Risk_{inhalation} = \sum_{i=1}^{n} IUR_i \times EC_i \qquad (3.5)$$

Where: IUR ($\mu g/m^3$)$^{-1}$ = Inhalation unit risk specific for each carcinogen ($\mu g/m^3$); and

EC ($\mu g/m^3$) = exposure concentration

The IUR can be defined as the upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of one (1) $\mu g/m^3$ in air. IUR values were obtained from databases provided by the EPA’s Integration Risk Information System (IRIS) and Provisional Peer Reviewed Toxicity Values (PPRTVs) (IRIS, 2015; IEc, 2009).

3.10 Determination of Particle Morphology and Elemental Composition Using Scanning Electron Microscope Coupled with Energy Dispersive X-ray (SEM-EDX)

The surface morphologies and elemental composition of airborne particles of $PM_{2.5}$ samples were examined by field emission scanning electron microscopy (FESEM, Hitachi, and SU-8020) coupled with energy-dispersive X-ray spectroscopy (EDX, Oxford X-Max^N). The 0.5 cm of the dry and loaded Teflon and glass fibre filter paper samples were cut off and mounted on aluminum stubs with carbon-conductive tape. A very thin film of platinum (Pt) was deposited on the surface of the samples using auto fine coating (Jeol JEC 3000PC). The fine coating of platinum makes the samples electrically conductive. The samples were placed in the corner of SEM-EDX chamber. Three images of one sample were taken at a magnification of X1500, X5000, X20000. EDX spectra of individual particles were obtained for determination of individual elemental composition of particles after scanning an electron beam with an accelerating voltage of 20 kV, a beam current of 10 µA and a Si (Li) detector 15 mm away from the samples to be analysed. Peaks were identified manually by entering the atomic symbol and then scrolling through the periodic table. The quantifying function of the computer programme was used to determine the peak intensities and the resulting intensities were converted to percentage weight (Pipal & Satsangi, 2015).

3.11 Statistical Analysis

The basic statistical parameters, correlation analysis, along with multivariate statistical methods comprising principal component analysis (PCA) and hierarchical agglomerative cluster analysis (HACA) were performed on the dataset using the XLSTAT PRO 2015 software.

3.11.1 Pearson Correlation Matrix

The trace metal concentrations of $PM_{2.5}$ samples were subjected to statistical analysis to determine the Pearson correlation matrix of the metals. Correlation was considered significant at the 0.05 level (Basha *et al*., 2014; Mustaffa *et al*., 2014).

3.11.2 Principal Component Analysis

Principal component analysis (PCA) is a multivariate statistical method used to identify possible sources for the detected elements. PCA reduces the number of elements into components by assembling a set of new variables based on the interrelations present in the original data set. Elements that were present at levels below the limit of detection in more than half of the samples were excluded from the PCA. In cases where an element was below the limit of detection in less than 50% of a particular sample, its concentration was assumed to be half the limit of detection. This was done to avoid having to further reduce the size of the data set (Mustaffa *et al*., 2014).

Dominick *et al*. (2012) stated that the principal components (PCs) can be obtained from equation (3.6):

$$Z_{ij} = a_{1i} x_{1j} + a_{2i} x_{2j} + \; .... \; + a_{ni} x_{nj} \qquad (3.6)$$

Where:

Z = component score,
a = component loading,
x = measured value of the variable,
i = component number,
j = sample number and
n = total number of variables.

The PCs were calculated by ordering the variables in a manner in which the first variable (PC) explains the highest proportion of variability within the original data. The second PC explains the highest proportion of the variability that was not explained by the first PC. Varimax rotation was applied to produce a better relationship between the PCs and the original variables. Varimax rotation ensures that each variable is maximally correlated with only one component and has a near zero association with the other components (Dominick *et al*., 2012). To obtain the new varimax factors, only PCs with significant values whose eigen value is more than one (1) were considered. The number of factors that were retained in each case was determined by the scree plot.

3.11.3 Hierarchical Agglomerative Cluster Analysis (HACA)

HACA is a statistical tool employed in the classification of variables into groups, or clusters. HACA was applied using Ward's method and Euclidean distance measurement to explore the spatial relationships among the objects. This involved examining their distances, obtaining a graphic display of how these objects are clustered, and reporting of results in the form of dendrogram (Latif *et al*., 2015; Shah *et al*., 2012).

3.12 Air Quality Index (AQI)

AQI was calculated using $PM_{2.5}$ concentration data, the two breakpoints that contain the concentration from the revised break-points table for fine particle pollutant (Table 3.4) and a standard formula developed by the EPA. The fine particle pollutant index was calculated using the mathematical expression as given in equation (3.7) (Mintz, 2012; US EPA, 2014):

Table 3.4: Revised AQI breakpoints

$PM_{2.5}$ ($\mu g/m^3$, 24-hour average)	Index Values	AQI Category
0.0 - 12.0	0-50	Good
12.1-35.4	51-100	Moderate
35.5-55.4	101-150	Unhealthy for Sensitive Groups
55.5-150.4	151-200	Unhealthy
150.5-250.4	201-300	Very Unhealthy
250.5-350.4	301- 400	Hazardous
350.5-500	401-500	Hazardous

Source: US EPA, 2014

$$I_p = \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} \left(C_P - BP_{Lo} \right) + I_{Lo} \qquad (3.7)$$

*w*here:

I_p = the index for pollutant p,

C_p = the rounded concentration of pollutant p,

BP_{Hi} = the breakpoint that is greater than or equal to C_P,

BP_{Lo} = the breakpoint that is less than or equal to C_P,

I_{Hi} = the AQI value corresponding to BP_{Hi} *and*

I_{Lo} = the AQI value corresponding to BP_{Lo}.

3.13 Quality Assurance/Quality Control

Comprehensive quality assurance/quality control (QA/QC) programme was ensured in the entire research work from sampling to data analyses and report. Field quality control, recovery test, reproducibility test and method detection limits were followed by strict adherence to documented standard operating procedures and comprehensive documentation of sampling notebook (US EPA, 1999a and US EPA, 1999b).

3.13.1 Quality Control of Filters, Sampler and Glasswares

Periodic cleaning of the sampler was ensured to avoid biased results. All filters for sampling were prepared on a clean surface to prevent any surface contamination to the filters. The filters were visually inspected in a dark room located in Physics Laboratory, Covenant University for defects such as pinhole, separation of ring, chaff, discolouration, filter nonconformity, irregular surface, before the initial weighing. Filters with identified defects were discarded. Filters were handled carefully at the edge with clean smooth, non-serrated forceps. The same micro balance was used for the pre-weighed and post-weighed Teflon/glass fibre filters. Two different desiccators were used for the pre-weighed and post-weighed filters in the laboratory. All filters were equilibrated in a desiccator while transporting from the field back to the laboratory. Laboratory and field blanks were used in the $PM_{2.5}$ filter processing procedure. The laboratory blanks were used to check for possible weight change between pre-sampling and post-sampling weighing which could result from contamination in the laboratory environment. The field blanks were used to check possibility of contamination occurring during sample transport, setup and recovery. They were transported to the sampling site, positioned in the sampler filter case, removed and stored in a covered petri dish container inside the sampler's case at the sampling site, until the exposed filters were retrieved for post sampling weighing. To avoid contamination in trace metal analysis, all the glasswares and filter assembly were soaked overnight in ultrasound cleaner (KQ 400KED), acid washed and oven dried. Blanks were analysed to check the interference from filter papers in the sample.

3.13.2 Recovery Test

Ten percent (10%) of the samples were evaluated by spiking with a known amount of metal to calculate the recovery efficiencies following the analytical procedure for the field samples. Percent recoveries were calculated in units appropriate to the matrix and the recovery values expressed in percentages as shown in equation (3.8) (US EPA, 1999b):

$$R = \left(\frac{Cs - C}{s} \right) \times 100 \qquad (3.8)$$

where:

R = percent recovery, %.
Cs = fortified sample concentration, µg/m^3.
C = sample background concentration, µg/m^3.
s = concentration equivalent of fortifier added to sample, µg/m^3.

3.13.3 Reproducibility or Duplicate Test

Duplicate analyses were used to determine reproducibility or consistency in the method. Three duplicate samples were processed following the analytical procedure for the field samples, analysed identically and expressed as relative percent difference (RPD). The relative percent difference was calculated by dividing the difference between the two results by their average as shown in equation (3.9) (Ventura *et al.*, 2014):

$$RPD = \frac{x - y}{\frac{1}{2}(x + y)} \times 100\% \qquad (3.9)$$

where:

x = result of first analysis,
y = result of second analysis.

3.13.4 Method Detection Limits (MDL)

MDL is the lowest measurable concentration of analyte that can be determined to be statistically different from a blank (99% confidence). MDL was determined for all analytes, using reagent water (blank) fortified at a concentration of five times the estimated detection limit. To determine MDL values, seven replicate aliquots of the fortified reagent water were processed through the entire analytical method and the concentration values were reported in appropriate units. The MDL was calculated from equation (3.10) (US EPA, 1999b):

$$MDL = t \times s \tag{3.10}$$

where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates).

s = standard deviation of the replicate analyses.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Spatio-Temporal Distribution of Fine Particulate Matter ($PM_{2.5}$) and Trace Metals in the Study Area

The characterization of spatial variability is usually done to give a representation of the background particle pollution. Spatial factors, such as topography, distance from a point source, and combination of other pollutants affects fine particle composition and levels from one location to the other. Temporal variation shows how fine particles and related component varies with time. Meteorological variables and traffic intensity amongst other factors are known to contribute to the dispersion of fine particles and associated components (Fang *et al*., 2016).

4.1.1 $PM_{2.5}$ Mass Concentrations ($\mu g/m^3$)

Table 4.1 presents the minimum and maximum value, average concentration and standard deviation of $PM_{2.5}$ collected from the four study areas. The mass concentration of sampled fine particles obtained from OTE, EWC, AGE and CUF ranged between 25.0-948.1 $\mu g/m^3$, 24.9-723.6 $\mu g/m^3$, 30-548.9 $\mu g/m^3$ and 25-673.6 $\mu g/m^3$, respectively. These values exceeded the WHO and US EPA National ambient air quality standard (NAAQS) $PM_{2.5}$ permissible daily limit of 25 and 35 $\mu g/m^3$, respectively, and the current annual WHO and US EPA guideline of 10 and 12 $\mu g/m^3$, respectively (Robert, 2013; US EPA, 2012a; WHO, 2006), for most of the sampling days.

Table 4.1: Average annual mass concentrations (μg/m^3) of PM$_{2.5}$ at different sites

Locations	OTE	EWC	AGE	CUF
N	36	36	18	36
Min	25.0	24.9	30.0	25.0
Max	948.1	723.6	548.9	673.6
Mean	263.0	222.5	215.1	146.2
Stdev	221.8	167.1	161.3	161.4

N= number of samples

From the observed results, average $PM_{2.5}$ concentration in the background site (CUF: agricultural site) was lower than the average results obtained from the three industrial sites (OTE, EWC and AGE), but higher than the regulatory agencies guidelines. The increase in fine particles observed at CUF may be attributed to a greater extent to the transportation of particles from the nearest industrial site (OTE) and to a lesser extent from the surrounding residential estate. Similar observations have been reported from literature (Zhao, Han, Lu, Zhang, Zhu, & Bai, 2015).

4.1.2 Spatial Distribution of $PM_{2.5}$ Concentrations

The spatial variations in the average concentration of $PM_{2.5}$ in the ambient air of the study area are in the following descending order: OTE > EWC > AGE > CUF as shown on Table 4.1. The average annual $PM_{2.5}$ mass concentrations measured were 15 – 26 times and 12 – 22 times higher than the current annual WHO and US EPA guideline of 10 and of 12 $\mu g/m^3$, respectively (Robert, 2013; US EPA, 2012a; WHO, 2006). This compares with the results reported in the literature for Egypt (Abu-Allaban, Lowenthal, Gertler, & Labib, 2007), China (Zhao *et al.*, 2013), India (Majumder *et al.*, 2012), Nigeria (Owoade *et al.*, 2015).

On the contrary, lower $PM_{2.5}$ concentrations in the range of 29 – 68 $\mu g/m^3$ were reported for Saudi Arabia (Shaltout, Boman, Al-Malawi, & Shehadeh, 2013). Also, a previous work done at Ewekoro community by Oguntoke, Awanu, and Annegarn (2012) recorded 116 ± 1.6 $\mu g/m^3$ as the highest concentration of $PM_{2.5}$. The reason for spatial variation in the levels of $PM_{2.5}$ observed in the different study locations is attributed to the high number of heterogeneous industrial emissions and enhanced by the nature of combined activities in the different study locations as earlier discussed in section 3.1, as well as contribution from long range transport (Luo, Ip, Li, Tao, & Li, 2014; Zhao *et al*., 2013).

4.1.3 Temporal Distribution of $PM_{2.5}$ Concentrations

Figure 4.1 illustrates the temporal trend of changes in $PM_{2.5}$ levels in Ota industrial estate (OTE), Ewekoro community (EWC), Agbara industrial estate (AGE) and Covenant university farm (CUF). The trend in $PM_{2.5}$ levels indicated seasonal dependence with dry season concentrations relatively higher than wet season concentrations. However, it was observed that two out of the four study areas, namely OTE representing the industrial area and CUF being the background site recorded the highest and lowest $PM_{2.5}$ level in both seasons, respectively.

The average concentrations of $PM_{2.5}$ in the wet and dry seasons were 191, 180, 144 and 67.9 μg/m^3 and 335.4, 264.8, 235.5 and 224.5 μg/m^3, respectively for OTE, EWC, AGE and CUF. These sites exhibited lower values in the wet season than those for the dry season. More so, fine particles were found to be almost two times higher in EWC and AGE, two times higher in OTE and three times higher in CUF in the dry season than in the wet season. The background site (CUF) and the surrounding neighbourhood is primarily occupied by agricultural land, and

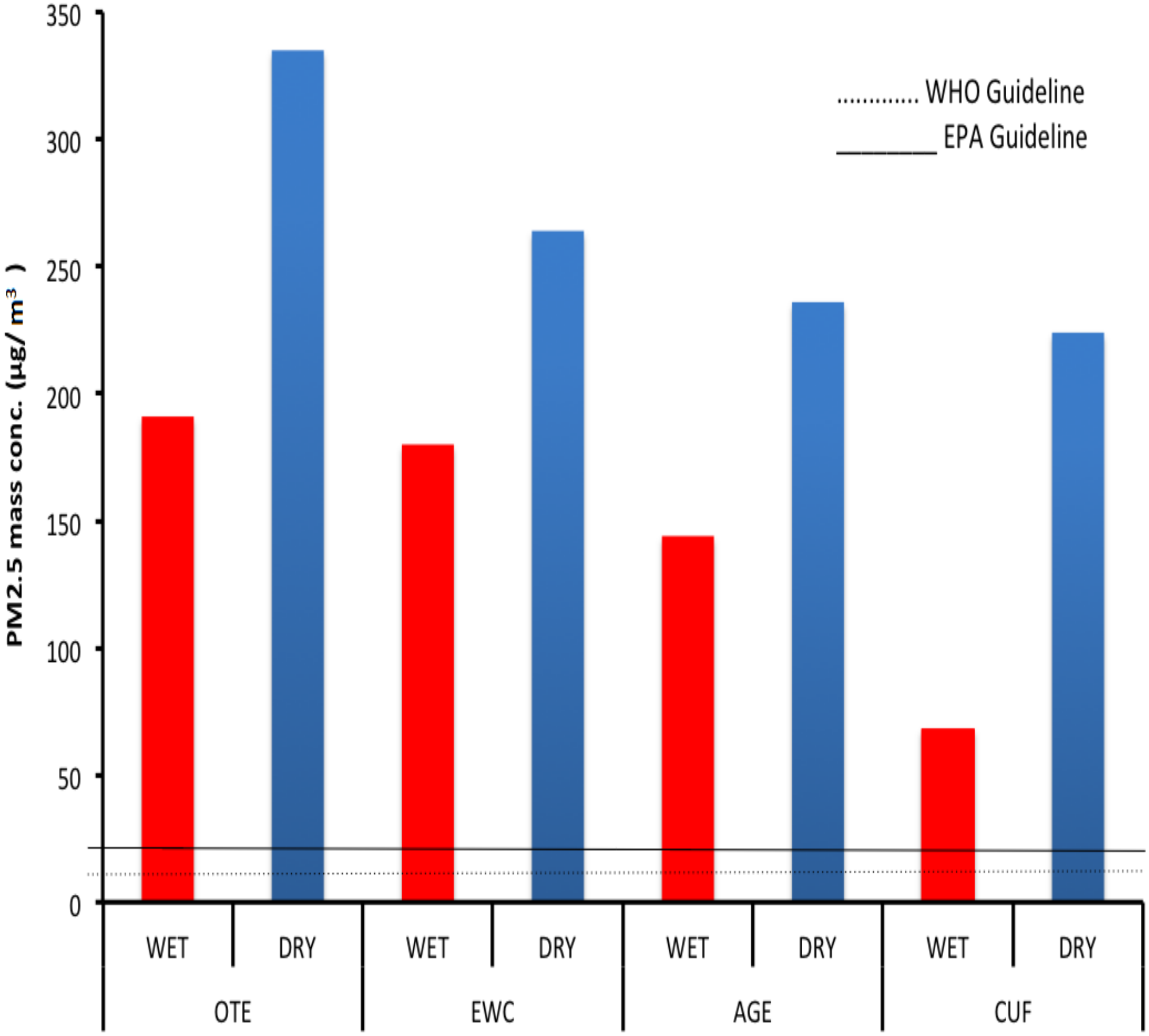

Figure 4.1: Average seasonal concentration of airborne $PM_{2.5}$ in all the study areas. Horizontal lines indicate the 24-h standard limits established by US-EPA and WHO

there could be high agro-related emissions from activities, such as farm ploughing, emissions from farm vehicles, fabrication of farm tools, fertilizer applications, herbicide/pesticide spraying and biomass burning especially from surrounding farmlands which can significantly contribute to the increase in the concentration of fine particles (Hu *et al*., 2013; Zhang, Hecobian, Zheng, Frank, & Weber, 2010). Also, the possibility of fine particle transport from the surrounding residential estate, the postgraduate hall construction, which was in proximity to the farm and Ota industrial estate, etc., may not be ruled out, coupled with the dry weather that acts as a catalyst in the suspension of airborne fine particles.

OTE results were pinned as the most polluted of the entire industrial site. The highest mass concentrations observed at OTE industrial sites, were not surprising considering the mixed sources of particle emission from surrounding industries (chemical, basic metals, scrap recycling). OTE environment is continuously saturated with noxious gases, fumes and smoke from chimney of industries and power plants, residential generators and firewood stoves, dust from unpaved rough roads, heavy traffic emissions within the estate and from the major Idiroko road, etc.

EWC result further corroborates a previous work done at Ewekoro in the dry season, which recorded $PM_{2.5}$ levels in the range 9.33 - 112.14 $\mu g/m^3$ (Bada, Olatunde, & Oluwajana, 2013). From Figure 4.1, it is clearly evident that, the level of $PM_{2.5}$ in both seasons in all the study area had exceeded the WHO and US EPA standards as earlier discussed.

The lower variations in particle accumulation during the wet season versus the dry season in the study area may be attributed to the washing effect on particulates from the atmosphere. Hence from the results shown, wet season accounted for only 35% of the inhalable particles while 65% was accounted for by dry season during the sampling period. Overall, the ambient $PM_{2.5}$ concentration far exceeds the 24-h and annual guideline limits established by US EPA (2012a) and WHO (2006).

4.2 Trace Metal Concentration in $PM_{2.5}$

4.2.1 Method Validation and Performance

The calibration of the ICP-MS instrument performed with multi-element calibration standards showed that the correlation coefficients (r^2) for all trace metals ranged from 0.998 to 1.0000, with exception of Al (0.994). Overall, a good linearity of $r^2 > 0.995$ was obtained. Field and laboratory blank filters analysed with samples to evaluate external elemental contamination introduced by sample handling were corrected by subtracting the blank amount from the sample concentration to obtain the actual concentration of metals present in the sample. Method detection limits (MDLs) values for trace metals were also obtained ranging from 0.0000429 to 0.0629 $\mu g/m^3$. Also, the method precision, expressed as relative percent difference (RPD) was in the range of 2 to 17% which falls in the expected range of <20% as specified by US EPA method IO-3.5, while the recovery test results done to evaluate the efficiency of the extraction procedure for the samples was in the range of 85% – 97% indicating that no significant loss or contamination was associated with any of the digestion procedures and ICP-MS measurements.

4.2.2 Spatial Variation of $PM_{2.5}$-BoundTrace Metals in the Study Area

In this section, the spatial variability of fine particle bound trace metals in the study areas are discussed by comparing their atmospheric average concentrations. Average trace metal concentrations of $PM_{2.5}$ in the four sampling locations in Table 4.2 show 22 trace metals: As, Cr, Pb, Ni, Cd, Mn, Ti, V, Ba, Fe, Al, Mo, Ca, Zn, Cu, Mg, Sr, Se, Ag, K, Na, and Sb that were detected and quantified at all the sampling sites.

The six most abundant atmospheric trace metal compositions in all the locations were Na, Zn, Ca, Al, K and Ba. The order of abundance in the atmosphere at the different study locations were presented as: OTE (Na > Al > Zn > K> Ca > Ba), EWC (Na > Ca > K > Al > Zn > Ba), AGE (Na > Al > Zn > Ba > K > Ca) and CUF (Na > Zn > K > Ca > Al > Ba), and the highest concentrations as shown in Table 4.2 were Na (265 $\mu g/m^3$), Zn (121 $\mu g/m^3$), Ca (115 $\mu g/m^3$), Al (114 $\mu g/m^3$), K (102 $\mu g/m^3$) and Ba (73.5 $\mu g/m^3$).

Furthermore, among all the four sampling sites the highest concentration of Pb (6.25 $\mu g/m^3$), Ni (0.12 $\mu g/m^3$), Fe (10.6 $\mu g/m^3$), and Sb (0.193 $\mu g/m^3$) were observed at OTE. This pollutant level is closely associated with the activities in the study location. Ota industrial estate has over 30 active production industries. It is burdened by different pollutant sources including open burning of solid waste, fleet of heavy duty vehicles, residential and commercial waste. But, top on the list are the industrial processing plants such as metal and steel, chemical, pharmaceutical, plastics, etc. Also, volatilization of inorganic compounds at very high temperature during production could generate most of the observed particles.

Table 4.2: Average concentrations and standard deviations for $PM_{2.5}$-bound trace metals in 3 significant figures across the study locations (μg/m^3)

Trace Metals	**OTE**	**EWC**	**AGE**	**CUF**
Na	119±89.5	177±174	223±183	265±210
Mg	9.40±89.5	14.5±15.5	6.88±3.8	7.11±4.03
K	47.2±37.3	58.9±64.3	56.2±56.7	102±76.6
Ca	44.1±26.9	115±166	51.1±35.2	64.9±49.2
Fe	10.6±9.88	9.00±8.57	5.65±4.23	10.1±9.90
Al	58.8±51.3	38.4±47.7	114±52.5	61.2±61.3
Ti	0.454±0.608	0.389±0.314	5.56±17.9	9.64±21.2
V	0.311±0.319	0.418±0.350	0.862±1.30	0.199±0.117
Cr	1.30±0.908	1.27±1.24	2.10±3.13	1.99±3.22
Mn	0.262±0.397	0.349±0.368	0.113±0.092	0.139±0.138
Cd	0.0900±0.130	0.0330±0.0230	0.131±0.238	–
Sb	0.193±0.501	1.31±2.02	–	–
Cu	0.108±0.120	1.97±4.07	0.897±1.88	0.0760±0.0537
Zn	53.8±44.2	34.7±39.4	83.3±70.5	121±92.0
As	0.402±1.10	1.93±2.13	0.206±0.272	0.117±0.0530
Se	0.0556±0.0695	0.0710±0.0620	0.0200±0.0190	0.0234±0.022
Sr	0.802±0.384	7.87±8.11	1.38±0.725	0.733±0.891
Mo	0.00674±0.0120	0.0160±0.0140	0.0300±0.0340	0.0179±0.0180
Ag	0.0447±0.0414	0.0330±0.0320	0.0630±0.0600	0.0325±0.0413
Ba	37.8±27.4	21.7±24.3	73.5±72.2	55.9±41.4
Pb	6.25±7.35	1.31±1.78	0.193±0.197	0.330±0.319
Ni	0.120±0.136	0.0790±0.0710	–	0.105±0.123

In line with these results, several metallic elements including Pb, Cd, As, Se, Cr, and Ni have been estimated in Ota industrial estate using industrial pollution projection survey (IPPS) model (Etim, 2012). The highest value of Ca (115 μg/m^3), Mg (14.5 μg/m^3), Sr (7.87 μg/m^3), Cu (1.97 μg/m^3) As (1.93 μg/m^3), Mn (0.349 μg/m^3), and Se (0.0710 μg/m^3), were observed at Ewekoro community (EWC). Possible sources of these elements include, the blasting of limestone, emission of dust from stacks and chimney of Lafarge cement WAPCO Nigeria Plc., paint industry, Dulphin steel industry, heavy vehicular traffic, open burning of waste and trailer tyres. Cement production by its nature is characterized by significant dust particle pollution, usually associated with some trace metals, such as Na, Ca, Mn, Mg, K, Cu, Al, Fe and Zn (Mlitan, Alajtal, & Alsadawy, 2013; Stanley, Odu, & Immanuel, 2014). The high level of Ca (115 μg/m^3), can be obtained from dolomite which is a major raw material used in the production of cement.

The Al (114 μg/m^3), Ba (73.5 μg/m^3), Cr (2.10 μg/m^3), Cd (0.131 μg/m^3), V (0.862 μg/m^3), Ag (0.0630 μg/m^3) and Mo (0.0300 μg/m^3) exhibited the highest levels of trace metals in Agbara industrial estate (AGE). This is a highly industrialized area, with several industries including pharmaceuticals, food and beverages, gas plant, confectionaries, savouries and detergents. Possible sources of these pollutants include, waste generated from these industrial processes, burning of fossil fuels from production plant and vehicles, road and building construction, open burning of waste materials and crustal emission from unpaved roads. More so, Fatoba, Ogunkunle, and Olawepo (2012) had attributed the high presence of Cd in Agbara to industries and several combustion processes such as vehicle emissions. At the background station (CUF), highest level of five trace metals namely, Na (265 μg/m^3), Zn (121 μg/m^3), K (102 μg/m^3), Ba (55.9 μg/m^3), and Ti (9.64 μg/m^3) were observed when compared with OTE, EWC and AGE.

These metals are suspected to be of mixed origin. Na, Ba, K and Ti metals are mostly associated with crustal origin, but higher concentration is an indication of anthropogenic contribution (Zhao *et al*., 2015). CUF is a farm with a farm building where occasional small scale fabrication of farm tools and repairs were carried out. Active construction was equally taking place in the nearby residential estate as at the time of sampling. Na was not only present in higher levels at CUF, but was also the highest when compared to the entire industrial site, confirming the suspicion of other anthropogenic influences.

4.2.3 Comparison with Ambient Air Quality Standards

In Nigeria, the limit set by National Environmental Standards and Regulations Enforcement Agency (NESREA) for atmospheric trace metals are not comprehensive, hence ambient air quality guidelines and standard limit values for trace metal species set by three regulatory agencies: United States Environmental Protection Agency(US EPA, 2014), European Commission Air Quality Standards (EC, 2015) and World Health Organisation (WHO, 2000) guidelines were employed as shown in Table 4.3.

Currently, guidelines and standards for only seven trace metal species (Pb, As, Cd, Cr, Ni, Mn, V) are available. A comparison of the 6 – months average concentrations of Pb, As, Cd, Cr, Ni, Mn, V trace metals in Table 4.2 to the appropriate standard limit values (Table 4.3) reveals that out of these 7 trace metals, only V (0.199 – 0.862 $\mu g/m^3$) was below the existing WHO limit of one (1) $\mu g/m^3$. Individual pollutants above the stipulated guideline limits are discussed in the following section.

Table 4.3: Trace metal standard in ambient air (µg/m^3)

Trace Metals	WHO	EU	US EPA
Lead (Pb)	0.5	0.5	0.15
Arsenic (As)	0.00066	0.006	
Cadmium (Cd)	0.005	0.005	
Nickel (Ni)	0.0025	0.02	
Chromium (Cr)	0.000025		
Manganese (Mn)	0.15		
Vanadium (V)	1		

Source: EC, 2015; US EPA, 2015c; WHO, 2000

4.2.3.1 Arsenic (As)

The levels of As in the $PM_{2.5}$ particles were in the range of 0.117 – 1.93 µg/m^3 for all the study locations, which appear conspicuously above the stipulated WHO and EU standards on Table 4.3. Arsenic is a chemical substance found naturally in soil and minerals in small concentrations and can be released into the air from windblown dust. It can also occur from industrial activities such as production of special types of glasses, wood preservation, Cu, Pb and Zn production and agriculture. Arsenic exists in two forms: the organic and inorganic with the latter form being considered more toxic. Inorganic arsenic concentrations are highest in ambient air in association with particulate matter close to industrial sources especially near non-ferrous metal smelters, in areas with natural geological contamination, and in soils or sediments near contamination sources. The level of particle bound As varies globally as follows: 7.0 x 10^{-6} – 1.9 x10^{-3} µg/m^3 in remote areas; 1.0 x 10^{-3}– 2.8 x10^{-2} µg/m^3 in rural locations, and 2.0 x 10^{-3} – 2.32 µg/m^3 in urban environments. Its major route is through ingestion, but it can equally be inhaled.

Toxic effects exerted by inhaled toxic inorganic As includes irritation of the stomach and intestines, decreased production of red and white blood cells, lung cancer, brain and DNA damage (Lenntech, 2016; WHO, 2010a). The possible reason for arsenic in the CUF may be from application of arsenic-containing pesticides to the farm (Lenntech, 2016; WHO, 2000; WHO, 2010a).

4.2.3.2 Chromium (Cr)

The Cr results are presented in Table 4.2 as follows, OTE (1.3 μg/m^3), EWC (1.27 μg/m^3), AGE (2.10 μg/m^3) and CUF (1.99 μg/m^3). The results exceeded the WHO permissible limit of 0.000025 μg/m^3 as shown in Table 4.3. Chromium is present in the atmosphere primarily in particulate form and its level in air is generally low. Likely sources of Cr from the investigated industrial area are chrome plating, the use of hexavalent chromium as a corrosion inhibitor, combustion of oil, coal, and municipal waste. The toxicity of chromium depends on the oxidation state. Chromium (VI) is more toxic and readily inhaled or ingested than chromium (III). Chromium (III) is an essential nutrient for humans, by maintaining the normal carbohydrate, lipid and protein metabolism. Deficiency of chromium (III) may cause heart conditions, disruptions of metabolisms and diabetes. However, chronic exposure to chromium (III) can cause weight loss, skin rashes, liver dysfunction and renal failure (Lenntech, 2016). On the other hand, exposure to some inhaled chromium (VI) mists can cause nose irritations and nose bleeding, lung cancer, respiratory irritation and inflammation. Removal of Cr from the atmosphere occurs by physical deposition processes. It is worth noting that only chromium (VI) compounds have been classified as known human carcinogen (Lenntech, 2016; US EPA, 2015d).

4.2.3.3 Lead (Pb)

The average concentration of Pb in all the study area ranged between 0.193 and 6.25 μg/m^3. It remarkably deviated from the WHO/EU and US EPA regulatory guidelines of 0.5 and 0.15 μg/m^3. The enhanced levels of atmospheric Pb in the study locations may have resulted mainly from industrial activities and emission from automobile using leaded gasoline, since only small amount of lead occurs naturally in the earth's crust. Active sources of Pb observed in the study locations include power plants, scrap recycling, metals processing, cement manufacturing, iron and steel foundries, pigments, paint, lead-acid batteries, solid waste combustion, and vehicular emission. The presence of this pollutant in the background site may be due to long range atmospheric transport from point sources. Adverse effects of Pb include: high blood pressure, kidney damage, diminished learning abilities of children, hyperactivity in children, brain damage, etc. Exposure of pregnant women to high levels of lead can cause miscarriage, stillbirth, premature birth and low birth weight, as well as minor malformations (Onunkwor, Dosumu, Odukoya, Arowolo, & Ademuyiwa, 2004; Tong, Von Schirnding, & Prapamontol, 2000; WHO, 2010b).

4.2.3.4 Cadmium (Cd)

Comparison of Table 4.2 to Table 4.3 indicates that OTE, EWC and AGE recorded Cd levels higher than 0.005 μg/m^3 set by WHO and EU air quality guidelines except for CUF where level of Cd was below the detection limit. The presence of high levels of Cd was attributed to anthropogenic activities. Though Cd can be released into the environment by natural activities, such as weathering and erosion, however, the extent of smelting and refining of nonferrous metals, recycling of cadmium containing materials such as cadmium-plated steel scrap and electronic waste, open burning of waste consisting of nickel-cadmium batteries, electronics, mobile phones and plastics, especially when waste sorting is yet to be practiced in these areas make anthropogenic activities in this region the chief culprits of Cd emission. Cadmium being a toxic metal, can affect the lungs, kidney and bones (WHO, 2010c). Inhalation is one of the main ways residents and workers are exposed to cadmium in these locations. An initial symptom of Cd begins with flu, fever and muscle pain, and graduates to cough, chest pain, shortness of breath, lung damage and death in severe cases (WHO, 2010c). Based on the overwhelming evidence that long-term occupational exposure to cadmium (e.g. through cadmium fume) contributes to the development of lung cancer, cadmium and cadmium compounds have been classified by IARC and US EPA as carcinogenic to humans (Group 1) (US EPA, 2015e; WHO, 2010c).

4.2.3.5 Nickel (Ni)

Ni was present in the range of 0.079 – 0.120 μg/m^3 in three locations implying levels higher than the threshold limit of WHO (0.0025) and EU (0.02) except for AGE where it was below the detection limit. Ni is naturally distributed uniformly in the soil, but it is accumulated on the surface from deposition by industrial and agricultural activities. From activities in the study area, especially in OTE, this finding can possibly be attributed to emissions from power plants, casting, welding, and recycling of used battery, waste burning and most especially, metallurgical activities associated with base metal refining. Ni released into the air can also travel long distances from the source of emission by atmospheric transport. Ni is essential in small quantities, but dangerous to human health in higher quantities causing sickness and dizziness after exposure to nickel gas, allergic reactions such as skin rashes, asthma and chronic bronchitis, respiratory failure, heart disorders and birth defects (Lenntech, 2016). The primary route of Ni exposure is by inhalation, followed by ingestion. Cempel and Nikel (2006) reported that typical average levels of airborne nickel are: 0.00001 – 0.003 µg/m^3 in remote areas; 0.003 – 0.03 µg/m^3 in urban areas having no metallurgical industry and 0.07 – 0.77 µg/m^3 in nickel processing areas.

4.2.3.6 Manganese (Mn)

Manganese exceeded the WHO allowable limit of 0.15 only in OTE and EWC. The principal sources of Mn in these industrial locations are emissions from ferroalloy production, iron and steel foundries, application of manganese pesticides, as well as combustion emissions from power plants and coke ovens. In addition, Mn can also occur from crustal sources since it is one of the most abundant metals in soils. It is mostly found in dust particles. Manganese is an essential trace metal necessary for man. However, it is toxic when too high concentrations are present in the human body. Prolonged inhalation of Mn dust and fume may result in manganese poisoning. Symptoms of Mn poisoning include sleepiness, weakness, recurring leg cramps, skin problem, and changes in hair colour, respiratory infections as well as paralysis (Lenntech, 2016).

4.2.4 Temporal Variation of $PM_{2.5}$-Bound Trace Metals in the Study Area

The seasonal average concentration of $PM_{2.5}$-bound trace metals is depicted in Table 4.4. From the observed results, distinct differences were observed for the individual components. In the wet season, Na, Zn, K, Ba, Ca, Pb, As and Cr trace metals exhibited comparable higher levels across the study locations while in the dry season, the trend of trace metals contamination in all the locations was: Na>Ca>Al>Zn>K>Pb>Cr>As>Mn>Ni>Cd. The average trace metal concentration observed in the dry season was expectedly higher than that of the wet season. This could be explained from the difference in meteorological conditions between the dry and the wet seasons, resulting in greater concentration of particle bound trace metals in the study area.

Table 4.4: Average concentrations and standard deviations in 3 significant figures for $PM_{2.5}$-bound trace metals across the season ($\mu g/m^3$)

	Wet Season				Dry Season			
Trace Metal	OTE	EWC	AGE	CUF	OTE	EWC	AGE	CUF
Na	89.3±95.8	159±240	287±180	238±234	133±87.6	184±163	226±185	292±205
Mg	2.54±3.23	8.41±10.9	7.58±5.00	6.53±3.94	11.7±17.9	17.6±17.2	6.56±3.45	7.69±4.49
K	26.7±32.7	61.1±81.5	34.2±41.2	100±76.7	56.3±37.2	58.0±63.3	71.4±60.4	114±76.8
Ca	22.9±25.4	51.8±48.0	56.2±48.2	59.3±46.6	52.0±24.2	139±191	49.4±33.3	69.4±56.2
Fe	4.02±2.18	7.01±8.48	3.01±2.99	8.33±10.5	11.9±10.4	10.3±8.96	6.83±4.29	12.0±10.5
Al	24.2±45.2	25.1±20.6	76.8±59.3	61.4±49.7	79.7±48.1	49.4±62.3	132±40.6	60.2±75.1
Ti	0.376±0.736	0.376±0.331	0.200±0.131	0.0790±0.0910	0.494±0.561	0.396±0.325	7.57±21.0	5.56±12.9
V	0.458±0.331	0.243±0.179	–	1.16±2.09	0.226±0.304	0.551±0.418	0.760±1.43	0.215±0.140
Cr	1.36±1.18	0.368±0.350	–	2.08±4.32	1.31±0.813	1.72±1.31	1.02±1.41	0.979±0.220
Mn	0.0660±0.0570	0.124±0.0740	0.200±0.163	0.141±0.102	0.351±0.456	0.462±0.410	0.0840±0.0330	0.164±0.173
Cd	0.104±0.147	–	–	–	0.0720±0.124	0.0350±0.0250	0.0120±0.0100	–
Sb	0.0390±0.0290	1.51±2.62	–	–	0.600±0.954	1.18±1.92	–	–
Cu	0.138±0.163	0.301±0.508	2.56±3.61	–	0.0820±0.0680	3.35±5.28	0.233±0.299	0.0710±0.0650
Zn	38.5±38.4	4.60±7.67	54.3±75.8	102±106	63.0±46.8	57.3±38.4	90.5±72.6	130±96.5
As	0.0970±0.0340	2.58±3.56	0.213±0.302	0.129±0.0170	0.621±1.45	1.61±1.70	0.204±0.284	0.105±0.0770
Se	–	0.0580±0.0480	–	0.0380±0.0230	0.0600±0.0770	0.0780±0.0740	0.0130±0.0110	0.00800±0.00200
Sr	–	8.69±12.1	1.25±0.511	0.612±0.279	0.801±0.414	7.44±7.74	1.43±0.816	1.04±1.31
Mo	0.00400±0.00400	0.0150±0.0190	–	–	0.0120±0.0190	0.0160±0.0150	0.0300±0.0340	0.0180±0.0180
Ag	0.0460±0.0380	–	–	0.113±0.141	0.0440±0.0490	0.0350±0.0350	0.0930±0.0430	0.0540±0.0560
Ba	25.2±30.3	–	62.9±15.8	25.1±35.3	47.8±23.0	19.4±26.4	80.6±95.3	59.7±58.1
Pb	7.94±4.81	1.32±1.69	0.140±0.229	0.240±0.294	5.49±8.76	1.30±1.92	0.216±0.191	0.344±0.249
Ni	–	0.0160±0.0190	–	–	0.0230±0.0260	0.111±0.131	–	

Also, Cd, Ni, Mn, and Al, trace metals showed a seasonal pattern in the order of dry > wet. These results were comparable to that reported by Owoade *et al*. (2015) where similar trend for same trace metals was observed. However, in both seasons OTE and EWC industrial sites showed elevated levels of Pb and As respectively, while CUF, being background also had enhanced levels of Na, Zn and K. The reason for observations at OTE and EWC is based on the emissions from mixed sources of pollution in the study area earlier discussed in section 3.2. At CUF, probable reasons may be resuspension of dust on the soil, long range transport of pollutants as well as fossil fuel combustion, power plant and small scale metallurgical fabrications in close proximity to the site.

Contrary, to similar trend of same trace metals in both seasons, CUF recorded higher concentrations of Ca and Cr in the wet season while EWC recorded higher concentrations of Ca and Cr in the dry season. The presence of Cr is attributed to airborne emissions from chemical plants, cement-producing plants, chromate pigments in dyes, paints, and plastics, chromium-based automotive catalytic converters and asbestos brakes, waste incineration and products of fossil fuel combustion (Cheng *et al*., 2014; Majolagbe, Yusuf, & Duru., 2013). The most significant contributors to Ca emissions are fuel combustion, buildings and road renovations/construction, glass production, quarrying, cement production and lime production (Gbadebo and Bankole, 2007; Hsu *et al*., 2016; Mustaffa *et al*., 2014; Wang *et al*., 2013). However, with respect to seasonal pattern Mg, Fe, Ti, Sb, V, Ag and Mo showed low concentrations in both seasons in all the study areas.

4.3 Influence of Meteorological Parameters on $PM_{2.5}$ Mass Concentration

Air quality differs from season to season everywhere due to the dynamics of the atmosphere. Also, meteorological parameters play a major role in the fate of air pollutants. To check the influence of meteorological parameters on $PM_{2.5}$ level, some variables such as temperature in degrees celsius (^oC); relative humidity in percentage (%); wind speed in metre per second (m/s); wind direction in degrees (^{o}) and rainfall in millimetres (mm) were statistically analysed. Table 4.5 presents the relationship between particle concentrations ($PM_{2.5}$) and meteorological factors during the wet and dry season.

Differences in meteorological conditions between the dry and the wet seasons could lead to the positive or negative differences in $PM_{2.5}$ concentrations. During the duration of the sampling, $PM_{2.5}$ mass concentration revealed a pattern of variation with high concentration in dry season (November- January) and low in the wet season (July, September, October).

Table 4.5: Average meteorological conditions at the study areas

Meteorological Parameter	Wet Season	Dry Season
$PM_{2.5}$ ($\mu g/m^3$)	146±126	269±231
Temperature (^oC)	26.0±0.904	28.0± 1.39
Relative Humidity (%)	86.8±3.37	71.8±13.7
Wind Speed (m/s)	2.05±0.62	2.70±1.05
Rain Fall (mm)	12.9±16.8	6.49±5.70
Wind Direction (^{o})	SW, NW	N,SW/NE

The elevated levels of particle in the dry season may be due to more re-suspended soil dust and harmattan occurrence and the combined effects of fossil fuel combustion, power plant, and industrial emissions, etc.

High relative humidity was observed in the wet season over the dry season, implying 55% increase in the wet season and 45% in the dry season. The average $PM_{2.5}$ was found to be lower with increased relative humidity. The $PM_{2.5}$ concentration of 146.0 μg/m^3 was recorded in relative humidity of 55% and as this decreased to 45% the $PM_{2.5}$ increases to 269.0 μg/m^3. As relative humidity increases there was an observable decrease in $PM_{2.5}$ (Figure 4.2). This explains the fact that high humidity may increase the removal processes of the particles. A similar work by Owoade *et al*. (2012) at a site in Ile Ife, Nigeria, had a relative humidity ranged between 65% and 87% representing the wet and dry seasons respectively. The $PM_{2.5}$ concentration for the wet season ranged between 9.86 and 28.41 μg/m^3, while that of dry season was in the range of 23.08 to 63.64 μg/m^3.

The rain fall exhibited a reverse relationship with $PM_{2.5}$, because increase in rain fall resulted in decreased $PM_{2.5}$ concentration. Large amounts of rainfall occurred in the wet season (12.9 mm) than in the dry season (6.49 mm). The cumulative rainfall value was minimal in the dry season and was only observed during the sampling in November. The $PM_{2.5}$ concentration of 146.0 μg/m^3 was recorded, when the rainfall was 12.9 mm and as it decreased to 6.49 mm, the $PM_{2.5}$ concentration increased to 269.0 μg/m^3 (Table 4.5). Rain causes large decrease in the concentration of accumulated particles due to its ability to wash out atmospheric particulates from the atmosphere. Also, it maintains the humid condition of the soil and atmospheric air thereby preventing the tendency of suspension of crustal particles and the effective accumulation of emitted particles (Owoade *et al*., 2012).

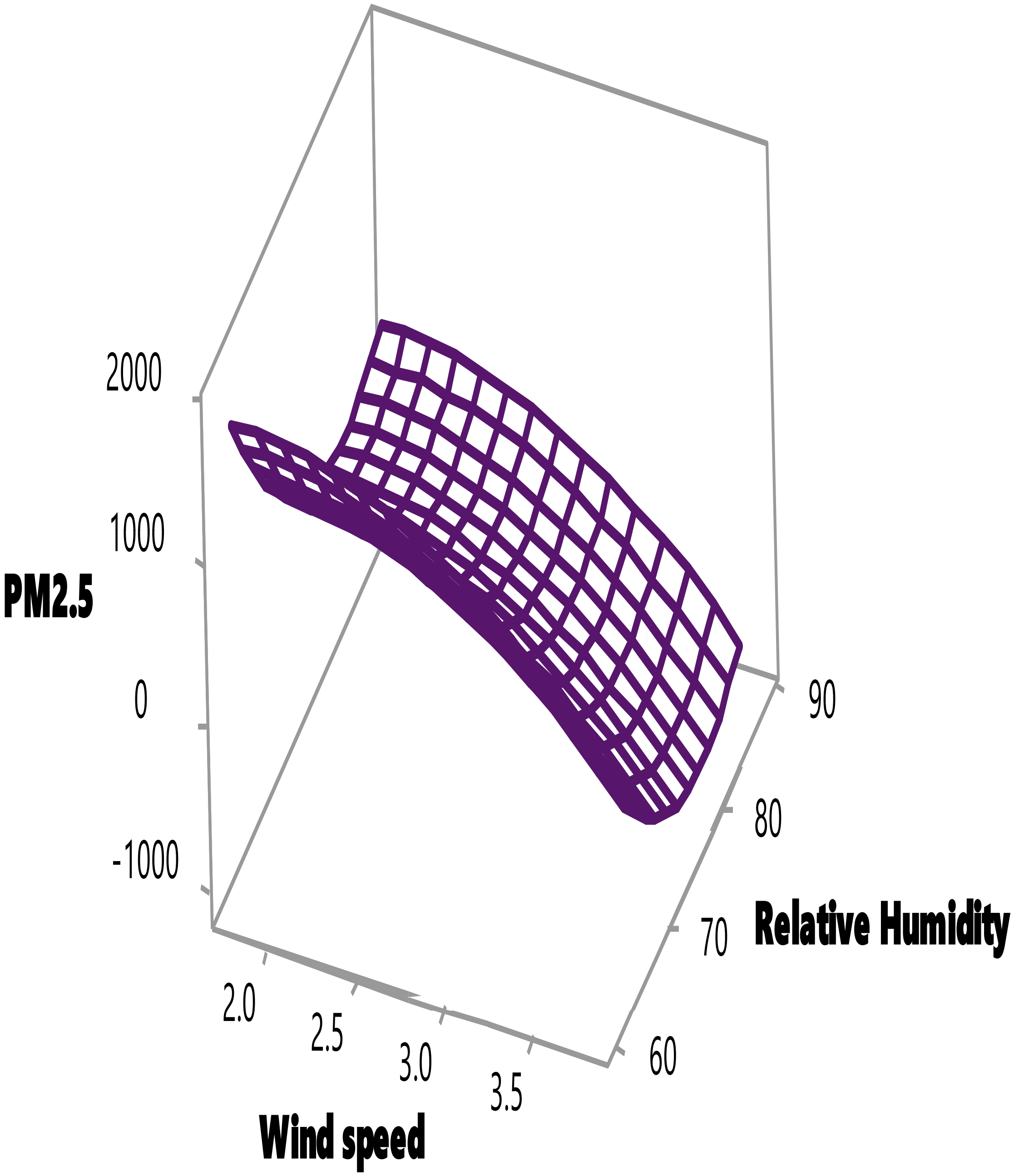

Figure 4.2: Surface plot of $PM_{2.5}$ vs relative humidity and wind speed

The average annual wind speed observed during the wet season was 2.05 m/s and its directions were predominantly south-westerly and north west wind while that of dry season was 2.70 m/s and the prevailing wind direction was North and south west for the months of December and January, while the South-westerly wind, prevailed only in the month of November. The level of $PM_{2.5}$ was 146.0 $\mu g/m^3$, when the wind speed was 2.05 m/s in the wet season and as this increased to 2.70 m/s the $PM_{2.5}$ increased to 269.0 $\mu g/m^3$.

Wind speed helps in increasing the level of $PM_{2.5}$. Low wind speed is characterized by calm or very stagnant air, which can persist for days during such period air pollutants tend to accumulate while high wind speed will cause dispersion of pollutants which dilutes in the direction of the wind (Ediagbonya, Ukpebor, Okieimen, & Okungbowa, 2012). Previous research conducted by Tecer *et al*. (2008) showed that increase in wind speed from 1.39 to 2.80 m/s, resulted in increase in the number of polluted days. This is in accordance with the wind speed results obtained in this work.

A positive relationship was observed between ambient temperature and $PM_{2.5}$ concentration. It shows that, in the wet season when the ambient temperature was low (26 ^oC), the $PM_{2.5}$ concentration was also low (146.0 $\mu g/m^3$) and in the dry season with increase of ambient temperature (28 ^oC) there was an increasing trend of 269.0 $\mu g/m^3$ $PM_{2.5}$ concentration. It is clear from Table 4.5 and Figure 4.3 that as the average annual temperature increased from 26 to 28 ^oC, subsequent increase in $PM_{2.5}$ concentration was observed from 146.0 $\mu g/m^3$ to 269.0 $\mu g/m^3$. Similarly, Amil, Latif, Khan, and Mohamad (2015) reported a positive correlation between $PM_{2.5}$ mass concentration and temperature.

In Sapele, the South-South geopolitical region of Nigeria, Ediagbonya *et al*. (2012) recorded average temperature of 29.9 ^{o}C in the wet season and further deduced that higher temperature increases the reactivity of gaseous constitutes in the ambient air leading to increase in particulate accumulation. Thus, the difference in PM concentrations between the wet and the dry seasons can be explained by the difference in pattern or meteorological condition for each specific season.

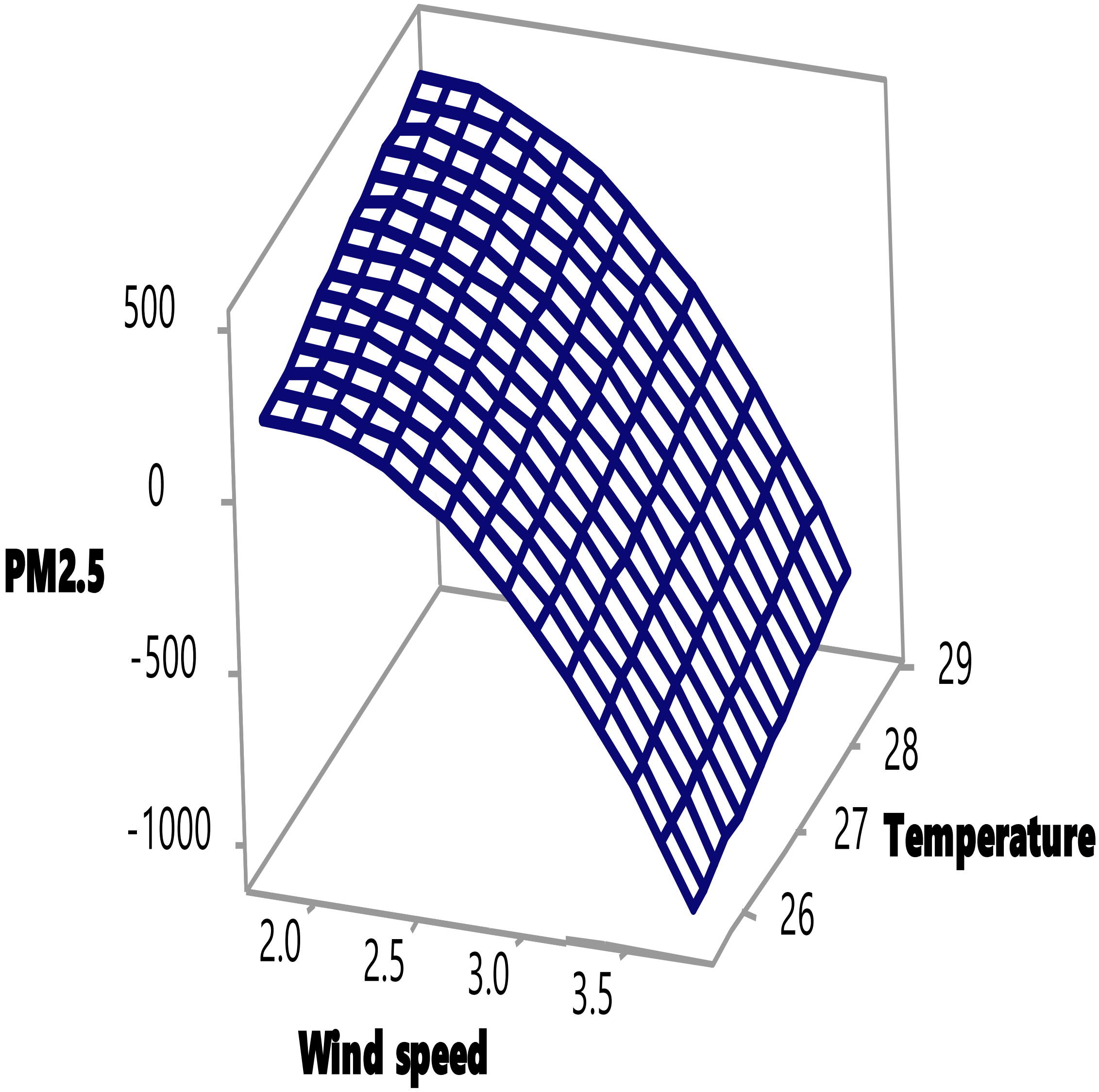

Figure 4.3: Surface plot of $PM_{2.5}$ vs temperature and wind speed

4.4. Chemical Speciation of $PM_{2.5}$ -Bound Trace Metals

The chemical speciation data for $PM_{2.5}$-bound trace metals obtained for this study are presented in Figures 4.4 and 4.5 as percentage distribution for OTE and EWC.

4.4.1 Ota Industrial Estate (OTE)

The import of easily released trace metals can only be known from determination of bio-available concentrations instead of total metal contents, which is very useful in risk assessment of metal toxicity (Mukhtar and Limbeck, 2013). In Ota industrial estate, speciation results were obtained for 12 trace metals: Pb, Cr, Ba, V, Al, Ag, Zn, Cu, Na, K, Mn and Cd (Figure 4.4). There was a dramatic difference in the pattern of relative distribution among the four fractions. Increased percentage distribution of soluble and exchangeable fraction (F1) obtained in OTE were Cr (46%), V (38%) and Cu (32%) while that of reducible fraction (F2) was Cd (67%) and Pb (37%).

Metals present in the soluble and exchangeable fraction amongst all other fractions pose the greatest risk to human health because they are easily adsorbed on particle surfaces and released into aqueous solutions (Feng *et al*., 2009). This implies that Cr, V and Cu would be readily bioavailable once inhaled into the respiratory system.

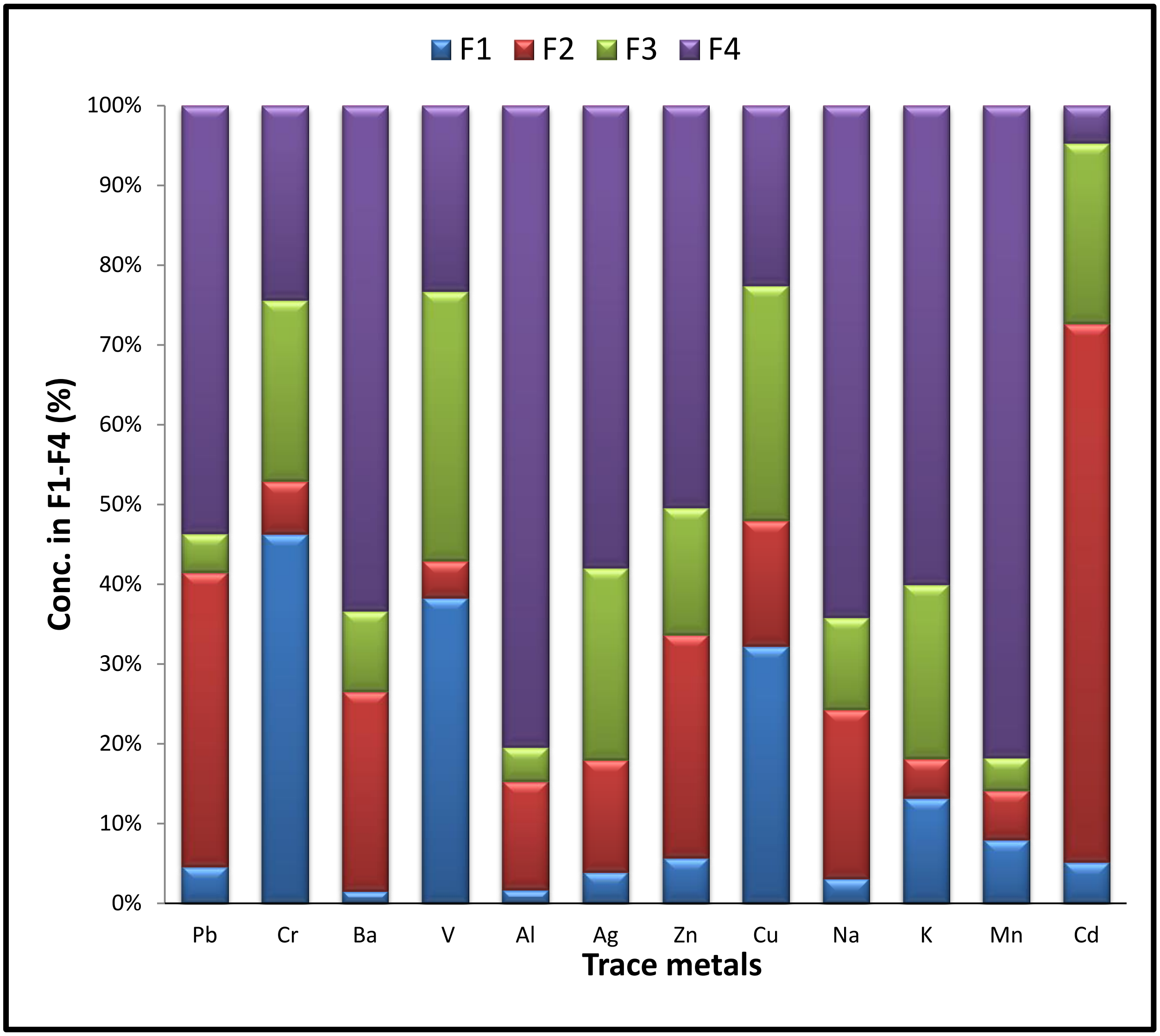

Figure 4.4: Chemical speciation distribution of OTE $PM_{2.5}$-bound metals as percentage (F1: soluble and exchangeable metals; F2: carbonates, oxides and reducible metals; F3: bound to organic matter, oxidisable and sulphidic metals; F4: residual metals)

However, even though Cd is present, it is only dominant in the carbonates, oxides and reducible fractions. Therefore, Cd can only be a threat to human health under acidic aquatic conditions. A combination of both F1 and F2 trace metals gave total percentage distribution of Cd (72%), Cr (53%), Cu (48%), and V (43%) when compared to the remaining fractions (F3 and F4). On comparing these FI and F2 results with chemical speciation results presented in Guangzhou, China, it showed that more than 40% of Zn, and Cd in the $PM_{2.5}$ samples were in the soluble and exchangeable (F1) form whereas more than 70% of Pb, more than 40% of Cd, Zn, Cu and more than 30 % of Mn were in carbonates, oxides and reducible forms (F2) (Feng *et al*., 2009).

It was observed that the trace metals bound to organic matter, oxidisable and sulphidic fraction did not record very high percentage distribution in any of the investigated metals. Majority of the trace metals were accounted for in the residual (F4) fraction in ascending order as follows: 82 % of Mn > 80% of Al > 64% of Na > 63% of Ba > 60% of K > 58% of Ag > 54% of Pb > 50% of Zn. Usually, trace metals present in the residual fraction have a stronger association with the crystalline structures of the minerals, as such are often very difficult to separate from the samples. Therefore, trace metals present in the residual fraction are said to be stable and of no threat to the human health. The chemical speciation trend in OTE $PM_{2.5}$-bound trace metal levels showed that F4 > F2 > F1 > F3. That notwithstanding, highest concentrations for the most toxic metals, of primary concern (Cr and Cd) were found in the soluble and exchangeable (F1) and reducible metals (F2) fractions of fine particles. Overall, the F1 and F2 represent 34%, while F3 and F4 represent 66% of the total metal concentration.

4.4.2 Ewekoro Community (EWC)

For Ewekoro community, speciation results were obtained for 12 trace metals: Pb, Cr, As, Ba, Ti, V, Al, Ag, Zn, Cu, Na, and K. The relative distribution of metals in different fractions is shown in Figure 4.5. As (89%), Ti (86%), Ag (77%), Pb (74%) Ba (56%) and Na (55%) were present mainly in the F4 compared to other three fractions.

These metals are not easily bioavailable since the residual fraction of metals in airborne particulate matter are relatively stable. The F2 fraction recorded Zn (68%), Cu (61%), V (55%), Cr (51%) and Al (44%), while Cr (43%) and V (39%) were present as highest fraction in the F1. More so, highest trace metals in the F3 fraction were K (40%) and Al (36%). Inhaled Zn, Cu, V, Cr and Al would only be bioavailable and a risk to health under very low body pH conditions (Betha *et al.*, 2013). But, Cr and V would be available in the body once inhaled. Conversely, K being in the oxidizable fraction is relatively stable as such would not be easily soluble in the body (Fernandez-Espinosa, Rodríguez, Rosa, & Sánchez, 2002).

The chemical speciation trend in EWC $PM_{2.5}$-bound trace metal levels shows F4 > F2 > F3 > F1. Overall, the F1 and F2 represent 46%, while F3 and F4 represent 54% of the total metal concentration. The results of sequential extraction procedure in both OTE and EWC indicated that majority of the bound metals were associated in the two stable phases (F3 and F4). However, the labile phases (F1 and F2) showed strong indication of the presence of Cr, V in both locations, while OTE, had Cu in addition. Hence, Cr, V and Cu are considered to be readily soluble once $PM_{2.5}$ is inhaled into the respiratory system of human being.

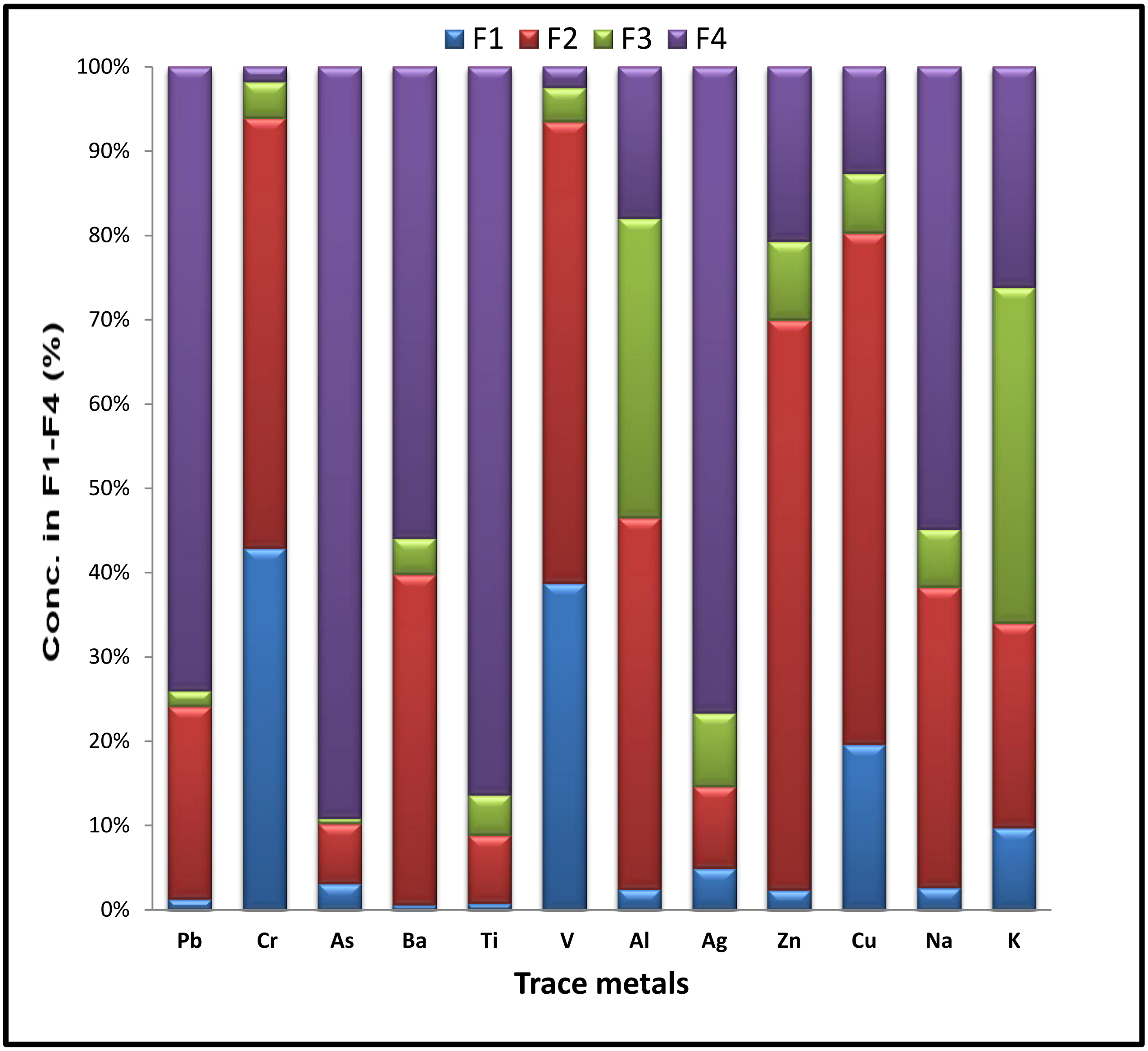

Figure 4.5: Chemical speciation distribution of EWC $PM_{2.5}$-bound metals as percentage (F1: soluble and exchangeable metals; F2: carbonates, oxides and reducible F3: metals; bound to organic matter, oxidisable and sulphidic metals; F4: residual metals)

4.5 Bioavailability Index (BI)

Bioavailability index of metals shows the amount of soluble fraction present in the cell membrane through inhalation pathway. Factor influencing the bioavailability of trace metals include surface properties of particles, the strength of the chemical bonds and the type of solutions in contact with the fine particles (Varshney, Saini, & Taneja, 2015). The calculated trace metals bioavailibity index results presented in Figure 4.6 for 14 trace metals (Pb, Cr, Ba, Cd, V, Zn, Ag, Al, Cu, Zn, Na, Mn, Ti and As) revealed that Cr and V recorded the highest bioavailability indexes of 0.9, closely followed by Cu (0.8) at EWC.

BI value of 0.7 was seen in Cd and Cr from OTE and Zn from EWC, while Al and Cu from OTE and EWC had BI value of 0.5 respectively. A slightly lower BI value of 0.4 was recorded by Pb, Ba, V and Na in OTE, EWC and CUF. Other metals recorded lowest BI values in the range of 0 to 0.3. However, CUF being an agricultural site which was chosen as a background for the industrial sites (EWC and OTE) had lower BI values in the range of 0.2-0.4. It is worth noting that amongst these metals Cd, Cr are the most toxic and their higher bioavailability index values indicate the possibility of their being fully available to physiological activities once inhaled into the respiratory system (Betha *et al.*, 2013; Feng *et al.*, 2009). This might pose significant health risks to humans and most especially residents and persons who by reason of their occupation spend most of their time in these affected areas.

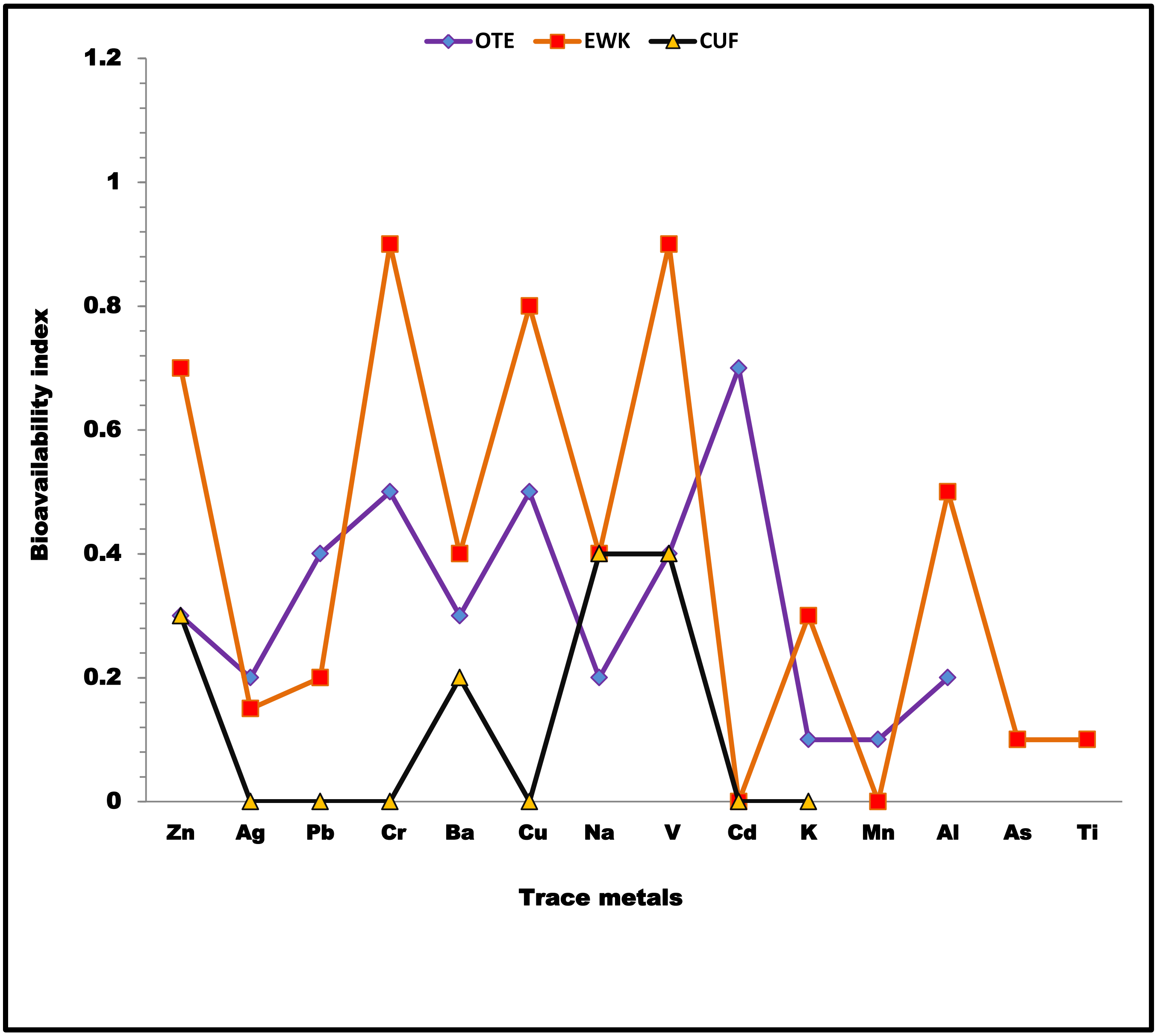

Figure 4.6: Bioavailability index of $PM_{2.5}$-bound trace metals

4.6 Cancer Risks Assessment of $PM_{2.5}$-Bound Trace Metals

Table 4.6 shows four (4) carcinogenic trace metals (arsenic, cadmium, chromium and nickel) selected among the twenty-two metals to calculate the incremental lifetime cancer risk (ILCR) at the study sites. As, Cd, Cr and Ni are capable of producing tumors of the respiratory tract, nasal passage, trachea, bronchus, and lung (Mulware, 2013). It is usually assumed that even a minute exposure to these trace metals is a potential risk.

EPA considers cancer risks between 1×10^{-6} (i.e., 1 in 1,000,000) and 1×10^{-4} (i.e., 1 in 10,000) to be generally acceptable (US EPA, 1991). Table 4.6 presents the concentration of the pollutants in the air, exposure concentration, inhalation unit risk, risk inhalation and sum of risk inhalation for all the carcinogens present in a particular study area.

Bioavailable form rather than total content of trace metal in airborne $PM_{2.5}$ was used in order to give a better and more accurate health risk estimate (Betha *et al.,* 2013; Feng *et al.*, 2009; Zajusz-Zubek, Mainka, Korban, & Pastuszka, 2015). Two approaches were considered: cumulative risks to adult and children aged 0-6 and 6-18 years at the site due to inhalation of trace metals in air. From results presented in Tables 4.6 and 4.7, the sum of the cumulative lifetime cancer risks across all investigated carcinogens due to inhalation exposures at each study site ranged as follows: adults ($1.52 \times 10^{-2} – 9.53 \times 10^{-2}$); children 1-6 years old ($1.09 \times 10^{-2} – 4.95 \times 10^{-4}$) and children 6-18 years old ($1.49 \times 10^{-3} – 3.27 \times 10^{-2}$). It is evident that the results obtained from all the study sites were above EPA’s acceptable risk range of 1×10^{-6} to 1×10^{-4}.

Table 4.6: Adults' cancer risks assessment of $PM_{2.5}$-bound trace metals

Sample site	Elements	CA	EC	IUR	$Risk_{inhalation}$	$\sum Risk_{inhalation}$
OTE	Cr	4.78	3.43	1.2×10^{-2}	4.11×10^{-2}	4.25×10^{-2}
	Cd	4.49×10^{-1}	3.22×10^{-1}	1.8×10^{-3}	6.00×10^{-3}	
	As	2.32×10^{-1}	1.67×10^{-1}	4.3×10^{-3}	7.00×10^{-4}	
	Ni	1.11×10^{-1}	8.00×10^{-2}	2.4×10^{-4}	1.91×10^{-5}	
EWC	Cr	1.08×10^{1}	7.72	1.2×10^{-2}	9.26×10^{-2}	9.53×10^{-2}
	Cd	1.31×10^{-2}	9.00×10^{-3}	1.8×10^{-3}	1.69×10^{-5}	
	As	8.79×10^{-1}	6.31×10^{-1}	4.3×10^{-3}	2.71×10^{-3}	
	Ni	1.67×10^{-2}	1.20×10^{-2}	2.4×10^{-4}	2.88×10^{-6}	
AGE	Cr	3.54×10^{-1}	2.54×10^{-1}	1.2×10^{-2}	3.05×10^{-3}	4.32×10^{-3}
	Cd	2.53×10^{-1}	1.82×10^{-1}	1.8×10^{-3}	3.27×10^{-4}	
	As	3.07×10^{-1}	2.20×10^{-1}	4.3×10^{-3}	9.48×10^{-4}	
CUF	Cr	1.74	1.25	1.2×10^{-2}	1.50×10^{-2}	1.52×10^{-2}
	Cd	1.88×10^{-1}	1.35×10^{-1}	1.8×10^{-3}	2.43×10^{-4}	

Table 4.7: Children cancer risks assessment of $PM_{2.5}$-bound trace metals

	Sample Site	Elements	CA	EC	IUR	$Risk_{Inhalation}$	$\sum Risk_{Inhalation}$
	OTE	Cr	4.78	3.93	1.2×10^{-2}	4.72×10^{-3}	4.87×10^{-3}
		Cd	4.49×10^{-1}	3.69×10^{-2}	1.8×10^{-3}	6.64×10^{-5}	
		As	2.32×10^{-1}	1.91×10^{-2}	4.3×10^{-3}	8.21×10^{-5}	
		Ni	1.11×10^{-1}	9.12×10^{-3}	2.4×10^{-4}	2.19×10^{-6}	
1-6 years	EWC	Cr	1.08×10^{1}	8.84×10^{-1}	1.2×10^{-2}	1.06×10^{-2}	1.09×10^{-2}
		Cd	1.31×10^{-2}	1.08×10^{-3}	1.8×10^{-3}	1.94×10^{-6}	
		As	8.79×10^{-1}	7.22×10^{-2}	4.3×10^{-3}	3.10×10^{-4}	
		Ni	1.67×10^{-2}	1.37×10^{-3}	2.4×10^{-4}	3.29×10^{-7}	
	AGE	Cr	3.54×10^{-1}	2.91×10^{-2}	1.2×10^{-2}	3.49×10^{-4}	4.95×10^{-4}
		Cd	2.53×10^{-1}	2.80×10^{-2}	1.8×10^{-3}	3.74×10^{-5}	
		As	3.07×10^{-1}	2.52×10^{-2}	4.3×10^{-3}	1.08×10^{-4}	
	CUF	Cr	1.74	1.43×10^{-1}	1.2×10^{-2}	1.72×10^{-3}	1.74×10^{-3}
		Cd	1.88×10^{-1}	1.55×10^{-2}	1.8×10^{-3}	2.79×10^{-5}	
	OTE	Cr	4.78	1.18	1.2×10^{-2}	1.42×10^{-2}	1.46×10^{-2}
		Cd	4.49×10^{-1}	1.12×10^{-1}	1.8×10^{-3}	2.02×10^{-4}	
		As	2.32×10^{-1}	5.73×10^{-2}	4.3×10^{-3}	2.46×10^{-4}	
		Ni	1.11×10^{-1}	2.74×10^{-2}	2.4×10^{-4}	6.58×10^{-6}	
6-18 years	EWC	Cr	1.08×10^{1}	2.65	1.2×10^{-2}	3.18×10^{-2}	3.27×10^{-2}
		Cd	1.31×10^{-2}	3.23×10^{-3}	1.8×10^{-3}	5.81×10^{-6}	
		As	8.79×10^{-1}	2.17×10^{-1}	4.3×10^{-3}	9.33×10^{-4}	
		Ni	1.67×10^{-2}	4.12×10^{-3}	2.4×10^{-4}	9.89×10^{-7}	
	AGE	Cr	3.54×10^{-1}	8.73×10^{-2}	1.2×10^{-2}	1.05×10^{-3}	1.49×10^{-3}
		Cd	2.53×10^{-1}	6.24×10^{-2}	1.8×10^{-3}	1.12×10^{-4}	
		As	3.07×10^{-1}	7.57×10^{-2}	4.3×10^{-3}	3.26×10^{-4}	
	CUF	Cr	1.74	4.29×10^{-1}	1.2×10^{-2}	5.15×10^{-3}	5.23×10^{-3}
		Cd	1.88×10^{-1}	4.64×10^{-2}	1.8×10^{-3}	8.35×10^{-5}	

The highest total cancer risks were experienced by residents living in proximity to the EWC site, representing the Ewekoro community, with risks of 9.53×10^{-2}, primarily due to exposures to chromium, arsenic, cadmium and nickel. The cancer risks for each individual carcinogen due to inhalation exposures at the various sites are discussed in details below.

4.6.1 Cadmium

The condition for estimating cadmium cancer risk according to US EPA explains that if a person continuously breathes air containing cadmium at an average of 0.0006 µg/m^3 over his or her entire lifetime, such a person would theoretically have a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical. Similarly, continuous breathing of cadmium contaminated air containing 0.006 and 0.06 µg/m^3 would result in a one-in-a-hundred thousand increased chance of developing cancer, and a one-in-ten thousand increased chance of developing cancer respectively. The estimations on Tables 4.6 and 4.7 show that the range of the incremental lifetime cancer risks of Cd due to inhalation exposures at all the investigated sites for adults (1.69×10^{-5}– $6.00 \text{ x } 10^{-3}$) and children 1 – 6 (1.94×10^{-6}– 6.64×10^{-5}); children 6-18 (5.81×10^{-6} – 2.02×10^{-4}) were within EPAs acceptable risk range (i.e., 6×10^{-4} to 6×10^{-2}). The highest cancer risks of 0.0006 µg/m^3 was observed for adults in OTE. This implies that for adults residing in OTE, one person out of a million has an increased chance of developing cancer as a direct result of breathing air containing cadmium over their entire lifetime (US EPA, 1999c).

4.6.2 Nickel

Incremental lifetime cancer risks of Ni in this study were within the EPA's acceptable risk range of 0.004 to 0.4 µg/m^3. Overall, the results obtained indicated that the highest Ni (1.91×10^{-5} µg/m^3) was estimated for adults, while the lowest was for children of ages 1 – 6 (3.29×10^{-7} µg/m^3) at EWC as shown in Tables 4.6 and 4.7.

4.6.3 Chromium

EPAs acceptable risk range of chromium is 0.00008, 0.0008 and 0.008 µg/m^3. OTE (4.11×10^{-2} µg/m^3), EWC (9.26×10^{-2} µg/m^3) and CUF (1.50×10^{-2} µg/m^3) for adults were above EPA's acceptable risk, with the exception of AGE (3.05×10^{-3} µg/m^3) as shown in Tables 4.6 and 4.7. Also, elevated levels of Cr in children within ages 1 – 6 and 6 – 18 were observed above the stipulated risk range for EWC (1.06×10^{-2} µg/m^3); OTE (1.42×10^{-2} µg/m^3) and EWC (3.18×10^{-2} µg/m^3). This would result in greater than a one-in-ten-thousand increased risk of developing cancer during one's lifetime.

4.6.4 Arsenic

EPA's acceptable risk range of arsenic is 0.0002, 0.002 and 0.02 µg/m^3. As shown in Tables 4.6 and 4.7, this study indicates that arsenic incremental lifetime cancer complied with the EPA acceptable risk value of 0.002 and 0.02 µg/m^3 with exception of 0.0002 µg/m^3 for some specified locations. These locations include: adults: OTE (7.00×10^{-4} µg/m^3) and AGE (9.48×10^{-4} µg/m^3); children ages 1-6: EWC (3.10×10^{-4} µg/m^3) and ages 6-18: OTE (2.46×10^{-4} µg/m^3), EWC (9.33×10^{-4} µg/m^3), AGE (3.26×10^{-4} µg/m^3). These results indicate that one (1) person out of a million people could get cancer after exposure to arsenic trace metals in ambient air inhaled from the investigated study area. In addition, a result for adults in EWC (2.71×10^{-3} $\mu g/m^3$), was slightly above the levels of 0.002 $\mu g/m^3$ which is tending toward an incremental lifetime cancer risk of one in a hundred thousand increased chance of developing cancer resulting from inhalation of arsenic polluted air. The above estimations show that the incremental lifetime cancer risks of As and Cr were higher in some study locations than the EPA acceptable risks range, while Cd and Ni were found within the acceptable risk range. The same findings were observed by Feng *et al*. (2009). Thus, air particle pollution may pose serious health risks to the residents in affected study area.

4.7 $PM_{2.5}$ Air Quality Index (AQI) Seasonal Variation in EWC, OTE, AGE and CUF

Air quality index is a colour-coded tool for notifying the public how clean or polluted the air is and steps to employ to cut down on their daily exposure to pollution. The US EPA AQI classification was used in the computation of AQI in this work. The AQI was divided into six levels of health concern namely: good (0–50), moderate (51–100*), unhealthy for sensitive groups (101–150), unhealthy (151–200), very unhealthy (201–300) and hazardous (301–500). A $PM_{2.5}$ level above 500 is known as (“beyond index”), but the U.S. AQI does not make provision for it. An AQI value of 100 as identified with the asterisk symbol, generally corresponds to the national ambient air quality standards (NAAQS) set by the EPA to protect public health. The index value of 100 is set at the level of the current 24-hour $PM_{2.5}$ standard, which is 35 $\mu g/m^3$ (Mintz, 2012). The discussion on the obtained results will be done based on the two seasons of sampling, considering the variation in AQI between weekday and weekend. A spatial map, obtained following the US EPA revised AQI breakpoints for $PM_{2.5}$ at 24-hour average as shown in Table 3.4 was used in the presentation of results.

4.7.1 $PM_{2.5}$ Air Quality Index in EWC, OTE, AGE and CUF for Wet Season

During the wet season (July, September, and October), monitoring of $PM_{2.5}$ air quality was carried out during weekdays and weekends to capture possible variation in the emitted air. As presented, the spatial map in Figure 4.7 shows that for a major part of the wet season, the weekday air quality for EWC and AGE remained in the "unhealthy" category with index value of 151 – 200. The percentage of occurrence of this category at EWC and AGE was 56 and 50% respectively, that of OTE location was in the "very unhealthy" category, with index value of 201 – 300 at 34% occurrence, while other categories are represented as follows: "unhealthy for sensitive group" [OTE (22 %), EWC (0 %) and AGE (15%)]; "unhealthy" OTE (22%); "very unhealthy" EWC (33%) and AGE (35%) and "hazardous" air quality was 22% for OTE and 11% for EWC.

It is quite revealing to note that the air quality category 'good to moderate', which represents the index value 0 – 100, was significantly absent in the weekdays of wet season, implying that the air quality was unhealthy for both the sensitive groups and for everyone in this location (US EPA, 2014).

Also, Figure 4.8 indicates that for the major part of the wet season, the weekend air quality was categorized as "unhealthy" in all the industrial sites. The percentage of occurrence of this category was 38% for OTE and EWC, and 50% for AGE. Other categories were represented as follows: moderate group OTE (25%); "unhealthy for sensitive group" EWC (25%) and AGE (15%); "very unhealthy" OTE (25%) EWC (25%) and AGE (35%) and hazardous air quality was 12% for OTE and 13% for EWC, respectively.

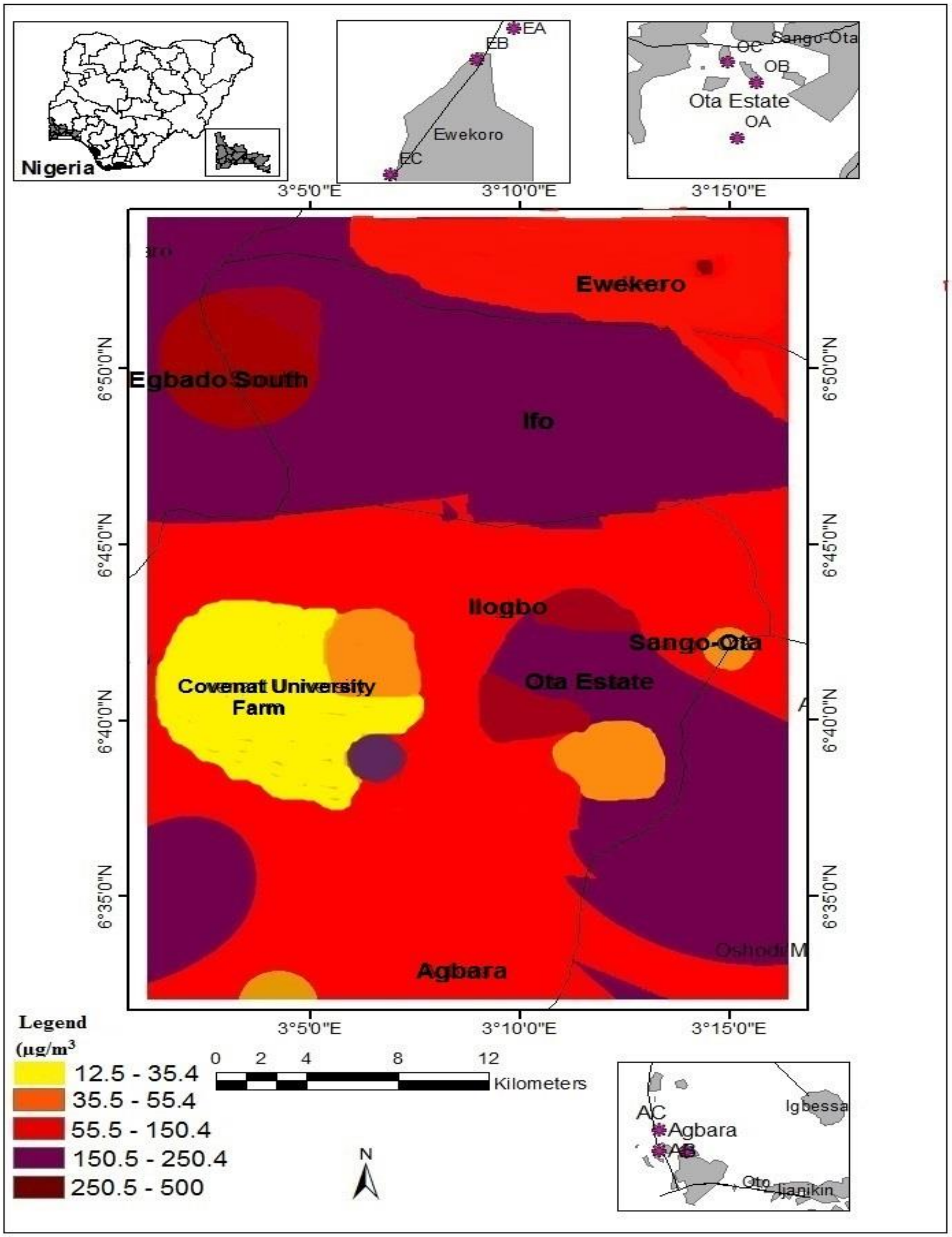

Figure 4.7: Spatial map of typical weekday $PM_{2.5}$ AQI in study area during wet season

When compared with quality of air at background site (CUF), a remarkable difference was seen in the category of “moderate” to “unhealthy for sensitive group” at about 50 and 60% occurrence in both weekday and weekend. Even though the air in CUF was of improved quality as compared to the industrial locations, there was the possibility of influence of pollution from the OTE, which is the closest to CUF.

Similar to the weekday results, most weekend AQI values were above 100, signifying poor air quality. The slight variation in weekend air quality from weekday air quality was the presence of moderate (51 – 100*) category, but it did not exist for any significant length of time. Only 11% of the rainy season weekend air quality reflected this category. Overall, the air quality of the weekend appears better when compared with that of the weekday, even though they both have strong tendency for possible adverse health concerns, especially for the sensitive group. The state of air quality in the industrial location can be explained from this underlying fact: OTE and AGE representing Ota and Agbara industrial/residential estate have the largest concentration of functioning industries in Ado-Odo/Ota local government area which borders on metropolitan Lagos. Being a mixed community, it is majorly influenced by industrial activities such as scrap recycling, production of chemicals, pharmaceuticals, food and beverages, plastics, woods, metals and steel as well as other activities: traffic congestion, fugitive dust from unpaved roads and residential heating using wood and stove amongst others. The pollutants emitted from chimney, stacks, and open burning of solid waste with little or no effective pollution emission control pose a threat to human health and the environment.

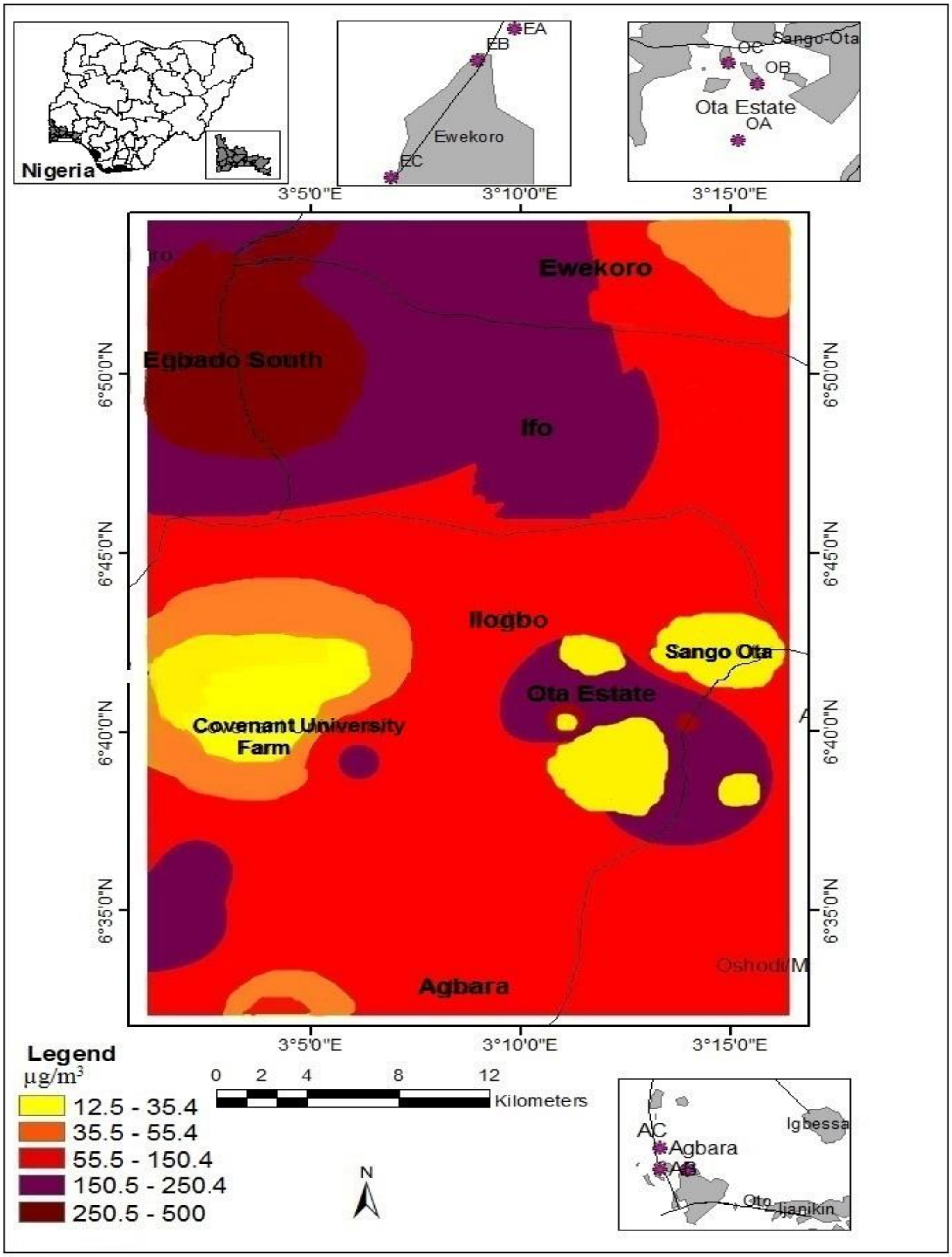

Figure 4.8: Spatial map of typical weekend $PM_{2.5}$ AQI in study area during wet season

The “very unhealthy’ category shown in the spatial map for OTE, is in line with the common occurrence of thick black and whitish emission from chimney, along with noxious gases, fumes, smoke and dust, causing itching of the throat, coughing, and irritation of the eyes and nose at site OB and OA while site OC had continuous direct emission of thick black, and whitish fumes from chimneys of the surrounding industries. This result compares favourably with previous results obtained by applying a modeled data on Ota industrial estate pollution loads (Etim, 2012) as well as that of Odesanya, Ajayi, Shittu, and Oshin (2012) on Ota and Agbara industrial estates.

Also, the state of Agbara (AGE) “unhealthy” air quality, can be attributed to a combination of particle emission from industries, buildings and roads construction, fugitive dust from unpaved roads, dust from the wood market, traffic congestion, residential heating using wood and stove and the frequent open burning of solid wastes along Atan/Agbara road.

In addition, the “unhealthy” air quality in Ewekoro (EWC) can be attributed to particle pollution caused by different industries, limestone quarrying, loading and unloading of cement, fossil fuel emission from heavy vehicles, woodstoves, power plants, unpaved roads, open burning of solid waste and tyres, reaction of gaseous pollutants such as sulphur dioxide (SO_2) and nitrogen oxides (NO and NO_2, referred together as NOx), etc. From interaction with residents during sample collection, frequently reported health conditions experienced include, coughing, wheezing, and asthma, itchy skin, eye problem, stomach ache, pneumonia, and respiratory tract diseases. Also, Afolabi, Francis, and Adejompo (2012) from their research on health and environmental challenges of cement factory on Ewekoro community residents confirmed incidences of air pollution amongst others above recommended minimum limits as well as four prevalent diseases namely asthma, heart disease, skin cancer and diarrhea.

4.7.2 Dry Season $PM_{2.5}$ AQI in EWC, OTE, AGE and CUF

The AQI spatial map results (Figures 4.9 and 4.10) obtained for dry season (November–January) showed that the weekday and weekend air quality varies for all the industrial locations (OTE, EWC and AGE). Results indicated that for major part of the weekday period (Figure 4.9), OTE was predominantly in the red and purple range at 66% occurrence, signifying an index of 151 – 300, which is in the category of “unhealthy” to “very unhealthy”. This implies that healthy people could be noticeably affected by particle pollution while people with breathing or heart problems could experience reduced endurance in activities. These individuals and the elderly are usually advised to remain indoors and restrict activities. This would trigger a health alert which signifies the possibility of everyone experiencing more serious health effects. The other 33% of OTE results for weekday dry season experienced a worse air quality scenario from “hazardous” to two incidences of “beyond index” (> 500) precisely at OB and OC.

The weekend AQI was in the red to marone range with two incidences of “beyond index” (> 500) which occurred at the same sites as that of weekday (OB and OC). The highest occurrence was observed at the purple range (37.5%), signifying an index of 201 – 300, which is in the category of “very unhealthy”.

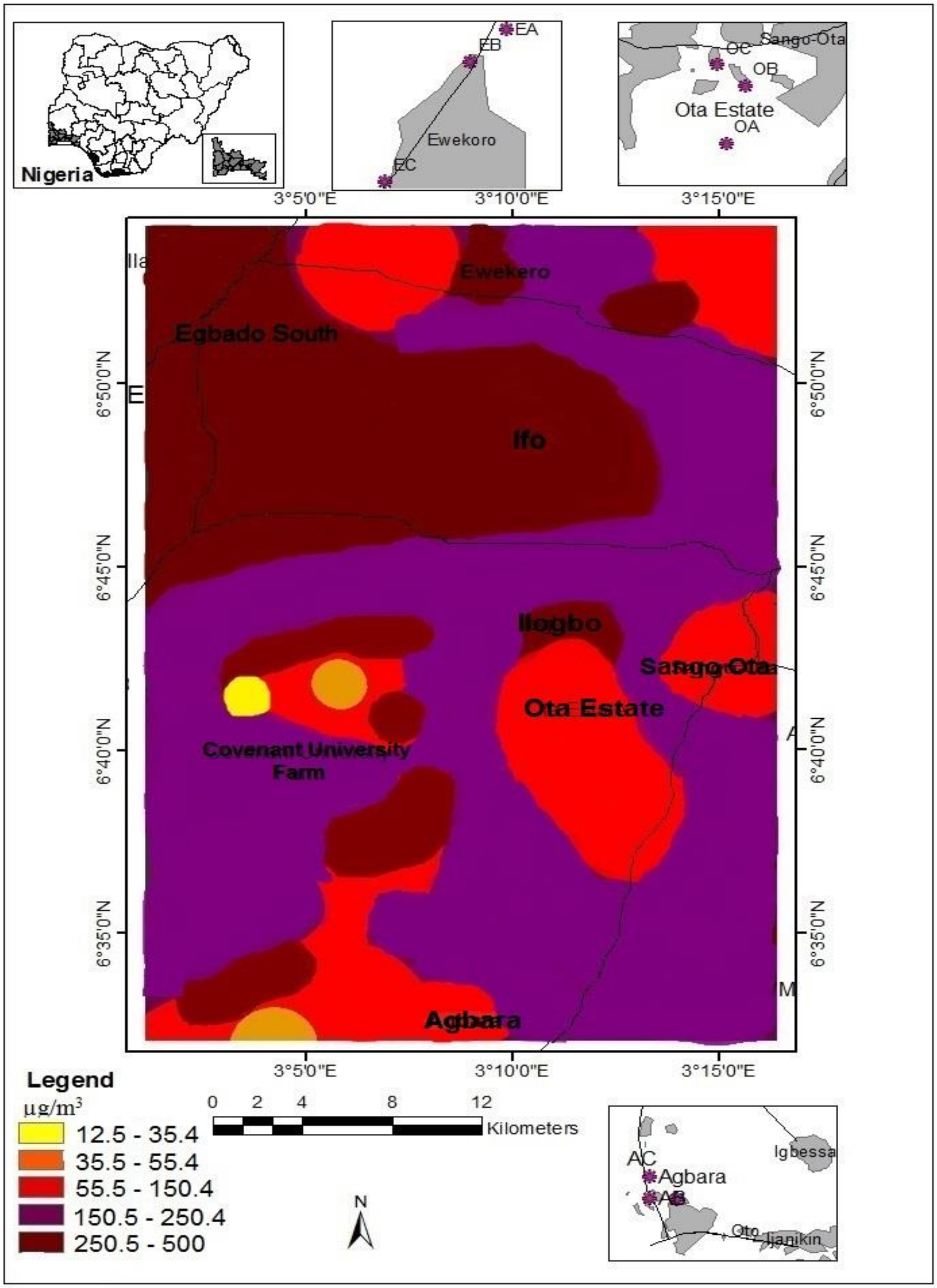

Figure 4.9: Spatial map of typical weekday $PM_{2.5}$ AQI in study area during dry season

The red range (12.5%) had the least occurrence while the marone and "beyond index" range had 25% occurrence respectively. At this level, everyone is at risk; these may cause strong irritations and symptoms and may trigger other illnesses.

AQI for EWC was in the red to marone range with two incidences of “beyond index (> 500)” which occurred at EA and EC. The marone range (33%) had the highest occurrence, signifying an index of 301-500, which is in the category of “hazardous”. The other period of this season had equal distribution of the red, purple and "beyond index" range.

Contrary to the weekday results, the weekend AQI as shown in Figure 4.10, was in the red to marone range with no incidence of “beyond index (> 500)”. The highest occurrence was observed at the purple range (44%), followed by marone range (33%) and the red range (12.5%). The effect of particle pollution is really obvious in dry season at EWC, based on the earlier identified sources of particles. But prominently, Larfage Cement Company stood out as the major culprit of particle emission during the dry season, starting from the blasting of limestone used in cement making to the obvious continuous release of huge quantity of whitish and grayish dust from their chimneys into the atmosphere which causes damage and leaves unappealing sights on the surrounding buildings, trees, lakes, plants, and soil. From interaction with residents during sample collection, frequent health hazards experienced include, coughing, wheezing, and asthma, itching on skin, eye problem, stomach ache, pneumonia, and respiratory tract diseases. This finding confirms similar reports by Afolabi, Francis, & Adejompo, 2012. Adekunle *et al*. (2015) have also reported the effects of these fine particles on the technical efficiency of cassava-based farmers in Ewekoro LGA.

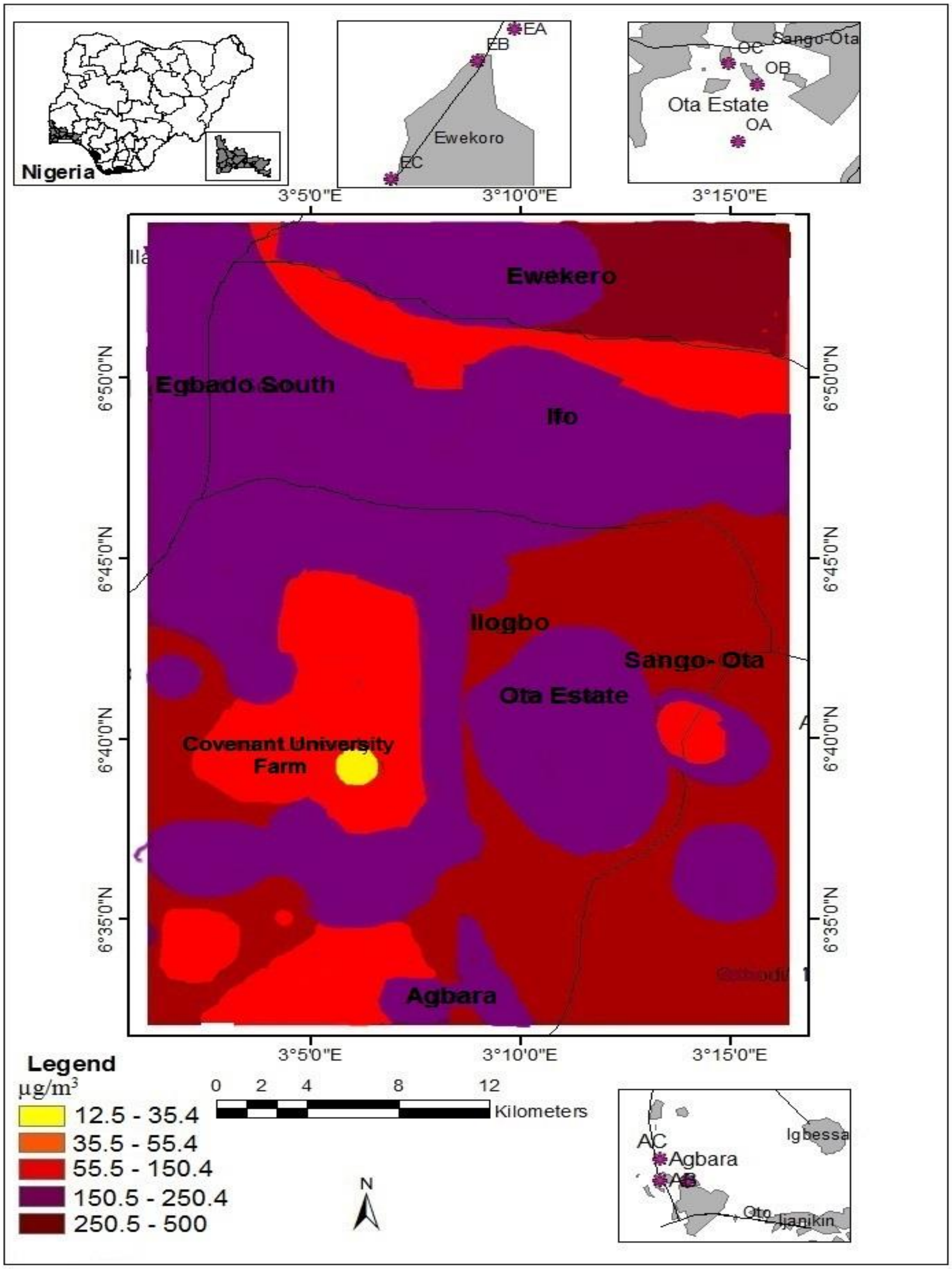

Figure 4.10: Spatial map of typical weekend $PM_{2.5}$ AQI in study area during dry season

The results revealed 139 illness episodes with 56% of the total illnesses due to respiratory disease. This, therefore, calls for caution to the public in general. Exposure to such high levels of particle pollution, increases susceptibility to respiratory infections and aggravate existing respiratory problem. Hence, people with heart or lung diseases and older adults are more likely to visit the emergency rooms, be admitted to hospitals, or in some cases, even die (US EPA, 2014).

Also, Figures 4.9 and 4.10 indicate that for the major part of the season, the weekday and weekend air quality for AGE had the highest percentage of occurrence of 43% and 37.5% respectively in the "unhealthy category", identified in the red range. For the week day, 14% occurrence was observed in the orange and marone range, while 29% was "beyond index", which is typical of site AB. The weekend results showed 25% occurrence for the marone range and 12.5% representing the yellow, purple and beyond index range at same site as weekday (AB). Red range means that everyone may begin to experience some adverse health effects, most especially members of the sensitive groups (the elderly, children and people with asthma or other respiratory diseases may experience more serious effects). This poor air quality can be attributed to particle emission from a combination of industrial, commercial, domestic sources as well as the close proximity of AGE to Lagos. Apart from these, the beyond index observed at site AB in the dry season for both week day and weekend, is a pointer to the contribution of particles generated in its immediate environment being outside the premises of Unilever Nigeria Plc., producers of savouries, toothpastes detergents etc., along with other surrounding industries, major unpaved roads, solid waste dump site, etc. Possible adverse health concerns which may be observed within a few hours or days after breathing polluted air includes unusual coughing, chest discomfort, wheezing, breathing difficulty and unusual fatigue. These symptoms, acts as caution to cut down on activity levels during this period (US EPA, 2015c).

The quality of air at background site (CUF), for week day throughout the dry season period ranged from the "moderate" to "hazardous" category with one incidence of "beyond index" at site CB and CC. The percentage of occurrence of these categories were 11% each for yellow, orange and red range and 22% for the purple, marone and "beyond index", whereas for the week end period the AQI ranged from the "unhealthy for sensitive group" to "hazardous" category with only one incidence of "beyond index" at site CC. The percentages of occurrence of these categories were 33% for the red range, 22% for the purple and marone and 11% for the orange and beyond index. Both weekday and weekend results indicated the deterioration in air quality. Possible sources that may contribute to this condition include emission from fabrication of farm tools, domestic and vehicular exhaust fumes from the residential estate close to the farm and long range pollution from Ota industrial estate. Even though the weekday and weekend AQI results for CUF was equally polluted, however, it still had less polluted air when compared with the three industrial sites.

Similar to the weekday results, most weekend AQI values were above 100, signifying poor air quality. The slight variation in weekend air quality from weekday air quality was the presence of moderate (51 – 100*) category, but it did not exist for any significant length of time. Only 4% of the dry season weekend air quality reflected this category. Overall, the air quality of the weekend appears slightly less polluted than that of the weekday, but both periods posed serious health threats to all categories of people resident in the study area.

It is quite revealing that the air quality category ‘good to moderate’ does not exist in week day for both seasons, in all the industrial sites. However, looking at the difference between wet and dry season, “beyond index” was absent, in the rainy season when compared to the frequency of its occurrence in the dry season. Moreover, it is clearly seen from the $PM_{2.5}$ AQI spatial map in Figures 4.7, 4.8, 4.9 and 4.10 that the air quality during the wet season was less polluted than the dry season. This is expected due to the washing effect of rain and relative humidity associated with the wet season (Megaritis *et al.*, 2014).

The state of AQI for these industrial areas is attributed to the diverse fine particle pollution sources, increased production during the dry season period and the contribution of harmattan from late December to mid-January. This period was characterized by very dry and dusty weather along with low humidity, linked to the dust laden North-east trade winds from the Sahara desert. In addition, the rise in AQI may also be attributed to stagnant air due to low wind speed. This allows air pollution to remain in a local area, resulting in high concentrations of pollutants and hazy conditions.

Overall, the AQI, for the fine particle pollution indices scaled from 51 to 500, reflecting six out of the seven AQI categories in varying proportions. The absence of 0 to 50 gradations representing the good AQI category was conspicuously highlighted. Results indicate that most AQI values were above 100. Possible adverse health concerns mostly for the vulnerable populations are indicated considering the unhealthy air quality state of studied locations.

4.8 Morphology and Elemental Composition of $PM_{2.5}$ Particle

The origin of fine particulate matter can be traced based on their microscopic morphology and chemical composition. This is possible because information obtained from the structures, sizes and chemical composition of particles can be used to further authenticate their sources (Anake, Benson, & Ana, 2016; Campos-Ramos, *et al*., 2010; Mummullage *et al*., 2016). The morphology and elemental composition results of atmospheric fine particles ($PM_{2.5}$) from four different sites (OTE, EWC, AGE and CUF) during different seasons are depicted in Figures 4.11 to 4.18. Based on the images and elemental composition of $PM_{2.5}$, the particles were classified into different categories namely: soil dust mineral, soot aggregation, alumino silicate and fly ash particles.

4.8.1 Soil Dust Mineral Particles

Mineral particles may be derived from both natural and anthropogenic sources. The natural sources include soil dust and suspension of dust from roads while anthropogenic sources include construction, coal combustion and vehicle emission (Li *et al*., 2010; Pipal & Satsangi, 2015). Two common types of mineral particles include the irregular shapes and elongated particles believed to originate from geological and secondary atmospheric reaction respectively (Yue *et al*., 2006). A type of ellipsoidal particle (Figure 4.11) was found in the background sampling point (CUF). On the basis of the distribution of the major elements in particulate matter, the atomic percentages of O, Si, C, Na, Ba, Zn, Al, K and Ca were 50.53%, 18.37%, 14.11%, 5.29%, 3.45%, 2.90%, 2.39%, 1.84% and 1.11%, respectively; among these elements, O and Si were the major components. Similar image have been confirmed in soil particles with surfaces that have a greater elastic particle adhesion (Wu, Liu, & Fan, 2015).

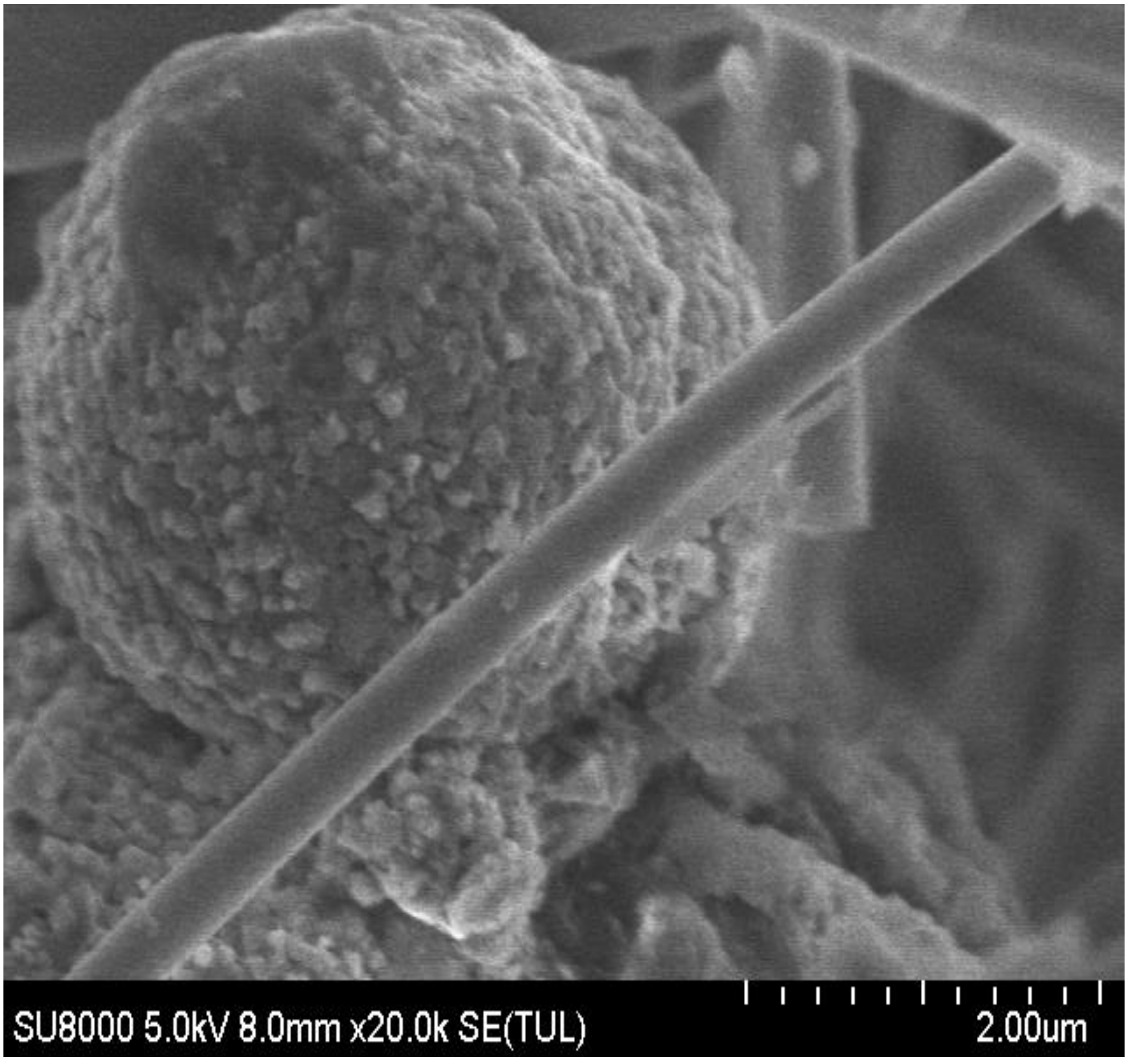

Figure 4.11:Morphology of $PM_{2.5}$ at CUF during the wet season

4.8.2 Soot Particles

The SEM photomicrographs of some characteristic soot particles are presented in Figures 4.12 – 4.14. Soot are formed in diverse ways, it could be from high temperatures through gas to-particle conversion or from emissions of combustion sources, such as, burning fuel oil, power plant, vehicle exhaust and biomass burning. Therefore, they are known markers of anthropogenic emission mainly from industrial and vehicular origin (Anake, Ana and Benson, 2016; Margiotta *et al*., 2015). It is present as agglomerates of many fine spherical primary particles. This kind of aggregate has an irregular morphology of various shapes. Soot particles were present in abundance in most of the samples especially in the industrial site (OTE, EWC and AGE) and were easily identified due to their unique morphology. $PM_{2.5}$ soot particles consisted of three dominant morphological types as follows: chainlike soot particles (EWC), cluster soot particles (AGE), and simple soot particles (OTE).

The SEM-EDX results of particulate matter collected at Ewekoro community (Figure 4.12) during the dry season revealed that the distribution of major elements in such aggregates included O, Si, C, Na, Ba, Zn, Al, Ca and Cl of which the atomic percentages were 50.7%, 18.9%, 12.9%, 5.69%, 3.57%, 2.43%, 2.43%, 1.94%, 1.14% and 0.23%, respectively, with high contents of O, Si, and C. The main sources of particulate matter were anthropogenic combustion. Soot particles of $PM_{2.5}$ collected at Agbara were characterized by clustered soot particles (Figure 4.13). The elemental composition of these particles included O, Si, C, Na, Ba, Al, Zn, K and Ca with atomic percentages of 51.4%, 18.8%, 12.5%, 5.68%, 3.65%, 2.66 %, 2.38%, 1.84%, and 1.07%, respectively. The main emission sources of soot particles at AGE were combustion of fossil fuel and biomass burning.

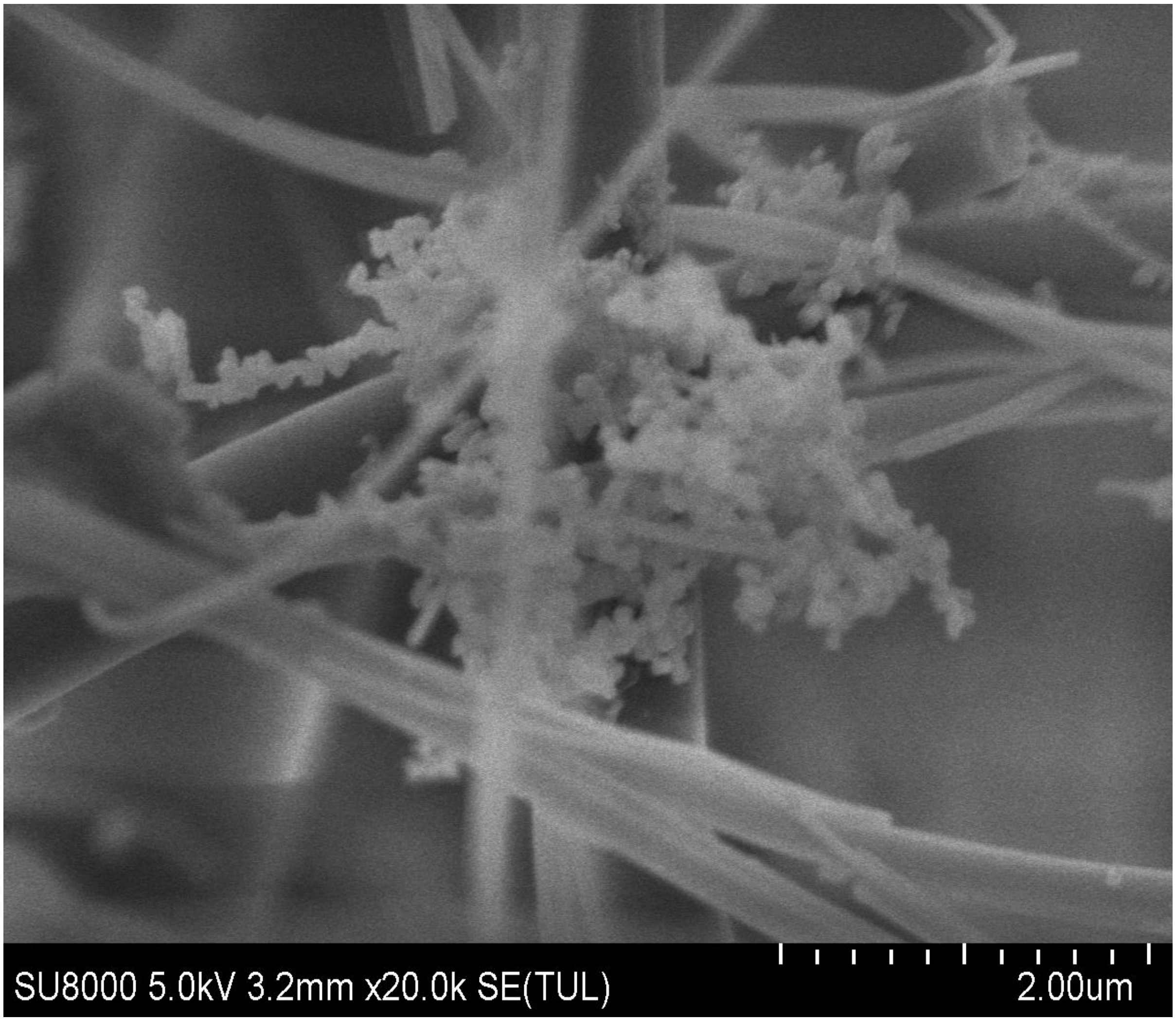

Figure 4.12: Morphology of $PM_{2.5}$ soot particles at EWC during the dry season

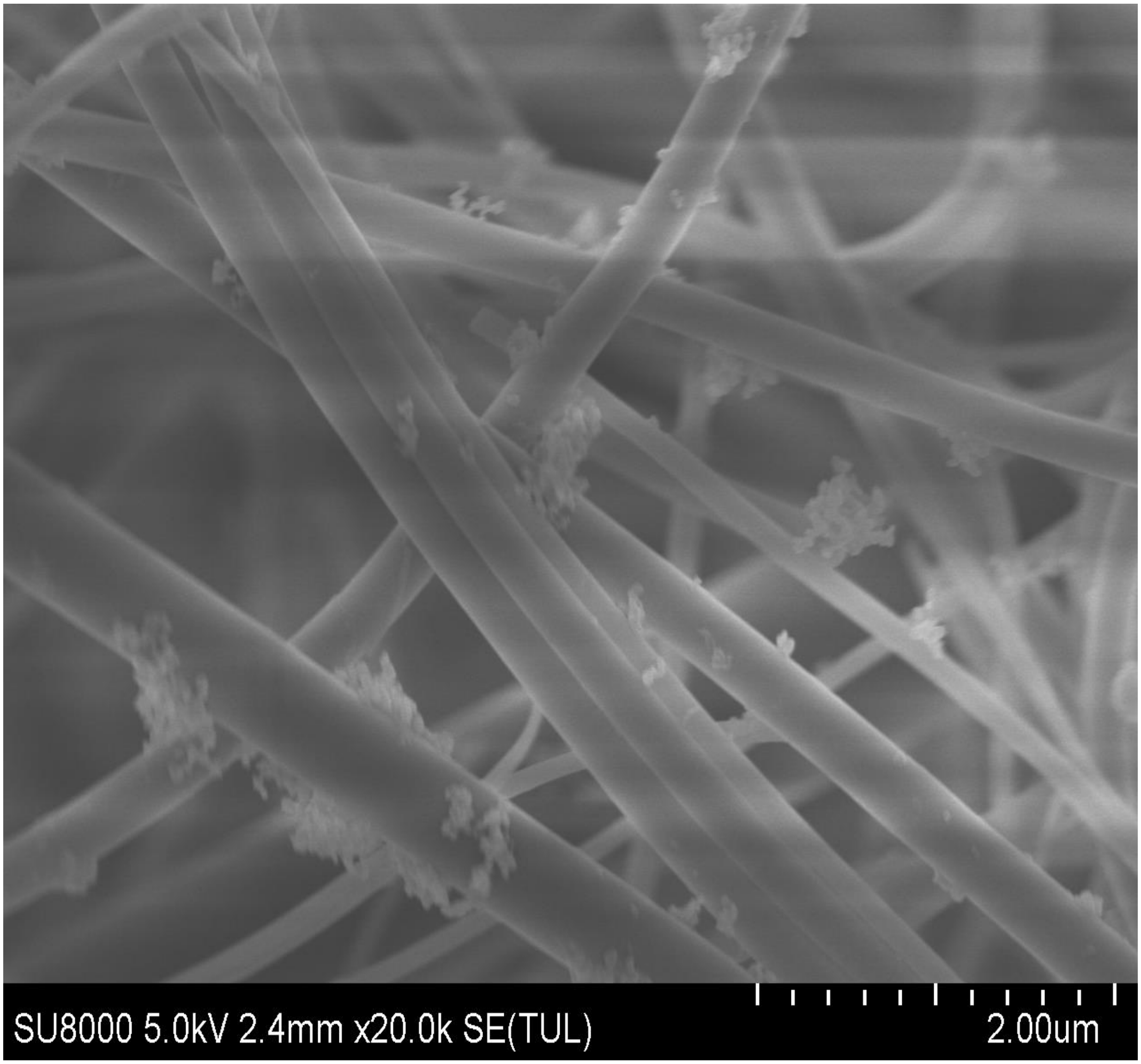

Figure 4.13: Morphology of $PM_{2.5}$ soot particles at AGE during the dry season

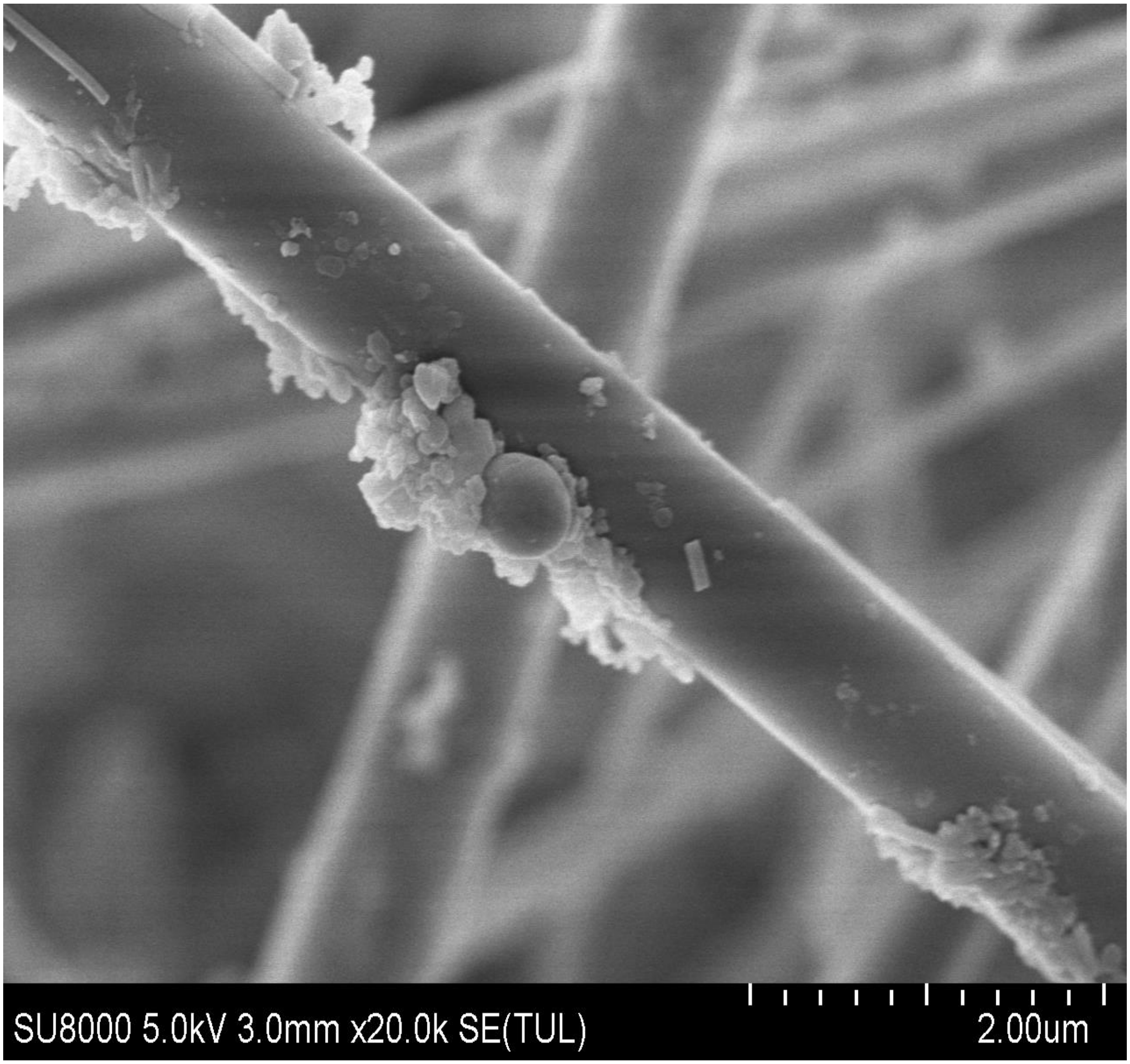

Figure 4.14: Morphology of $PM_{2.5}$ soot particles at OTE during the wet season

OTE soot particles are shown on Figure 4.14. The distribution of the major elements associated with the fine particulate showed that the atomic percentages of O, Si, C, Na, Ba, Zn, Al, K and Ca were 50.7%, 17.5%, 16.0%, 4.93%, 3.28%, 2.65%, 2.19%, 1.66% and 1.05%, respectively; among these elements, O, Si and C were dominant. The variation in the morphology of soot particles was a function of the different types of fuels, incomplete fossil fuel combustion, industrial and residential combustion, biomass burning as well as atmospheric processes (Pipal & Satsangi, 2015).

4.8.3 Fly Ash Particles

Fly ash particles originate from diverse combustion processes including vehicular emissions and coal burning. Aluminosilicates dominate in the finer fraction as anthropogenic fly ash due to fossil fuel combustion process. Industrial combustion generates Si containing fly ash; these types of particles are usually abundant in heavily industrialized areas (Singh *et al*., 2014a). According to Lu *et al*. (2011), fly ash particles comprise of amorphous, spherical, and irregular shape and are of utmost concern since they are regarded as respirable with the potential of causing damage to the human respiratory system.

The morphology of OTE fly ash particles is shown on Figure 4.15a SEM image. The distribution of the major elements associated with the fine particulate showed that the atomic percentages of O, C, Si, Na, Al, Ba, Ca, Zn, K, Fe, Cl and S were 49.8%, 18.5%, 14.7%, 3.95%, 2.82%, 2.73%, 2.42%, 2.18%, 1.39%, 0.59%, 0.31% and 0.31%, respectively. Also, Figure 4.15b presents fly ash particles of $PM_{2.5}$ collected at EWC. The elemental composition of these particles includes O, Si, C, Na, Ba, Zn, Al, K, Ca, Cl and Mg with atomic percentages of 50.9%, 17.4%, 16.1%, 4.01%, 2.95%, 2.94%, 2.03%, 1.61%, 1.41%, 0.63% and 0.23%, respectively. Fly ash particles are rated as being very toxic due to the presence of enhanced levels of bioavailable trace metals and other chemical contaminants (Pipal & Satsangi, 2015).

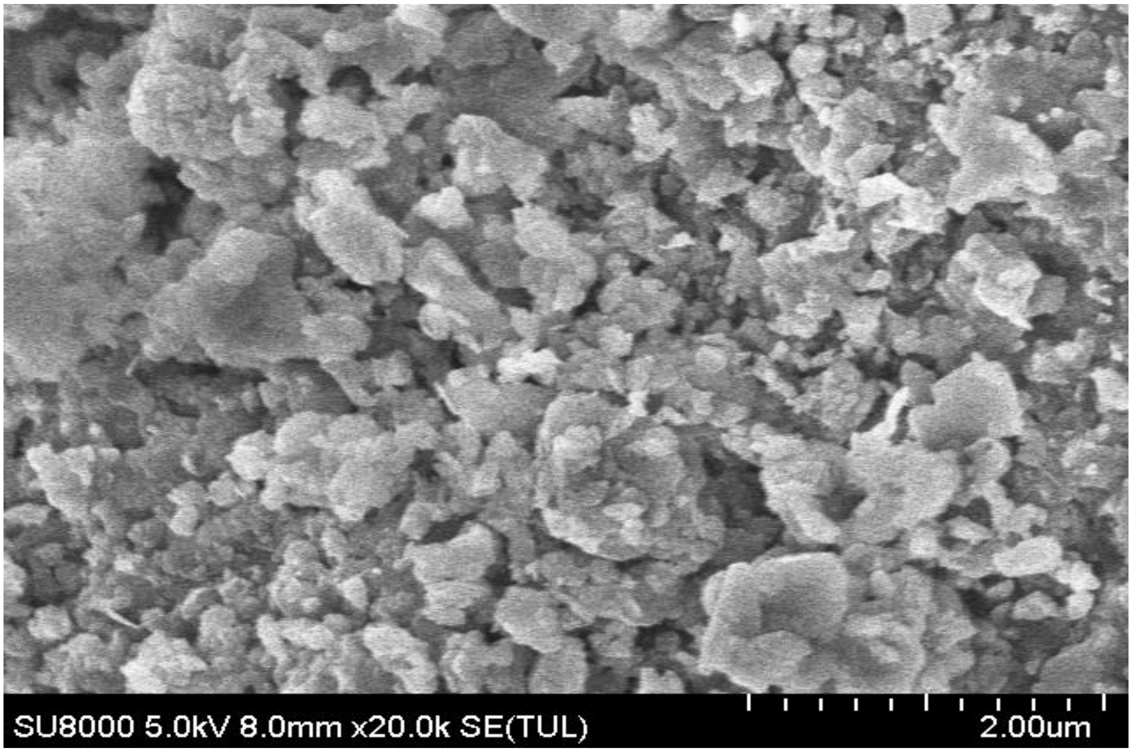

Figure 4.15a: Morphology of $PM_{2.5}$ fly ash particles at OTE during the dry season

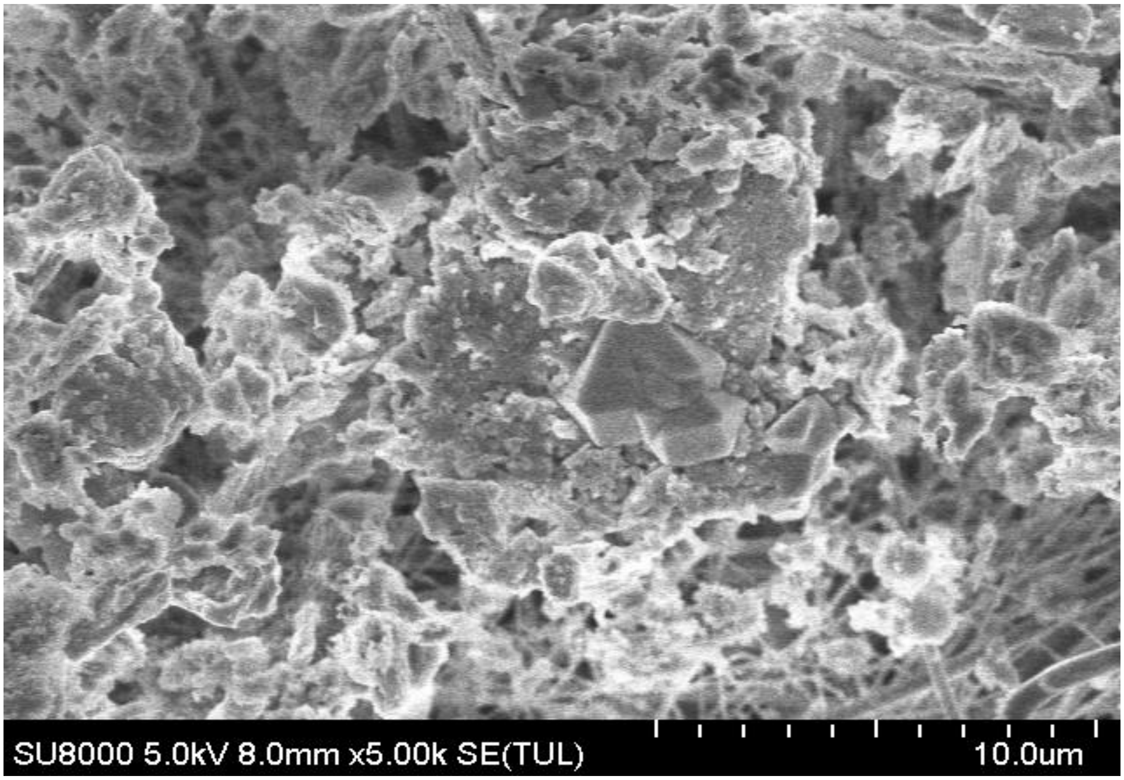

Figure 4.15b: Morphology of $PM_{2.5}$ fly ash particles at EWC during the dry season

4.8.4 Alumino-Silicates Particles

Alumino-silicates are formed basically from natural sources, such as erosion of local geological formations. Most of alumino-silicates (containing Al, Si, K, Fe, and Ca) and silica particles (Si oxides) present in the fine fraction have irregular forms and are classified as dispersion of soil dust. Alumino-silicates with significant levels of Al, Si and K can also originate from crustal sources, agricultural activities, fuel and biomass burning (Byeon, Willis, & Peters, 2015; Satsangi & Yadav, 2014).

Figure 4.16a presents alumino silicate mixed with soot particles of $PM_{2.5}$ collected at EWC. The elemental composition of these particles include O, Si, C, Na, Ba, Al, Zn, K and Ca with atomic percentages of 49.3%, 18.5%, 14.4%, 5.01%, 3.62%, 3.35%, 2.27%, 1.93% and 1.1%, respectively.

CUF alumino-silicate particles are shown on Figure 4.16b SEM image. On the basis of the distribution of the major elements in particulate matter, the atomic percentages of O, C, Si, Na, Ba, Al, Zn, K, Ca, Fe, Mg and Cl were 49.4%, 19.5%, 16.3%, 4.14 %, 2.79%, 2.62%, 1.78%, 1.47%, 1.02%, 0.58%, 0.2% and 0.14%, respectively.

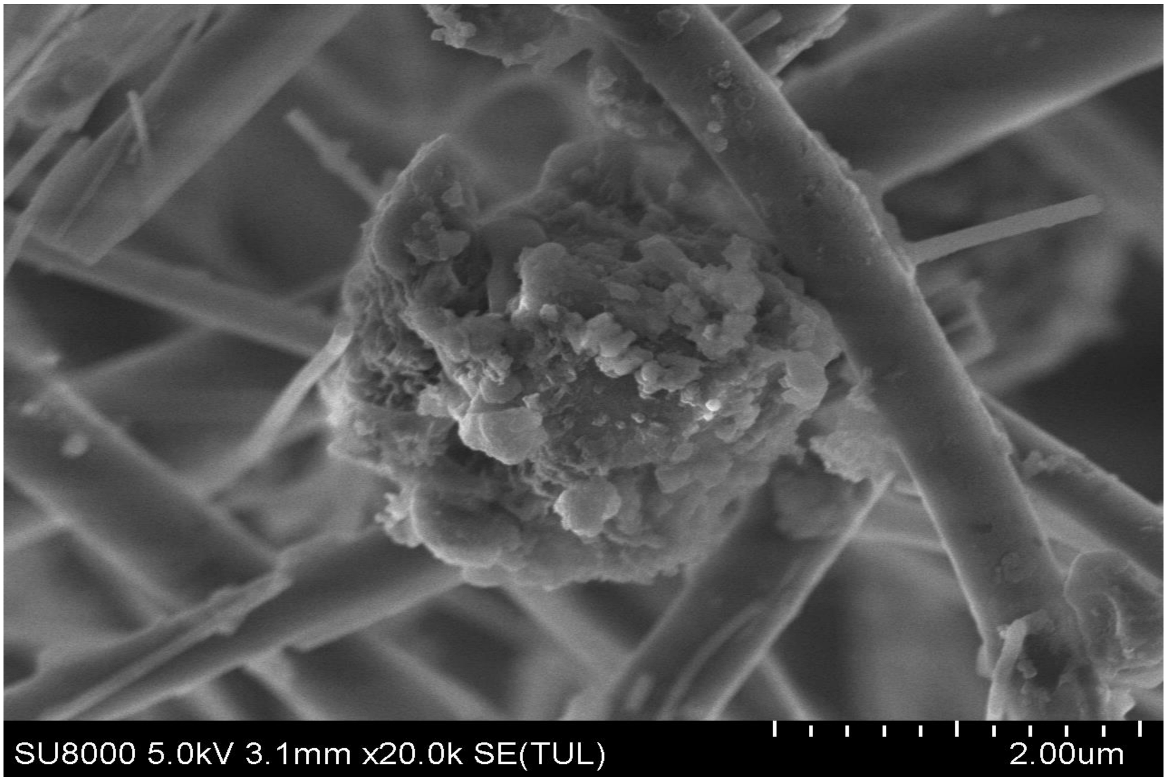

Figure 4.16a: Morphology of $PM_{2.5}$ aluminosilicate mixed with soot particles at EWC during the wet season

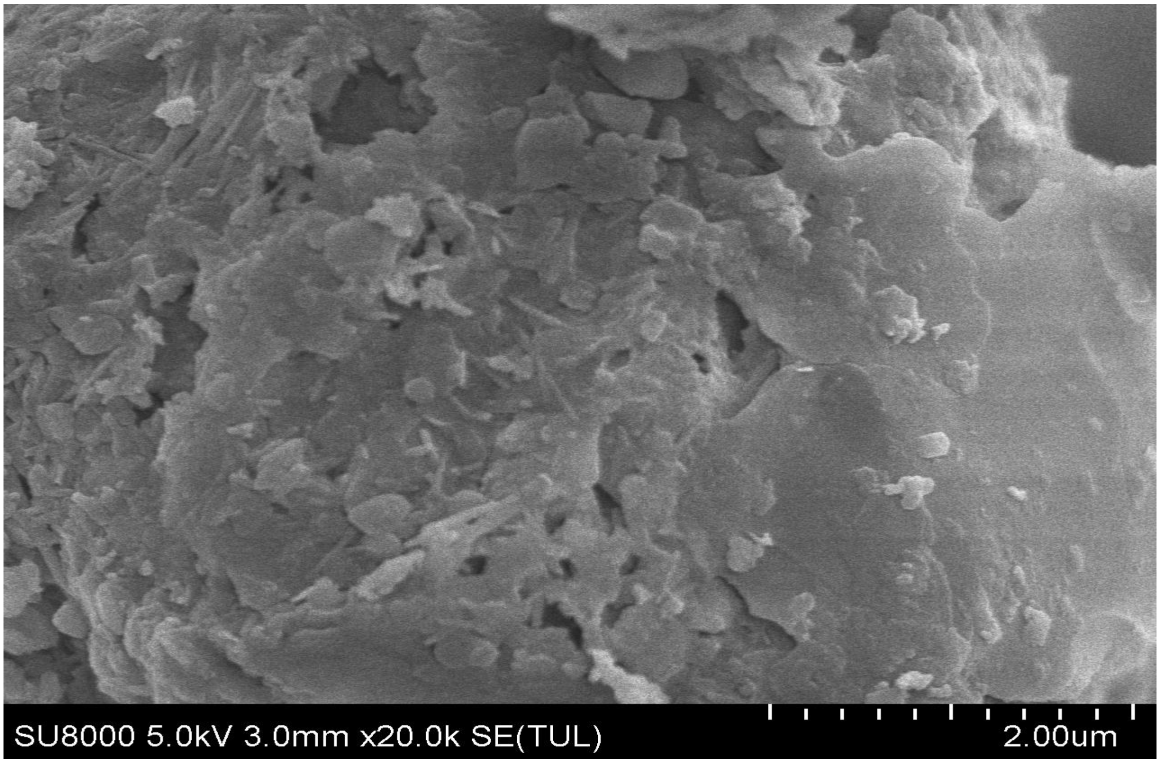

Figure 4.16b: Morphology of $PM_{2.5}$ aluminosilicate at CUF during the dry season

The SEM-EDX results of particulate matter collected at Agbara industrial estate (Figure 4.17) during the dry season indicated that the distribution of major elements in such aggregates included O, Si, C, Na, Ba, Zn, Al, Ca, Fe and Mg of which the atomic percentages were 51.0%, 20.6%, 9.49%, 5.63%, 4.25%, 2.93%, 2.4%, 2.13 %, 1.13%, 0.22% and 0.2% respectively, with high contents of O, Si, and C.

Figure 4.18 shows alumino-silicate particles of $PM_{2.5}$ collected at Ota industrial estate. The elemental composition of these particles included O, C, Si, Na, Ba, Zn, Al, Pb, K Ca, Cl and Mg with atomic percentages of 48.1%, 16.9%, 16.6%, 4.92%, 3.39%, 2.74%, 2.2%, 1.84%,1.75%, 0.95%, 0.53% and 0.2%, respectively. These particles contribute to the highest proportion of global aerosol mass in the atmosphere due to the ease at which they are dispersed into the air (Pipal & Satsangi, 2015).

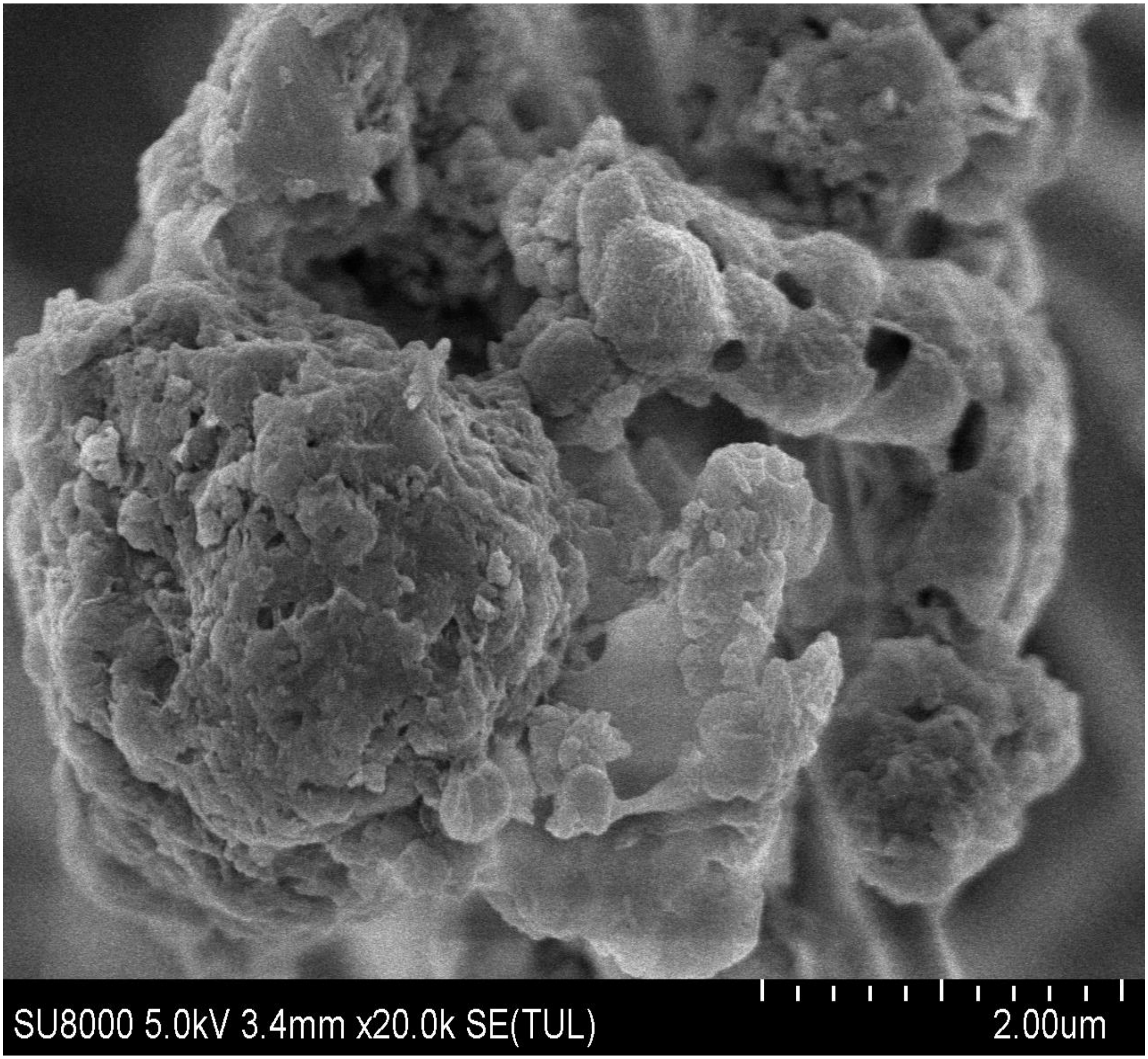

Figure 4.17: Morphology of $PM_{2.5}$ aluminosilicate at AGE during the dry season

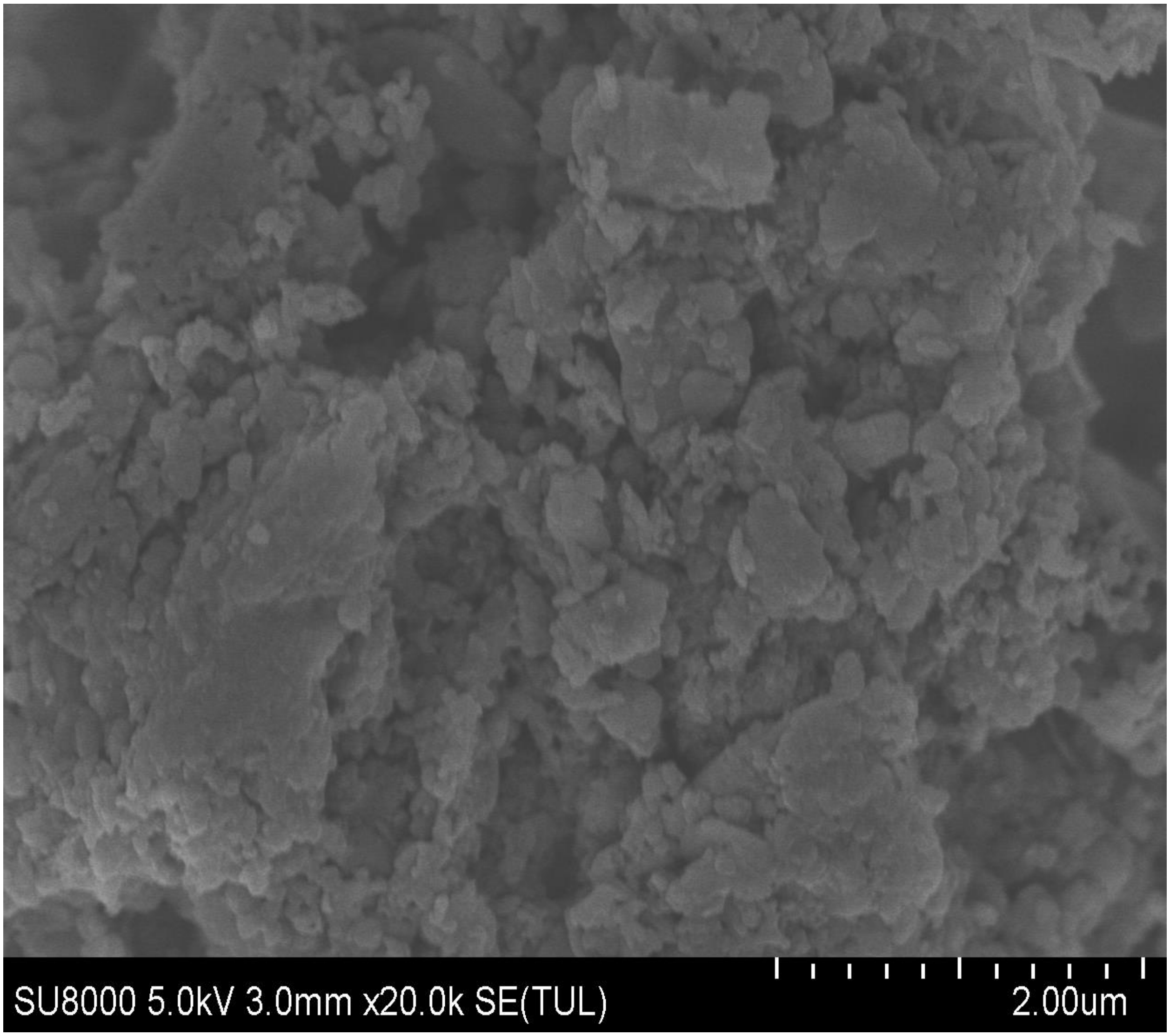

Figure 4.18: Morphology of PM$_{2.5}$ aluminosilicate at OTE during the wet season

4.9 Inter-Relationship between $PM_{2.5}$ Trace Metals Obtained in Study Locations

Correlation coefficient measures the degree of linear relationship between two or more variables. It provides information on the possible sources of elements in the study area. The Pearson correlation coefficient matrix was used to establish interrelationship between trace metals in EWC, OTE, AGE and CUF as shown in Tables 4.8 to 4.11. A strong positive, significant, moderate and negative correlation will be discussed for some selected trace metals.

As shown for EWC, in Table 4.8, a strong positive correlation was found between Ca-Cu (r = 0.979), Na-K (r = 0.957), Ca-Ni (r = 0.809), Mn-Ni (r = 0.900), Mn-Cu (r = 0.897), Mg-Ca (r = 0.884), Mg-Mn (r = 0.864), Mg-Cu (r = 0.862), Mn-Ag (r = 0.837), and Ca-Ni (r = 0.844). A significant correlation was found between Na-Mn (r = 0.672), Na-Cu (r = 0.654), and Na-Fe (r = 0.601); Mg-Fe (r = 0.601). It is also found significant for K with Mn (r = 0.634), Fe (r = 0.600), K-Al (r = 0.503), Ca-Fe (r = 0.665), Fe-Ni (r = 0.608), and Zn-Ni (r = 0.541), Mn-Ni (r = 0.60), Al-Ti (r = 0.516), Ti-V (r = 0.524), V-Pb (r = 0.691) and Sb-Pb (r = 0.611). K-Ni (r = 0.465), Fe-Al (r = 0.443), T-Pb (r = 0.489) and V-Zn (r = 0.402) showed the moderate correlation while the negative correlation was found between Na-Pb, K-Ti, Ca-Zn, Al-Ni, Sb-Cu and Pb-Ni etc. Based on the findings from the strong positive and significant associations, it may be concluded that Ca, Cu, Na, K, Ni, Mn, Mg, Ag, Fe, Al, Ti, V, Pb and Sb were contributed by mixed sources, both of natural and anthropogenic origin. This corroborates the information on the activities at Ewekoro earlier discussed.

Table 4.8: Pearson correlation coefficients ($p<0.05$) of PM$_{2.5}$-bound trace metals at EWC study area

Variables	Na	Mg	K	Ca	Fe	Al	Ti	V	Mn	Sb	Cu	Zn	Ag	Pb	Ni
Na	**1**														
Mg	0.733	**1**													
K	0.957	0.709	**1**												
Ca	0.755	0.884	0.774	**1**											
Fe	0.601	0.601	0.600	0.665	**1**										
Al	0.553	0.127	0.503	0.101	0.443	**1**									
Ti	0.064	0.112	-0.034	-0.119	0.525	0.516	**1**								
V	-0.033	0.074	-0.179	-0.216	0.024	0.088	0.524	**1**							
Mn	0.672	0.864	0.634	0.906	0.818	0.223	0.257	-0.042	**1**						
Sb	-0.105	0.251	-0.154	-0.160	-0.240	-0.179	0.222	0.672	-0.130	**1**					
Cu	0.654	0.862	0.681	0.979	0.635	-0.055	-0.153	-0.219	0.897	-0.157	**1**				
Zn	0.320	0.127	0.171	-0.066	0.285	0.821	0.700	0.402	0.185	0.130	-0.199	**1**			
Ag	0.597	0.796	0.435	0.721	0.567	0.191	0.262	0.113	0.837	0.095	0.692	0.325	**1**		
Pb	-0.068	0.180	-0.195	-0.182	0.061	-0.040	0.489	0.691	-0.033	0.611	-0.160	0.250	0.191	**1**	
Ni	0.501	0.771	0.465	0.809	0.608	-0.075	0.135	-0.098	0.900	-0.083	0.844	-0.009	0.759	-0.134	**1**

Table 4.9: Pearson correlation coefficients ($p<0.05$) of $PM_{2.5}$-bound trace metals at OTE study area

Variables	Na	Mg	K	Ca	Fe	Al	Ti	V	Cr	Mn	Cd	Sb	Cu	Zn	As	Ba	Pb
Na	**1**																
Mg	0.126	**1**															
K	0.926	0.149	**1**														
Ca	0.860	0.006	0.938	**1**													
Fe	-0.061	-0.008	0.034	0.234	**1**												
Al	0.813	0.040	0.901	0.858	0.108	**1**											
Ti	0.238	0.264	0.253	0.280	0.597	0.168	**1**										
V	-0.125	0.196	-0.370	-0.467	-0.418	-0.507	-0.245	**1**									
Cr	-0.024	0.159	-0.308	-0.368	-0.360	-0.406	-0.258	0.926	**1**								
Mn	-0.296	-0.102	-0.211	-0.112	0.718	-0.013	0.149	-0.309	-0.170	**1**							
Cd	-0.126	-0.170	-0.365	-0.371	-0.020	-0.280	-0.266	0.316	0.504	0.369	**1**						
Sb	-0.093	0.961	-0.095	-0.226	-0.063	-0.199	0.193	0.311	0.263	-0.090	-0.061	**1**					
Cu	-0.444	-0.188	-0.420	-0.373	0.136	-0.388	0.022	-0.007	-0.029	0.294	0.302	-0.055	**1**				
Zn	0.929	0.062	0.965	0.907	-0.077	0.887	0.198	-0.359	-0.280	-0.286	-0.274	-0.159	-0.288	**1**			
As	-0.067	0.968	-0.069	-0.213	-0.096	-0.166	0.151	0.329	0.281	-0.099	-0.063	0.997	-0.079	-0.134	**1**		
Ba	0.061	0.234	-0.168	-0.244	-0.038	-0.264	0.125	0.678	0.589	-0.140	0.173	0.219	-0.133	-0.235	0.232	**1**	
Pb	-0.044	-0.065	-0.037	-0.070	-0.185	-0.151	0.147	-0.158	-0.208	-0.142	-0.111	-0.032	-0.037	0.030	-0.051	-0.204	**1**

Table 4.10: Pearson correlation coefficients ($p<0.05$) of PM$_{2.5}$-bound trace metals at AGE study area

Variables	Na	Mg	K	Ca	Fe	Al	Ti	Mn	Cu	Zn	As	Sr	Ba	Pb
Na	**1**													
Mg	0.671	**1**												
K	0.693	0.691	**1**											
Ca	0.439	0.703	0.816	**1**										
Fe	0.013	0.149	0.306	0.251	**1**									
Al	0.495	0.768	0.805	0.839	0.505	**1**								
Ti	-0.353	-0.453	-0.242	-0.365	-0.037	-0.531	**1**							
Mn	-0.245	0.324	0.119	0.545	0.315	0.333	-0.073	**1**						
Cu	-0.181	-0.580	-0.270	-0.347	-0.287	-0.543	0.052	-0.244	**1**					
Zn	0.572	0.619	0.984	0.818	0.342	0.778	-0.126	0.190	-0.256	**1**				
As	-0.337	-0.717	-0.354	-0.475	-0.152	-0.704	0.810	-0.239	0.590	-0.262	**1**			
Sr	0.669	0.835	0.919	0.817	0.347	0.875	-0.416	0.267	-0.440	0.881	-0.615	**1**		
Ba	0.631	0.593	0.734	0.534	0.241	0.522	-0.241	0.082	0.026	0.691	-0.242	0.781	**1**	
Pb	-0.533	-0.704	-0.357	-0.382	0.069	-0.345	0.143	-0.169	0.461	-0.285	0.383	-0.395	-0.206	**1**

Table 4.11: Pearson correlation coefficients (p<0.05) of $PM_{2.5}$-bound trace metals at CUF study area

Variables	Na	Mg	K	Ca	Fe	Al	Ti	V	Cr	Mn	Zn	As	Sr	Pb
Na	**1**													
Mg	0.958	**1**												
K	0.997	0.955	**1**											
Ca	0.985	0.963	0.984	**1**										
Fe	0.290	0.363	0.327	0.321	**1**									
Al	0.907	0.898	0.909	0.941	0.265	**1**								
Ti	-0.227	-0.298	-0.217	-0.276	-0.251	-0.275	**1**							
V	0.362	0.376	0.392	0.314	0.201	0.278	-0.182	**1**						
Cr	0.597	0.528	0.584	0.484	0.033	0.449	-0.089	0.394	**1**					
Mn	0.435	0.496	0.474	0.467	0.915	0.344	-0.281	0.400	0.050	**1**				
Zn	0.996	0.946	0.995	0.981	0.279	0.920	-0.188	0.346	0.576	0.416	**1**			
As	0.341	0.376	0.367	0.297	0.250	0.371	-0.232	0.909	0.499	0.304	0.333	**1**		
Sr	0.768	0.769	0.759	0.839	0.208	0.896	-0.232	-0.038	0.086	0.262	0.791	0.026	**1**	
Pb	-0.028	-0.138	0.019	-0.015	-0.101	0.024	0.614	0.038	-0.167	-0.069	0.024	-0.032	0.012	**1**

The OTE data in Table 4.9 manifested a strong positive correlation between Na-K (r = 0.926), Na-Ca (r = 0.860), Na-Al (r = 0.813), Na- Zn (r = 0.929); Mg- Sb (r = 0.961), and Mg-As (r = 0.968); K-Ca (r = 0.938), Al-Ca (r = 0.901), Zn-Ca (r = 0.965); Ca-Al (r = 0.858) and Zn-Al (r = 0.907), Fe-Mn (r = 0.718), Al-Zn (r = 0.887), V-Cr (r = 0.926), and Sb-As (r = 0.997) suggesting similar origin. Significant correlation was found between V-Ba (r = 0.678), Cr-Cd (r = 0.504), and Cr-Ba (r = 0.589). No moderate correlation was observed in OTE trace metals. However, there were several negative correlated trace metals, few of which were Na-Cu (r = -0.444), K-Cu (r = -0.420), Ca-V (r = 0.467), Fe-V (r = 0.418), and Ba-Pb (r = 0.204). Correlation results in OTE show relationship between Na, K, Ca, Al, Zn, Mg, Sb, As, Fe, Mn, V, Cr, Ba and Cd indicating a common source, which is pointing more to industrial emitted trace metals with few tendency of resuspended dust majorly due to the unpaved roads.

A strong positive correlation between Mg-Ca (r = 0.703), Mg-Al (r = 0.768); K-Ca (r = 0.816), and K-Al (r = 0.805); Al-Zn (r = 0.778), Ti-As (r =0.810), Zn-Sr (r = 0.881) and Sr-Ba (r = 0.781) was found in AGE as shown in Table 4.10. Significant correlation was found between Na-Mg (r = 0.671), Mg-K (r = 0.691), Mg-Mn (r = 0.545), Fe-Al (r = 0.505), Al-Ba (r = 0.522) and Cu-As (r = 0.590). Only Na recorded moderate correlation between Ca (0.439) and Al (0.495). Also, some of the negative correlated trace metals were, Mg-Cu (r = -0.717), Na-Pb (r = -0.704), K-As (r = -0.354) and K-Pb (r = - 0.357). It was observed that Mg, Ca, Al, K, Zn, Ti, Sr, Ba, Na, Mn, Fe, Cu and As exhibited a strong positive to significant correlation which equally implies same source of emissions.

In addition, Table 4.11 shows interrelationship of trace metals at CUF. A strong positive correlation was seen between Na-Mg (r = 0.958), Na-K (r = 0.997), Na-Ca (r = 0.985), Na-Al (r = 0.907), Mg-Zn (r = 0.946), Ca-Sr (r = 0.839) and V-As (r = 0.909). Also, significant correlation was established between Na-Cr (r = 0.597), Mg-Cr (r = 0.528), K- Cr (r = 0.584) and Cr-Mn (r = 0.576). Na-Mn (r = 0.435), Ca- Cr (r = 0.484), Al-Cr (r = 0.449), V-Mn (r = 0.400), Cr-As (r = 0.499) and Mn-Zn (r = 0.416). A lot of negative correlations were equally observed, such as Na-Ti, Na-Pb, Fe-Ti, Ti-Cr, Mn-Pb and As-Pb. From the strong positive to significant correlated metals in CUF, it can be inferred that possible trace metals from same sources include Na, Mg, K, Ca, Al, Zn, Sr, V, As , Cr and Mn.

4.10 Hierarchical Agglomerative Clustering Analysis of Trace Metals

Classification of the pollutant sources were determined using hierarchical agglomerative clustering analysis (HACA). HACA was used to group the trace metals into clusters so that those within a cluster are similar to one another while trace metals located in other clusters are different from one another.

The dendrogram produced by HACA on trace metals clustering patterns for EWC location is shown in Figure 4.19. Ten trace metals have been categorized into three clusters. The strongest trace metal cluster for the $PM_{2.5}$ airborne particulates was cluster 1 and had only Na trace metal; this was closely followed by cluster 3 with only Ca. However, all the remaining trace metals in the dendrogram namely Mg, K, Fe, Al, Ti, Mn, Zn and Pb made up Cluster 2. Each of the trace metals were classified into different groups most probably because of the similarities in their concentrations. Every group had their own range of concentrations. This is in agreement with similar research work done by Latif *et al*. (2015).

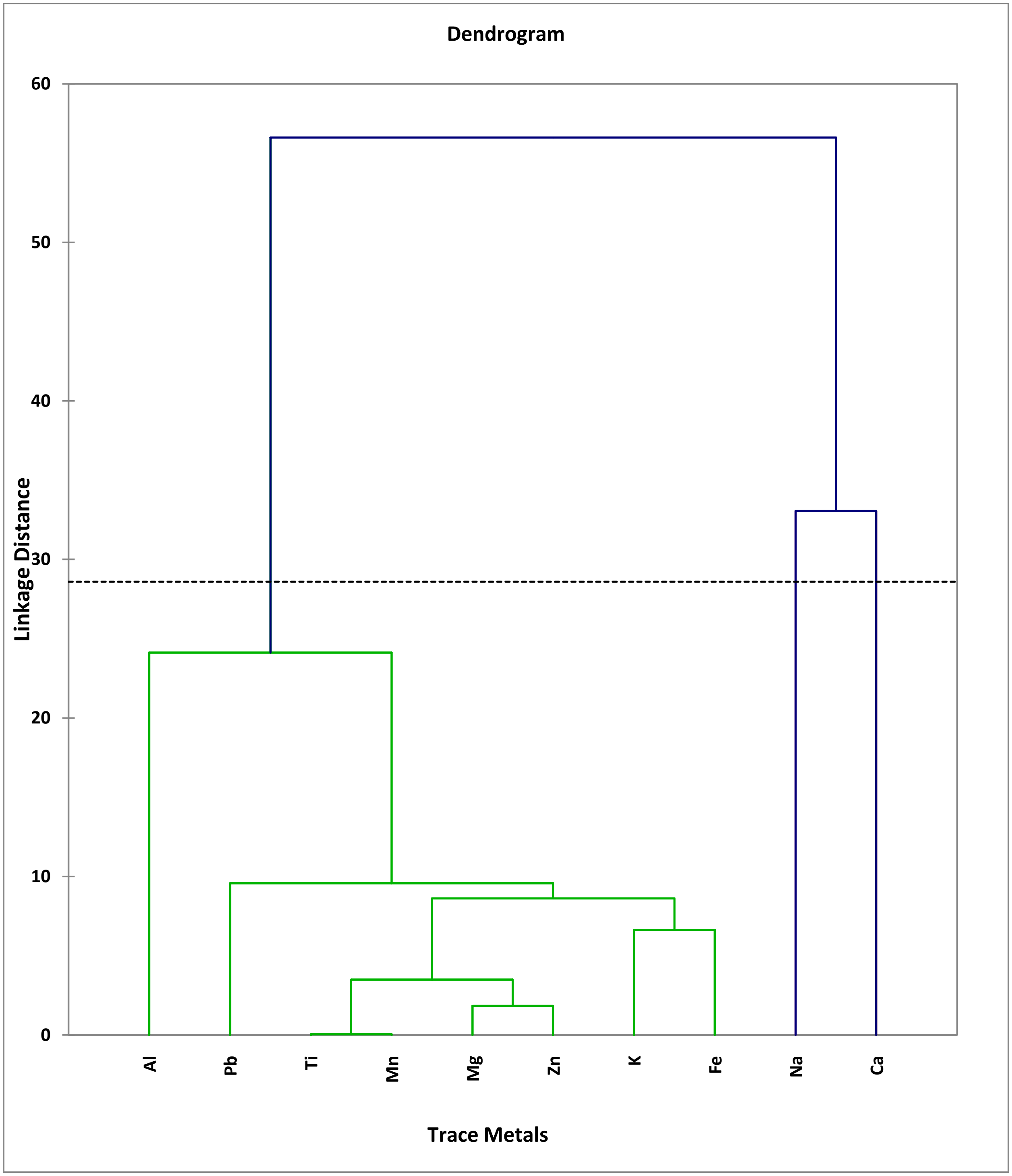

Figure 4.19: Dendrogram showing different trace metals clusters in EWC

The OTE location dendrogram produced by HACA on trace metals clustering patterns as presented in Figure 4.20 was also grouped into three clusters. Similar to EWC, ten trace metals have been categorised into three clusters. Cluster 1 consists of Na, Cluster 2 consist of Mg, K, Ca, Fe, Ti, Mn and Pb whereas Cluster 3 comprised of Al and Zn. Since each group had their unique range of concentrations, extremely high concentration was recorded for Na closely followed by Al and Zn. The high similarities within the groups implied that the members of each group had a common source.

The highest categories of dendrogram presentation of $PM_{2.5}$-bound trace metals were observed in AGE location (Figure 4.21). Ten trace metals were categorized into five clusters. Cluster 1, recorded only Na; Cluster 2 consist of Mg, Fe, Mn and Pb; Cluster 3 comprised of K, Ca and Zn while Cluster 4 and 5 had only Al and Ti, respectively. Different trace metals clusters reflected similar concentration range. The clusters were observed to occur in the following ascending order Cluster 1 > Cluster 4 > Cluster 3 > Cluster 2 > Cluster 5. The high similarities within the groups implied that the members of each group had a common source.

Furthermore, four categories of $PM_{2.5}$- bound trace metals dendrogram were observed in CUF location (Figure 4.22). In CUF, Cluster I was also in line with observations from the industrial locations. Only Na metal was observed in Cluster 1; Cluster 2 recorded Mg, Ca, Fe, Ti and Mn; K, Al and Zn were grouped in Cluster 3 while Cluster 4 had only Pb. The Clusters for CUF were found in the following range Cluster 1 > Cluster 3 > Cluster 2 > Cluster 4. The HACA results are comparable with other investigated works such as Shah *et al*. (2012), Silva *et al*. (2015) and Latif *et al*. (2015).

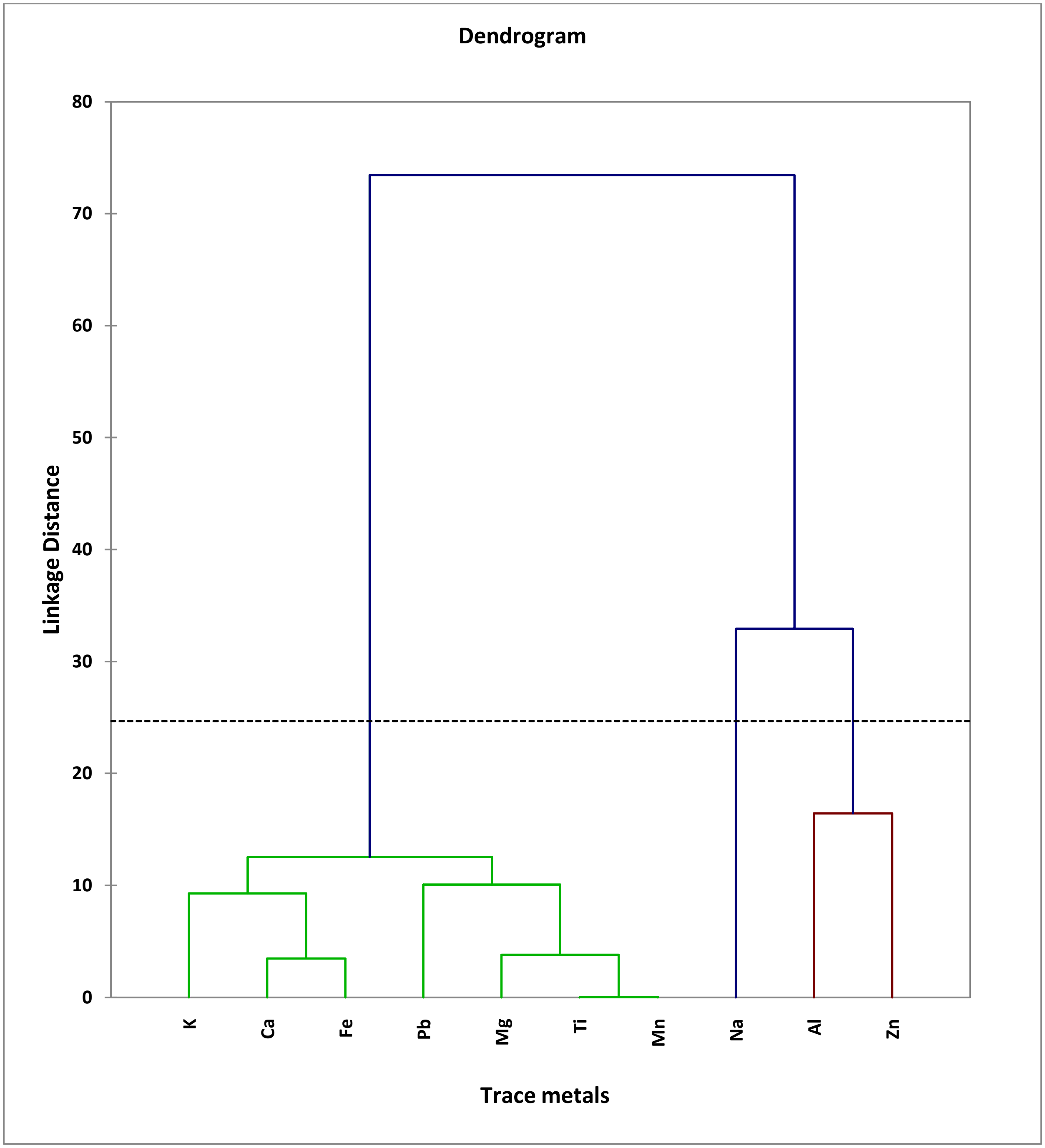

Figure 4.20: Dendrogram showing different trace metals clusters in OTE

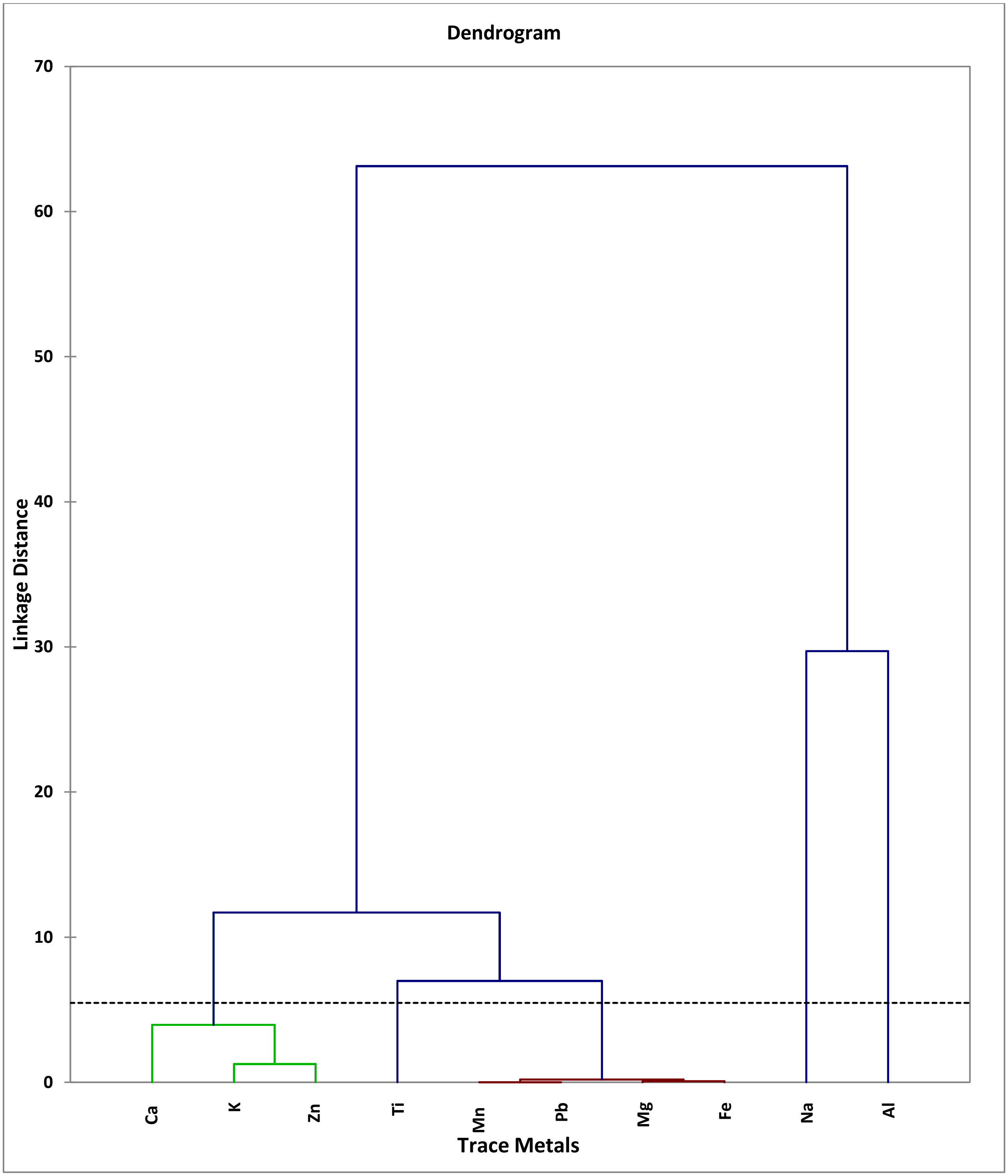

Figure 4.21: Dendrogram showing different trace metals clusters in AGE

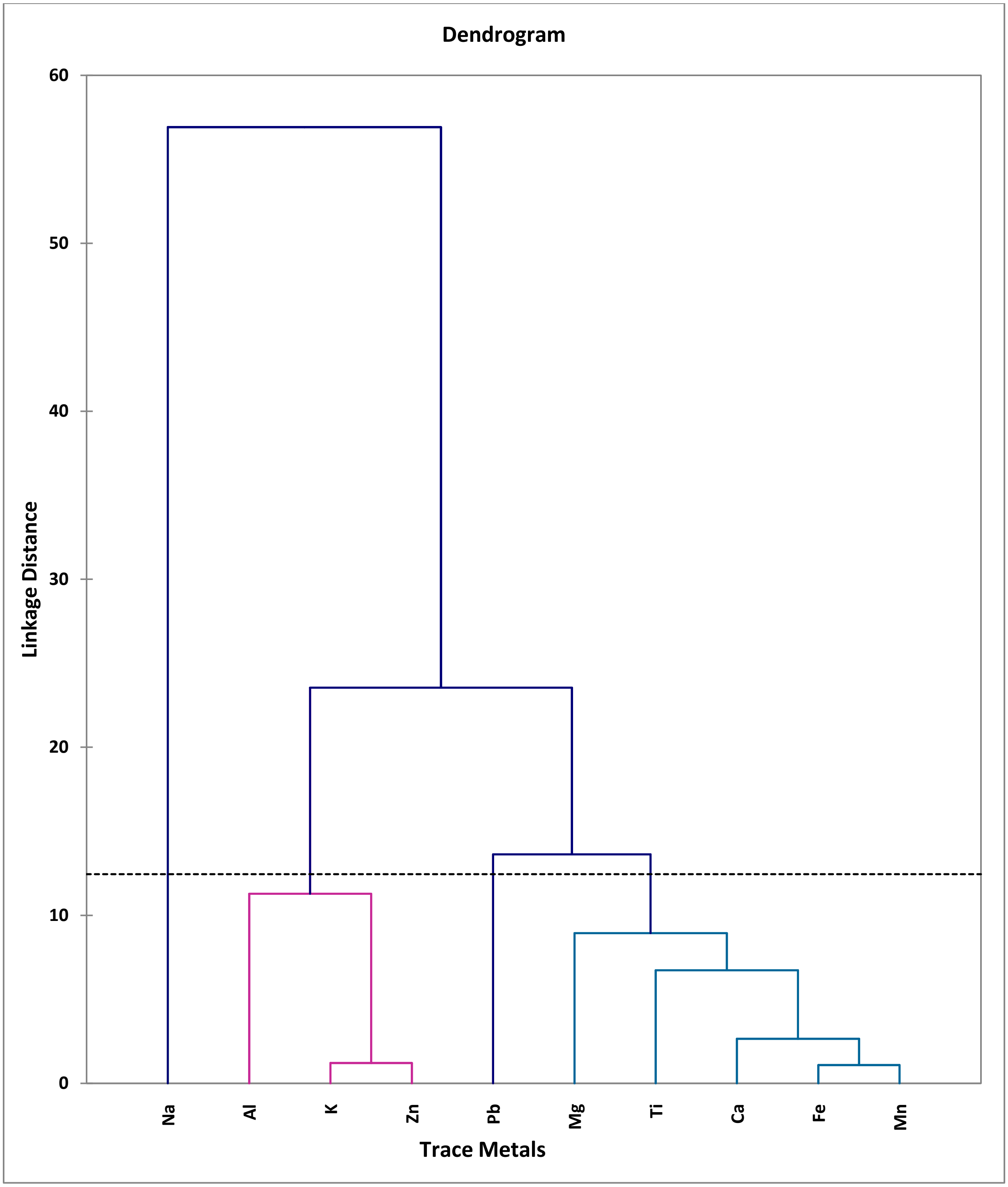

Figure 4.22: Dendrogram showing different trace metals clusters in CUF

4.11 Source Apportionment of $PM_{2.5}$-Bound Trace Metals

Metals in the atmosphere can be linked with specific pollutant sources, and these are often used as tracers in order to identify the source of atmospheric particulate (Chen *et al*., 2013). PCA was applied to determine the correlation between pollutants and to identify the source profile of trace metals in $PM_{2.5}$. Table 4.12 describes the significant principal component (PC) loadings for the trace metals in ambient $PM_{2.5}$ samples from all sites with corresponding eigen values and variances. The method of Kaiser criterion, which retain only factors having eigen value greater than one (1) was adopted for the interpretation of the result (Kaiser, 1960).

The PCA revealed two (2) components that accounted for 67.0%, of the overall variance in Ewekoro (EWC). PC1 had high loadings for Mn, Ca, Mg, Cu, Na, Ni, K, Ag and Fe which explained 46.2% of the total variance (Figure 4.23). This factor is associated with fossil fuel, road dust and industrial emissions, especially the metal processing, and solid waste combustion activities in the industrial area (Ni, Cu, Fe). Also, Ca, Mg and Mn were identified as emission from mining of limestone and cement production by Lafarge Cement WAPCO being primary raw materials for the production of cement (Akpan, Amodu, & Akpan, 2011; Gbadebo and Bankole, 2007). K was associated with vegetation and biomass burning (Yu, Wang, & Zhou, 2014). Thus, PC1 can be identified as mixed sources of industrial activities and traffic emissions.

Table 4.12: Factor loadings of trace metals after PCA varimax rotation at the study area

	OTE		EWC		AGE		CUF	
Trace Metals	F1	F2	F1	F2	F1	F2	F1	F2
Na	**0.810**	0.406	**0.838**	0.070	**0.692**	0.227	**0.977**	0.155
Mg	-0.073	**0.863**	**0.910**	0.068	**0.902**	-0.204	**0.967**	0.066
K	**0.936**	0.308	**0.805**	-0.082	**0.898**	0.406	**0.983**	0.124
Ca	**0.942**	0.125	**0.945**	-0.284	**0.846**	0.061	**0.980**	0.192
Fe	0.178	-0.312	**0.777**	0.198	0.321	0.048	0.414	-0.457
Al	**0.907**	0.122	0.328	0.534	**0.926**	-0.117	**0.925**	0.218
Ti	0.274	0.127	0.181	**0.850**	-0.489	0.554	-0.306	0.273
Mn	-0.105	-0.438	**0.962**	0.007	0.293	-0.194	**0.546**	-0.517
Zn	**0.910**	0.249	0.207	**0.756**	**0.844**	0.462	**0.973**	0.193
Pb	0.028	-0.077	-0.047	**0.644**	-0.506	0.184	-0.070	0.296
Cu	**-0.328**	-0.321	**0.903**	-0.355	**-0.480**	0.388	**0.000**	0.000
V	**-0.635**	0.485	-0.067	**0.736**	0.000	0.000	0.450	**-0.665**
As	-0.297	**0.823**	0.000	**0.000**	**-0.679**	0.677	0.463	**-0.656**
Ba	-0.349	0.404	0.000	**0.000**	**0.674**	0.384	**0.000**	0.000
Cr	**-0.563**	0.442	0.000	**0.000**	0.000	0.000	**0.527**	-0.117
Sb	-0.311	**0.800**	-0.106	0.510	0.000	0.000	0.000	0.000
Cd	-0.408	-0.136	0.000	**0.000**	0.000	0.000	0.000	0.000
Ag	0.000	0.000	**0.790**	0.182	0.000	0.000	0.000	0.000
Ni	0.000	0.000	**0.820**	-0.153	0.000	0.000	0.000	0.000
Sr	0.000	0.000	0.000	0.000	**0.974**	0.126	**0.753**	0.442
Eigenvalue	5.50	3.44	6.92	3.12	7.17	1.64	7.46	1.89
Variability (%)	32.3	20.2	46.2	20.8	51.2	11.7	53.2	13.5
Cumulative %	32.3	52.6	46.2	67.0	51.2	62.9	53.2	66.8

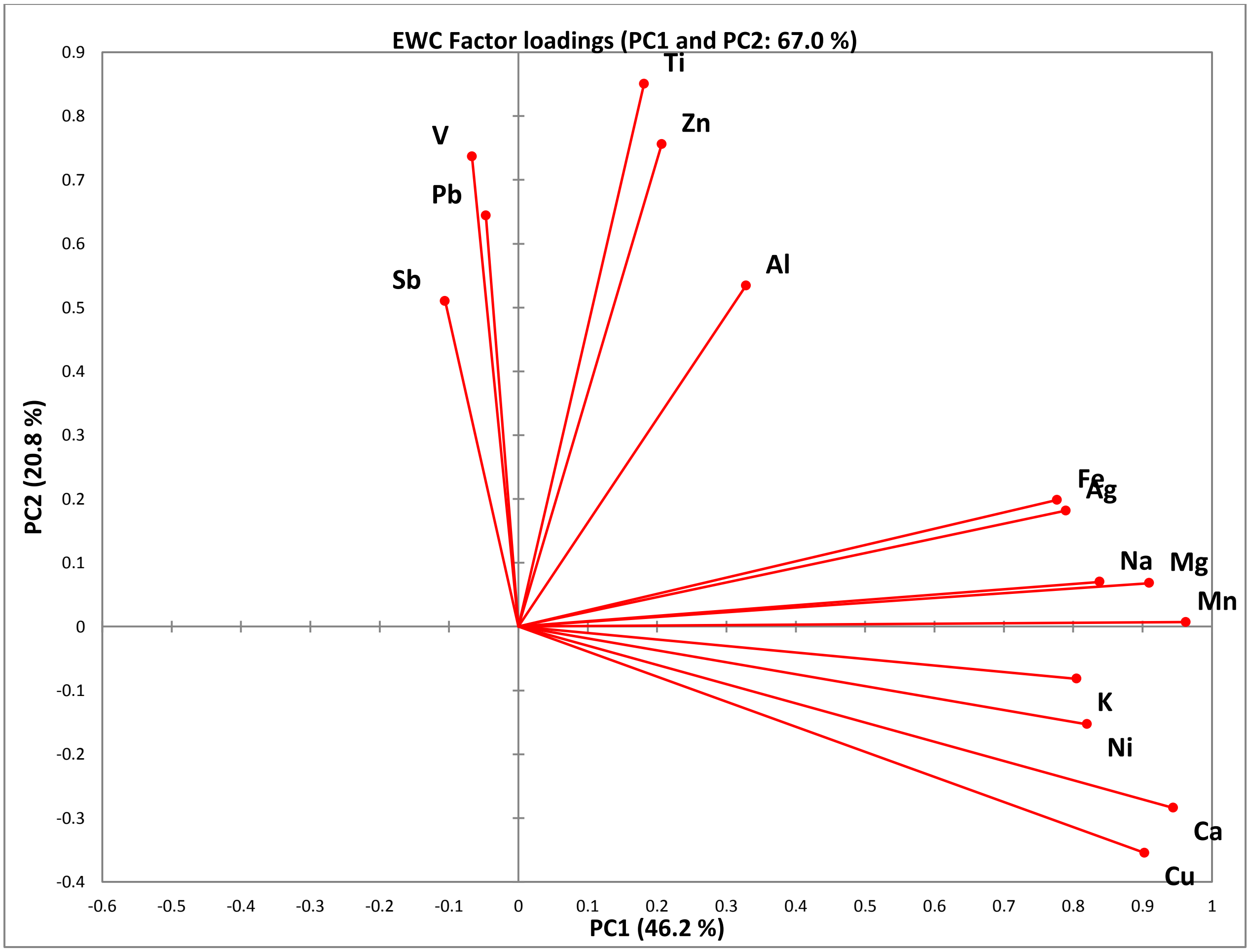

Figure 4.23: Loading plot for principal components obtained for trace metals at EWC

PC2 explained 20.8% of the total variance and correlated with high loadings on Ti, Zn, V and Pb, (Figure 4.23). This factor represented traffic emission, waste combustion, uncontrolled burning of heavy duty vehicle tyres to extract wires and metal processing (Zn, V, and Pb) as well as soil dust (Ti). Based on principal component analysis, some sources from either re-suspended dust or industrial process sources could increase metals concentrations in particles (Kothai, Saradhi, Pandit, Markwitz, & Puranik, 2011). However, vehicle emission including tailpipe, tire wear and brake emissions was also a predominant source of metals.

In OTE, two factors obtained in the PCA analysis of trace metals in $PM_{2.5}$ accounted for 52.6% of the overall variance. As shown in Figure 4.24, PC1 (32.3%) had high loadings for Al, Ca, K, Zn, and Na which can be attributed to nonferrous metal melts, coal oil combustion, dust associated with construction, vehicle wear and tear, crustal soil dust and biomass burning and Zn smelting in nonferrous metal (Wang, Hu, Chen, Chen & Xu, 2013). PC2 (20.2%) with very high loadings on Mg, As and Sb could be assigned as soil dust and industrial emissions. Major sources of Sb include brake and tyre wear, coal consumption by industrial boilers, ferrous and nonferrous metal smelting industries; Mg is one of the crustal elements used as tracers for soil dust while As is associated with metallurgical production and solid waste combustion (Figure 4.24), (Owoade *et al*., 2015; Shah *et al*., 2012; Tian *et al*., 2015).

In AGE site, PC1, (Figure 4.25), accounted for 51.2% of the variance and had significant loadings on Sr, Al, Mg, K, Ca, Zn, Na and Ba. The presence of Na, Al, Ca, Mg, and Sr which is an indication of crustal trace metals from soil dust (Na), markers of mineral dust due to buildings and road renovations/construction (Mg, Ca and Al), while Sr was identified to be associated with both crustal and industrial activities (Hsu *et al*., 2016; Khan *et al.*, 2016; Li *et al*., 2013, Mustaffa *et al*., 2014; Wang *et al*., 2013). Zn, K and Ba emissions are also linked to transportation emission such as brake and tire wear, metallurgical production, biomass burning, frequent open air solid waste burning coupled with multiple industrial activities from AGE, as pointed out earlier (Qiao *et al*., 2013).

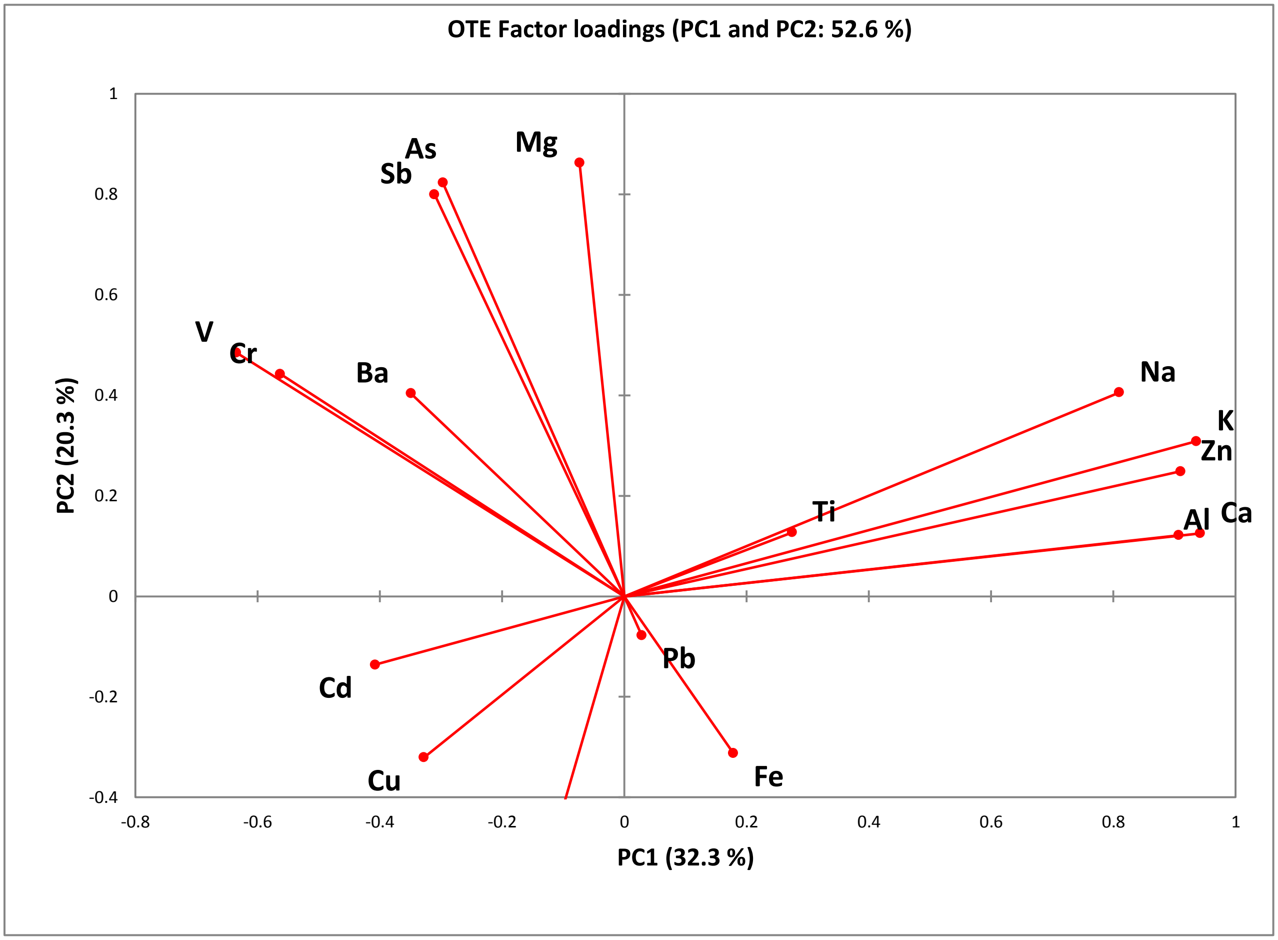

Figure 4.24: Loading plot for principal components obtained for trace metals at OTE

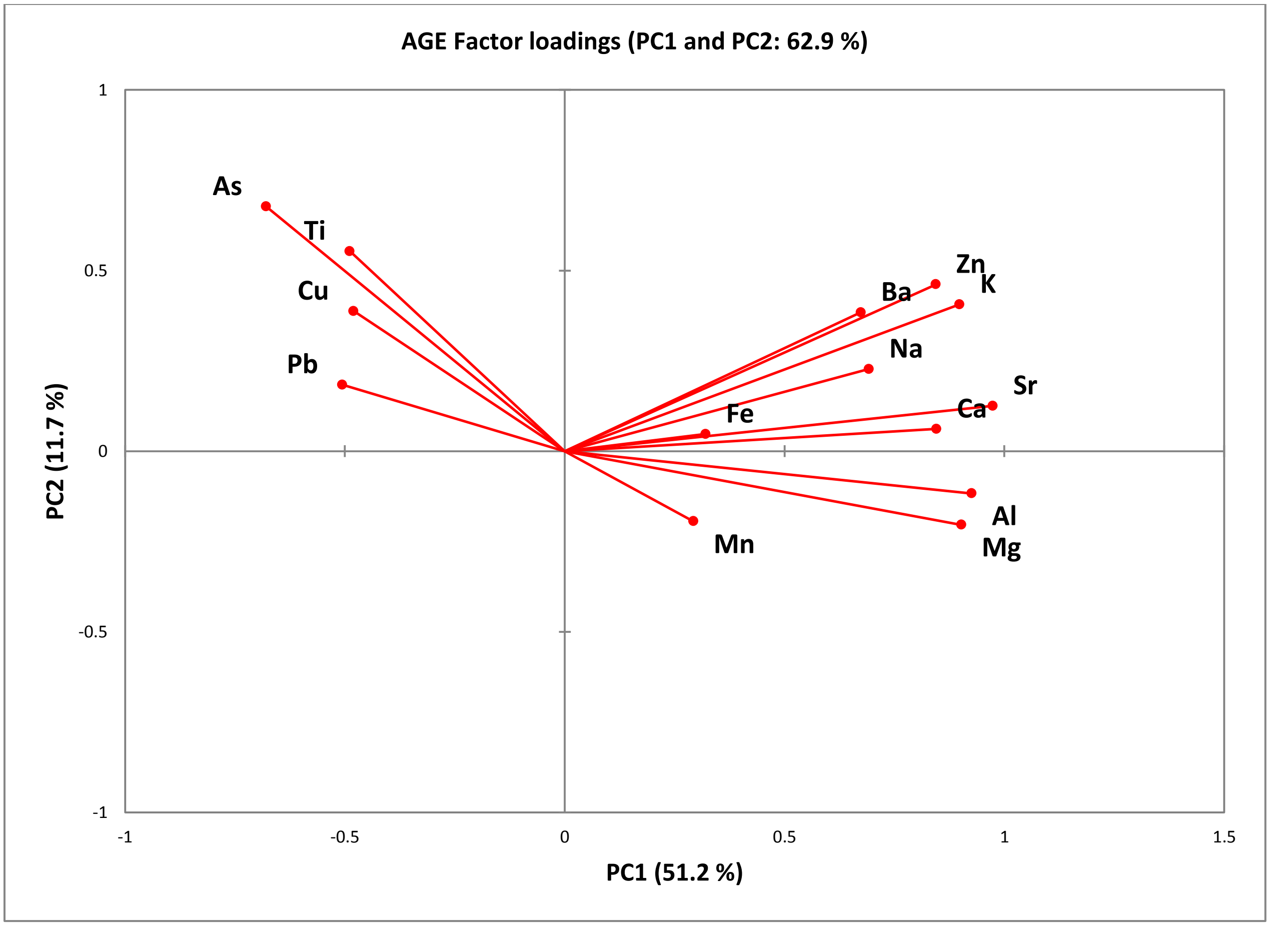

Figure 4.25: Loading plot for principal components obtained for trace metals at AGE

The PC2, (Figure 4.25), which presents the high loadings for As and Ti, accounts for 11.7% of the total variance representing fossil fuel combustion and industrial activities for As while Ti was attributed to soil dust (Chen *et al*., 2013).

For samples collected in the control site, CUF, two factors accounted for 66.8% of the total variance in the data. As shown in Figure 4.26a, PC1 showed high loading for K, Ca, Zn**,** Na, Cu, Al, Sr, Mn and Cr. The presence of Cr, Cu, and Zn was suspected to come from wear and tear in brake line and tyres associated with vehicular emission sources (Grigoratos & Martini, 2015; Khanna, Khare, & Gargava, 2015; Li *et al*., 2013), Al, Ca and K pointed to building construction emission, biomass burning from surrounding farm land (Karnae & John, 2013; Wang *et al*., 2013), while Sr and Mn can be associated with natural crustal sources (Celo & Dabek-Zlotorzynska, 2010; Li *et al*., 2013) and anthropogenic emission, such as secondary aluminum smelter for Sr (Hsu *et al*., 2016), while Mn has been identified with vehicle brake wears (Grigoratos & Martini, 2015).

However, PC2 showed strong negative factor loadings for V and As (Figure 4.26). For the control site, it can be seen that vehicle emission, re-suspended dust, building construction emission, biomass burning and influence from surrounding industrial activities were the sources with different factor loading of 53.2% and 13.5%, respectively.

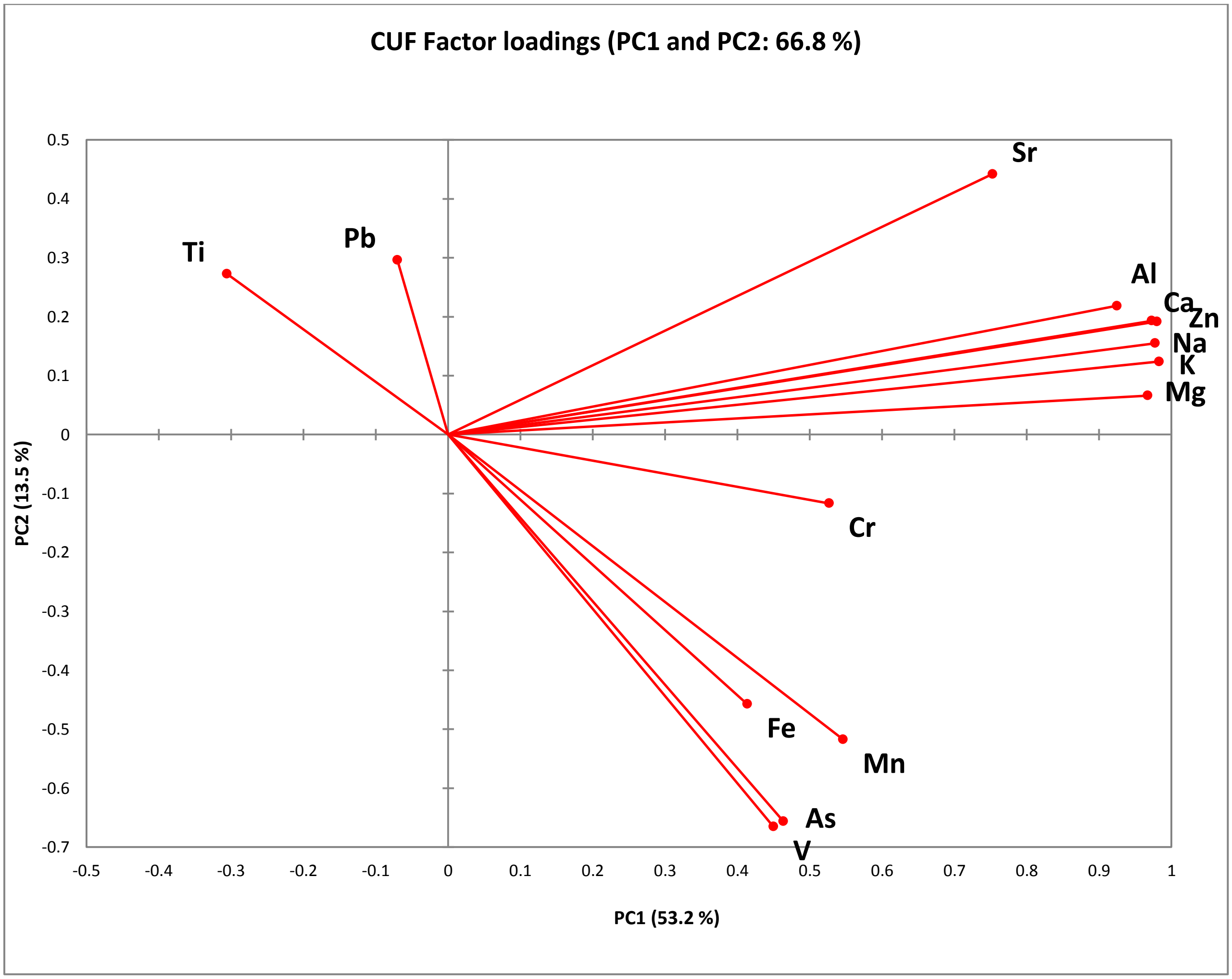

Figure 4.26: Loading plot for principal components obtained for trace metals at CUF

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The spatio-temporal variability of trace metals in atmospheric fine particulate matter from Ota industrial estate (OTE), Ewekoro community (EWC), Agbara industrial estate (AGE) and Covenant University Farm (CUF) was investigated. The results obtained for spatial and temporal variations of $PM_{2.5}$ in the ambient air across the study locations were as follows: OTE > EWC > AGE > CUF. The average concentrations of $PM_{2.5}$ in the wet and dry seasons were 191, 180, 144 and 67.9 $\mu g/m^3$ and 335.4, 264.8, 235.5 and 224.5 $\mu g/m^3$, respectively for OTE, EWC, AGE and CUF. Wet season accounted for only 35% of the inhalable particles while 65% was accounted for by dry season during the sampling period. OTE, was the most polluted of the industrial sites. Overall, the ambient $PM_{2.5}$ concentration far exceeds the 24-h and annual standard limits established by US EPA and WHO.

A comparison of the 6-month average concentrations of Pb, As, Cd, Cr, Ni, Mn, V trace metals with the appropriate standard limit values revealed that out of these 7 trace metals, only V (0.199 – 0.862 $\mu g/m^{-3}$) was below the existing WHO limit of one (1 $\mu g/m^{-3}$). The average trace metal concentration observed in the dry season was higher than that of the wet season. This has been associated with difference in meteorological conditions in both seasons, since relative humidity and rainfall were found to decrease the accumulation of fine particles in the wet season due to wash-out effects, whereas, the reverse was observed with wind speed and temperature during the dry season in the investigated sites.

Significantly, speciation phases in OTE and EWC $PM_{2.5}$-trace metal level revealed 34% and 46% metals respectively in the (F1 and F2) fraction. Most importantly, the labile phase (F1), trace metals in OTE (Cr, V, Cu) and EWC (Cr, V) will be readily soluble once $PM_{2.5}$ is inhaled. Also, trace metals bioavailability index results revealed that the highest bioavailability index occurred only at EWC [Cr and V (0.9), Cu (0.8), Zn (0.7)] and OTE [Cd and Cr (0.7)]. Furthermore, the sum of the cumulative lifetime cancer risks due to inhalation exposures across all investigated carcinogens for adults ($1.52 \times 10^{-2} – 9.53 \times 10^{-2}$) and children of ages 1- 6 ($1.09 \times 10^{-2} – 4.95 \times 10^{-4}$) and ages 6-18 ($1.48 \times 10^{-3} – 3.27 \times 10^{-2}$) were above EPAs acceptable risk range of 1×10^{-6} to 1×10^{-4}, notably the highest risk was recorded at Ewekoro community (9.53×10^{-2}).

More so, fine particulate matter AQI spatial map of all investigated sites for wet and dry season revealed that in the wet season, the weekday air quality for EWC, AGE and OTE was found in the "unhealthy" to "very unhealthy" category while the weekend air quality was categorized as "unhealthy". A better AQI was observed for background site (CUF), in the "moderate" to "unhealthy for sensitive group" category. The dry season was not any better, though the air quality of the weekend appears slightly less polluted than that of the weekday. Overall, there was no good category observed across the locations and seasons.

Finally, the Pearson correlation analysis showed the existence of a strong positive and significant correlation between some selected trace metals in the different study locations. SEM images of fine particles indicate that they are clustered into the following groups: soil dust mineral, soot aggregation, alumino silicate and fly ash particles. HACA provided information about the similarities and differences among the $PM_{2.5}$-bound trace metals while the PCA highlighted the possible sources of $PM_{2.5}$-bound trace metals in all the investigated sites such as industrial processes, vehicular emission, fossil fuel, solid waste combustion and construction activities.

5.2 Recommendations

Sufficient attention has not been given by the government, environmental legislative authorities and the public on the deteriorating state of atmospheric pollution in the country in spite of several cries from communities directly affected by particle pollution. In view of this, the following recommendations are being proposed:

1. A permanent network of air quality monitoring stations and reporting system for on-time information on criteria pollutants and hazardous air pollutants should be established by government. Data generated from these monitoring stations would be helpful in achieving air quality management goals.
2. Government should ensure smooth operation of municipal solid waste incineration coupled with sophisticated air pollution control equipment in the study sites.
3. NESREA should come up with Nigerian standards for fine particulates and other associated chemical pollutants.
4. NESREA should also come up with a workable enforcement strategy that will enhance better vehicle maintenance, stop indiscriminate bush burning, stop open solid waste combustion, and stop burning of wood timber for generating charcoal in order to abate particle pollution levels.
5. Immediate attention should be given to industries in Ota, Ewekoro and Agbara by NESREA in order to evaluate their existing manufacturing technologies and practices,

and recommend suitable process changes that generates less dust in their production operations.

6. In trace metal studies, chemical speciation analysis should be given wide publicity, since a better predictive insight on the bioavailability and fate of metallic contaminants can be obtained, which can help in cutting down remediation costs.
7. More sensitization on cultivation of green belts (trees and shrubs) should be done since they are capable of playing active role in air pollution attenuation.
8. The use of air cleaners at home will help in reducing exposure to particle pollutants.
9. Industries should endeavour to switch from obsolete facilities to energy efficient and ecofriendly manufacturing plants as well as control pollution at source by using cyclone separator, electrostatic precipitator, and spray tower to scavenge out particulate matter.

5.3 Contributions to Knowledge

The following are the contributions of this study to the body of knowledge:

1. Elevated levels of fine particulate matter

   The investigated industrial areas are confirmed to be highly polluted with Ota Industrial Estate taking the lead during the wet and dry seasons. Higher concentrations of fine particulate matter were dominant in the study locations at levels higher than what is obtainable in the developed countries.

2. Presence of $PM_{2.5}$ bioavailable trace metals

   The presence of multi-selective speciation phases of trace metals in air-borne fine particles was confirmed. Speciation and bioavailability studies identified Cr, V, Cu, Cd and Cr, V Cu, Zn as the most kinetically labile metals present in Ota Industrial Estate and Ewekoro Community, respectively.

3. Cancer risks

   Trace metals associated with the fine particles were found at enhanced concentrations including carcinogenic elements such as Cd, Cr, Ni, and As. Estimation of the sum of the cumulative lifetime cancer risk of inhalation exposure route were found above EPA's acceptable risk range of 1×10^{-6} to 1×10^{-4} for both adults and children with the highest occurrence (9.53×10^{-2}) in Ewekoro Community. Also, the individual carcinogenic trace metals (As and Cr) were found in concentrations above the EPA acceptable lifetime cancer risk range especially within the industrial sites.

4. Influence of meteorological parameters in the study areas

   Increased relative humidity and rainfall in the wet season resulted in reduced concentrations of fine particulate matter during the wet season.

5. Air quality index spatial map generated

   Spatial maps of $PM_{2.5}$ air quality for the duration of study were generated. The air quality in the study area with respect to fine particle pollution was poor during both seasons, with the worst case scenario reported more during the dry season. In addition, no record of 0 to 50 gradations representing the good air quality index category was found in the study area.

6. Key pollutant sources identified

   The major source of air pollution in the industrial areas was principally from anthropogenic activities (industrial processes). However, pollution from industrial sources was exacerbated by emissions from traffic congestion, inefficient vehicles, resuspension of dust mainly due to untarred roads, solid waste combustion, biomass burning and construction activities.

7. Generation of Data on $PM_{2.5}$-bound trace metals in the study areas

   Observed data on fine particulate matter-bound trace metals have been obtained for the study locations. The inferences from the data will give enhanced understanding and guidance on policy formulation for community-based environmental control and abatement programmes through the Covenant Universities Community Development Impact Initiatives (CUCDII). Also, it would contribute to the on-going development of abatement policies on airborne particulate matter in Nigeria if incorporated into the national database.

8. Peer Reviewed journals

   Two journals and one accepted manuscript have been produced from this research before the Ph.D oral examination. They are:

   a. Anake, W. U., Benson, N. U., & Ana, G.R. E. E. (2016). Characterisation of airborne fine particulate matter ($PM_{2.5}$) and its air quality implications in Ogun State, Nigeria. *Proceedings of 3rd* Covenant University International Conference on African Development Issues, 543-547.
   b. Anake, W. U., Ana, G.R. E. E. & Benson, N. U. (2016). Study of Surface Morphology, Elemental Composition and Sources of Airborne Fine Particulate Matter in Agbara Industrial Estate, Nigeria. International Journal of Applied Environmental Sciences, 11 (4), 881-890.
   c. Anake, W. U., Ana, G.R. E. E. & Benson, N. U. (2016). Spatial variation and source apportionment of fine particulate-bound trace metals in industrial and agricultural area: A case study in Ogun State, Nigeria. Research Journal of Applied Sciences (accepted)

5.4 Challenges Encountered during Research Work

(i) Delay in taking delivery of ordered filters

Early purchase of filters in sufficient quantity before the sampling is important to forestall delay in delivery and abrupt termination of sampling. There was a delay in taking delivery of filters.

(ii) Difficulties in securing approvals for the industrial study sites

Formal permission is expected to be obtained from the authority overseeing the proposed designated site prior to embarking on the research. There were difficulties in securing approval from the management of the industrial sites.

(iii) Disturbance/interruption during the field work

Threats and hostility were encountered from security personnel and local area boys around the industrial sites. Diplomacy and formal authorisation letter were used to assuage restive situations.

(iv) Movement of sampling equipment around the different study sites was tedious and capital intensive.

(v) Non-availability/ease of access to state of the art analytical equipment in the country.

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APPENDICES

Plate 1: $PM_{2.5}$ Sampling at site EA, Ewekoro Community

Plate 2: $PM_{2.5}$ Sampling at site OB, Ota Industrial Estate

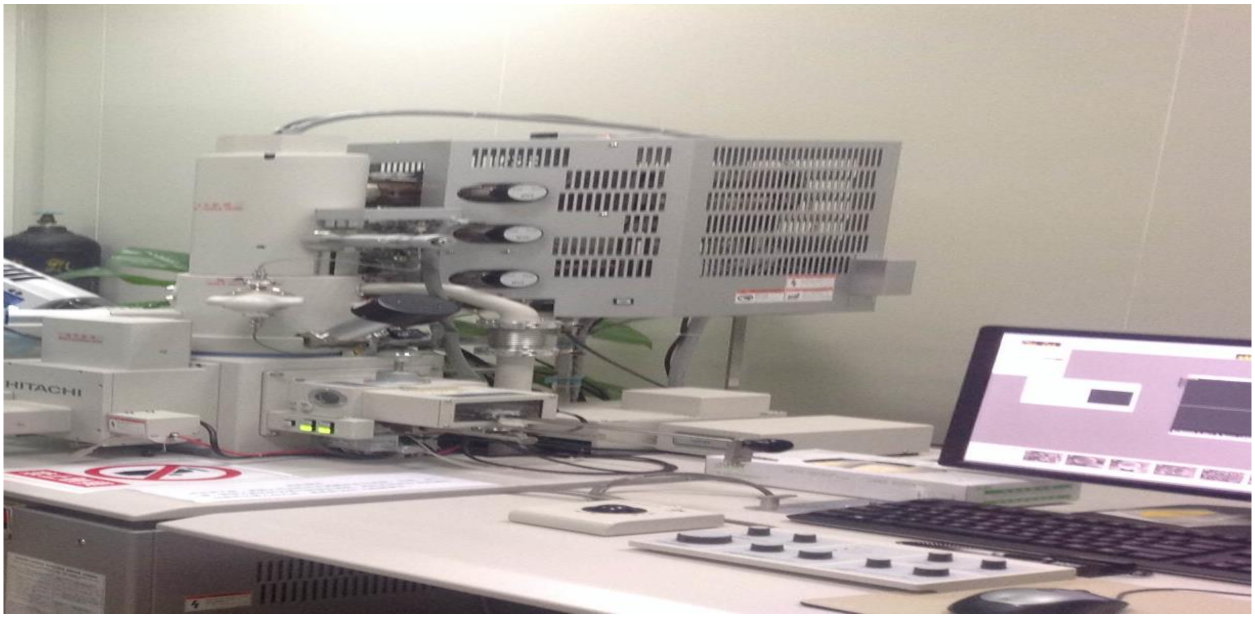

Plate 3: Field emission scanning electron microscopy- energy-dispersive X-ray spectroscopy (Hitachi, SU-8020).

Plate 4: Morphology analysis of $PM_{2.5}$ filters using Field emission scanning electron microscopy-energy-dispersive X-ray spectroscopy (Hitachi, SU-8020).

Plate 5: Samples of filters for trace metals analysis

Plate 6: Sequential extraction analysis using CEM MARS 6 microwave reaction system

Plate 7: Supernatant from microwave assisted extraction

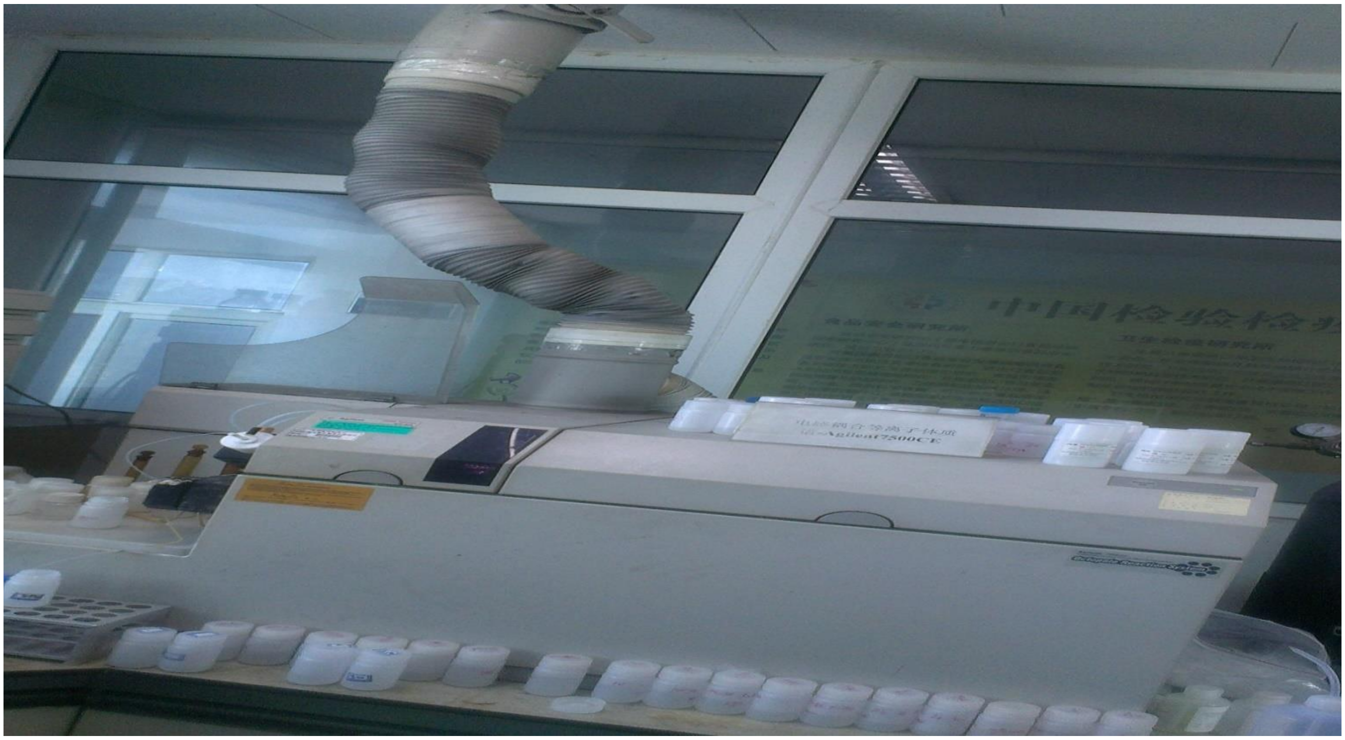

Plate 8: Trace metal analysis with lCP-MS (Agilent 7500ce Series)

Plate 9: Bench space for analysis at Institute of Process Engineering, Beijing, China.