LEVELS AND CHARACTERISTICS OF AIRBORNE PARTICULATE MATTER IN DAMMAM, DHAHRAN AND KHOBAR, SAUDI ARABIA

BY

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This thesis is dedicated to my parents for their prayers and supports

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LIST OF ABBREVIATIONS

AAS	- Atomic Absorption Spectroscopy
EAD	- Aerodynamic Diameter
BC	- Black Carbon
EDX	- Energy Dispersive Spectrometry
EDXRF	- Energy Dispersive X-Ray Fluorescence
EU	- European Union
ICP-OES	- Inductively Couples Plasma Optical Emission Spectroscopy
FESEM	- Field Emission Scanning Electron Microscope
FIB	- Focused Ion Beam
NO_X	- Nitrogen Oxides
CO	- Carbon monoxide
OSHA	- Occupational Safety and Health Administration
OC	- Organic Carbon
NAAQS	- National Ambient Air Quality Standards
PM	- Particulate Matter
PME	- Presidency of Meteorology and Environment
SO_2	- Sulphur (iv) oxide

SO_X - Oxides of Sulphur

SIA - Secondary Inorganic Aerosol

SEM - Scanning Electron Microscope

SEM-EDX - Scanning Electron Microscope coupled with Energy Dispersive Spectrometry

TSP - Total Suspended Particulate

TXRF - Total Reflection X- Ray Fluorescence

USEPA - United State Environmental Protection Agency

VOC - Volatile Organic Compound

XRD - X-Ray Diffraction

XRF - X-Ray Fluorescence

WHO - World Health Organization

ABSTRACT

Full Name: **LAWAL, Taoreed Taiwo**

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Health studies have linked a number of human respiratory problems to the high levels of particulate matter (PM) in the atmosphere. In Saudi Arabia, there are few information on the assessment of PM with respect to their geochemical and morphological characteristics. This study was carried out to assess the levels and characteristics of airborne particulate PM_{10} matter in cities of Dammam, Dhahran and Khobar in the Eastern Province of Saudi Arabia. PM samples were collected from three (3) different locations within each city over a period of 3 months (Oct. – Dec. 2015). PM samples were collected using ECOTECH Air Sampling device and concentration levels in $\mu g/m^3$ were obtained using the difference in corrected volume and the change in weight. The samples were characterized using analytical techniques such as Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDXs), X-ray Fluorescence (XRF), X-ray Diffraction (XRD) and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The results of the study showed that the average concentrations of PM_{10} were 126.00 $\mu g/m^3$, 177.00 $\mu g/m^3$, and 379.85 $\mu g/m^3$ in Dammam, Dhahran, and Khobar respectively. The Morphological analysis showed that the shapes of PM samples collected from Dhahran

were predominantly rod-like and platy with size between 2 – 6 µm, and the samples from Khobar were mostly irregular and size range between 2 – 8 µm and those from Dammam are nearly spherical with size ranging from 1 – 3 µm. The elemental composition showed the presence of carbon (C), oxygen (O), fluorine (F), sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), potassium (K) and calcium (Ca) at varying percentage by weights in all sampling locations. The elemental compositions were confirmed with XRF. The mineralogical analysis obtained from XRD showed that calcite and montmorillonite clay minerals are the main constituents of the PM. Finally, trace metal analysis showed the presence of Mn, V, Zn and Ni at levels higher than what was obtainable from literature.

Based on the results, it appears that most of the PM in the study area are from crustal materials which have biogenic or natural origin.

ARABIC ABSTRACT

(ملخص الرسالة)

الاسم الكامل: تايو توريد لاوال

عنوان الرسالة: معدلات وخصائص الجسيمات المحمولة جوا بالظهران، الخبر، والدمام بالمملكة العربية السعودية

التخصص: علوم البيئة

تاريخ الدرجة العلمية: مايو 2016

تشير الدراسات الصحية إلى ارتباط العديد من المشكلات التنفسية التي تصيب الإنسان بارتفاع مستويات الجسيمات المحمولة جوا بالغلاف الجوي. وتوجد قلة في الدراسات، في المملكة العربية السعودية، حول التوصيف الجيوكيميائي والمعدني لهذه الجسيمات. هذه الدراسة إلى تقدير مستويات الجسيمات المحمولة جوا (10) وتوصيفها في مدن الدمام، الخبر، والظهران بالمنطقة الشرقية بالسعودية. جمعت العينات من ثلاثة مواقع بكل مدينة على مدى ثلاثة أشهر (أكتوبر- ديسمبر 2015). وتم أخذ عينات الهواء من هذه المدن باستخدام جهاز إيكوتيك (ECOTECH) وقياس معدلات تركيزها بالميكروغرام/م3 عن طريق قياس التغير في الحجم والوزن. وتم التحليل المعدني والكيميائي للعينات باستخدام جهاز حيود الأشعة السينية، جهاز فلورة الأشعة السينية، الميكروسكوب الالكتروني، و مطياف الانبعاث الضوئي البلازمي التقارن الحثي. وتشير هذه النتائج أن متوسط نركيز الجسيمات المحمولة جوا (10) إلى 177.00 ميكروغرام/م3 بالظهران، 379.85 ميكروغرام/م3 بالخبر، و126.00 ميكروغرام/م3 بالدمام. ويشير تحليل الشكل للجسيمات تنوع أشكالها من موقع لآخر؛ حيث يغلب شكل العيدان على جسيمات الظهران، شكل الصفائح على جسيمات الخبر، والشكل غير المنتظم القريب إلى الكروي لجسيمات الدمام. وتشترك الجسيمات بالمناطق الثلاث بصغرحجمها عن ال10 ميكرون. وتشير نتائج التحاليل الكيميائية إلى تواجد عناصر الكربون، الأوكسجين، الفلور، الصوديم، الماغنسيوم، الألمونيم، السيليكون، البوتاسيم، والكالسيوم بجميع المواقع مع اختلاف نسبها من موقع لآخر. ويكون معدني الكالسيت والمونتموريلونيت الجزء الرئيس من الجسيمات. وترتفع معدلات العناصر الدقيقة (المنجنيز، النيكل، الفاناديوم، الزنك) عن المعدلات المذكورة في الدراسات السابقة. تشير النتائج النهائية أن معظم الجسيمات في المناطق المدروسة مصدرها القشرة الأرضية ذات اللأصل الطبيعي أو الحيوي.

CHAPTER 1

INTRODUCTION

1.1 Particulate Matter (PM)

The generic term for a general group of substance of physical and chemical diversities which exist as discrete particles (liquid droplets or solids) over a wide range of sizes is called Particulate Matter. Particulate matter which is a complex blend of very small particles and liquid droplets have been found to be composed of organic, inorganic, and several other components that could cause damage to human lungs through inhalation of air from the atmosphere, and this could be released from natural or man-made sources (Engel-Cox et al. 2013; Taiwo et al. 2014).

Anthropogenic stationary and mobile sources, as well as natural sources are the various sources from which PM originates. They could be by direct emission (primary emission) or may be formed secondarily in the atmosphere by reaction of some other gaseous emissions such as SOx, VOCs and NOx. Their properties hugely differ depending on time, region, source of emission and meteorology. Particulate matter sizes vary from as small as 5 nm to as large as 100 µm (Cao, 2013). Particulate matters are classified on the basis of their sizes –equivalent aerodynamic diameters (EAD) by USEPA.

Total Suspended Particulate (TSP) is used to describe PM with EAD within the range of 10 – 100 µm. This includes dusts and pollens. TSP measurement phased out by USEPA (World Bank Group, 1998) because they are filtered by nose and have less health effects. PM_{10} refers to particles with aerodynamic diameter or size of 10 microns (10 µm) or less,

and this is assigned for fine and coarse particles with EAD less than 10 μm. They are trapped in mucus linings and are referred to as “inhalables” because they are small enough to penetrate the thoracic region of the respiratory tract hence, they have significant health effects. Their diameter that is less or equal to an average of 1/7 of human hair and they include dust, soot, smog and fumes as shown in Figure 1.

Ultrafine and fine parliculates having EAD less than 2.5 μm are designated as $PM_{2.5}$ and called “respirables”. They can get deep into lungs, hence the main health problems associated with PM is related to fine and ultrafine particles.

While fine particles are produced primarily by combustion processes such as power plants, gas and diesel engines, wood combustion, and many industrial processes and reaction of various gaseous pollutants in the atmosphere, PM_{10} particles are generally released from mechanical processes that crush or grind larger particles, or by resuspension of dusts in the atmosphere.

1.1.1 Effects of PM

There is global concern about atmospheric dust pollution, especially of pollutant particles below 10 μm, because of their adverse health effects associated with their inhalation (Prabhat, 2016). Effects associated with PM exposures include mortality, aggravation of respiratory and cardiovascular disease (Cascio et al., 2014). PM also have neurological effects because they have the ability to transport neurotoxicants such as lead and mercury, to complex organic compounds that are usually formed or synthesized to harm the nervous system (Vallero, 2014). For instance, PAHs and halogenated compounds like the polychlorinated biphenyls (PCBs) which are neuro toxic are formed in the atmosphere from

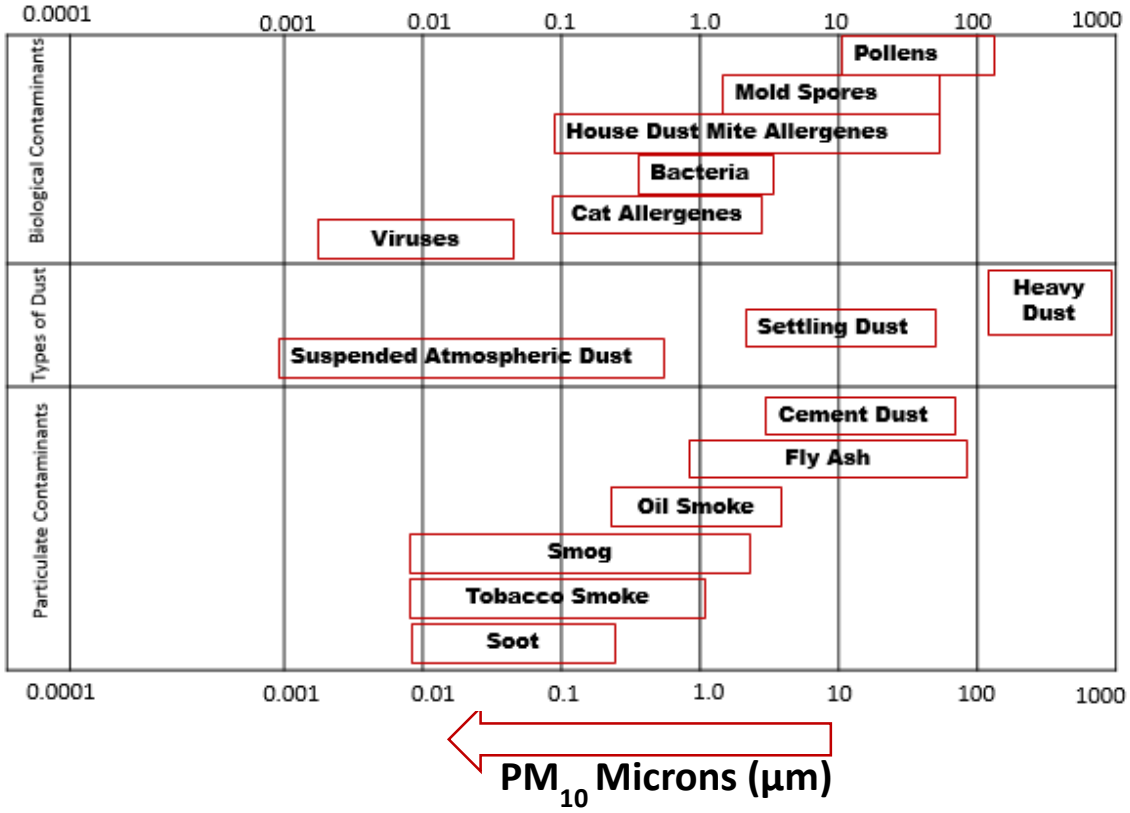


Figure 1. PM Types and Size Distribution

organochlorine and organophosphorus insecticides.

Air transport through airborne PM is the main route of human exposure. PM also affects the ecosystem such as the coral reefs because they transport microbes from one region to another which can invade and destroy corals. PM have also been implicated to be responsible for reproductive disorders in developing or newly conceived pregnancy from the womb. This is because they have the tendency to transport developmental and reproductive toxic chemicals such as teratogens. Other effects of PM include aggravation of allergic symptoms, decreased development of lung function and evidence of subtler indicators of cardiovascular health (Cascio et al., 2014).

1.1.2 PM Standards

To protect human health, standards are set for maximum allowable composition of PM in air especially for $PM_{2.5}$ (Buczyńska et al., 2014; European Commission, 2014). Due to its importance in human health and ecosystems, different countries and international bodies have set out regulatory standards to ensure protection of human health and public welfare. Standards and guidelines are given in 24-hour mean and annual mean. The unit of measurement is microgram per cubic meter (μgm^{-3}). It is also worthy of note that PMs are the only group air pollutant that have the same standards for ambient and indoor air quality. Theoretically, no standard is available for indoor PM but in workplace and for research purposes, ambient air quality standards are adopted by OSHA, WHO (2005), and PME Standard (2014). $PM_{2.5}$ standards according to PME, WHO, USEPA and EU over a 24-hour period is 25 $\mu g/m^3$, 35 $\mu g/m^3$, 35 $\mu g/m^3$ and 25 $\mu g/m^3$, respectively, while the maximum allowable limit for PM_{10} is 50 $\mu g/m^3$, 340 $\mu g/m^3$, 150 $\mu g/m^3$ and 50 $\mu g/m^3$ according to WHO, PME, USEPA and EU.

1.2 Significance of the Study

In Kingdom of Saudi Arabia, studies have shown the importance of the sources of particulate matter on their morphological and chemical characteristics (Rushdi et al. 2014; Shaltout et al. 2015). However, little studies have been published on the morphology and characteristics of particulate matter samples in Eastern Province of the Kingdom despite being the site of many industries, oil production, petro-chemical, and research institutions.

Owing to all the problems that PM causes in our environment and the importance of the Eastern Province as base of many industries, this study aims to assess the concentration levels and main geochemical characteristics of PM in the Eastern Province, Saudi Arabia.

1.3 Research Objectives

The main objective of the study will be to assess the chemical and morphological characteristics of the particulate matter in selected sites in the Eastern Province of Saudi Arabia. The specific objectives include:

1) To determine the concentration levels of airborne particulate matters (PM) in the selected sites.
2) To assess the morphological and mineralogical characteristics of the airborne particulates in the selected sites.
3) To assess the spatial distribution of the particulate matter in the selected sites

CHAPTER 2

LITERATURE REVIEW

2.1 General Studies on PM

Goldberg et al., (2013), explained that there is no clear evidence to illustrate that there were seasonal associations for respiratory and cardiovascular diseases but there is high correlation between daily non-accidental mortality and airborne PM. Lim et al., (2012), explained that PM poses great challenge to both environment and human populations and several researchers have sought the various outdoor sources of PM in the environment. Belis et al., (2013), reported that there are six different individual sources of PM and they include atmospheric formation of secondary inorganic aerosol (SIA), traffic, biomass burning, industrial point sources, sea/road salts and resuspension of crustal/mineral dust. Taiwo et al., (2014), reviewed the different models for source apportionment of PM from industries and they found out that the models are mostly appropriate for mineral constituents. Particulate matter occurs both indoor and outdoor depending on the probable source (Kuo and Shen, 2010).

There are various sizes of particulate matter but $PM_{2.5}$ has been given more priority over the years, unlike other particles greater than 2.5 μm, because it has a higher tendency of penetrating deeper into the human lung which may worsen breathing states and cause diseases in the lung (Shaltout et al., 2015). $PM_{2.5}$ has also been reported to be responsible for visibility impairment and poor vegetation as well as physiological, biological and genetic damage in children (World Bank Group 1998; Xue and Feingold 2006; Ee et al., 2013). Several research has focused on the effects of $PM_{2.5}$ in the environment with little

emphasis on PM10. Meanwhile, attention should be given to PM_{10} as it contains particles that may have aerodynamic sizes as low as 2.5microns (Stephanou, 2012; Pascal et al., 2014).

2.2 International Studies on PM Levels and Characteristics

Globally, PM has been considered to be of great importance hence the establishment of various agencies to enforce air quality standards and monitor air quality levels (World Bank Group, 1998; WHO, 2005; PME Standard, 2014; USEPA, 2014). This has also led researchers around the world to carry out various researches on PM. Moschandreas in 1985, reviewed the purpose of air pollution studies, and in the review, he identified residence with major pollutant emitting source as well as residence without the emitting sources as the two categories of inhabited environments from the data base he gathered. Based on collected information, he concluded that air pollution control is purely based on the desire to estimate total individual exposure and reduce the exposure to air pollutants. Fromme et al., (2008) studied the chemical and morphological properties of PM in some school classrooms using gravimetric data, scanning electron microscopy (SEM) and energy dispersive microanalysis (EDX) data. The study showed that physical activities of students led to resuspension of primarily indoor coarse particles and hugely contributes to increased PM_{10} level in classrooms. They also found out that PM concentration caused by indoor and outdoor combustion processes are comparable and based on their findings, they concluded that aside from outdoor particles, PM measured in classrooms have other sources. Their findings corroborated the hypothesis that ambient air PM is more toxic than indoor-generated PM. Pachauri et al., (2013) classified the groups of particulate matter based on their morphology as shown in Table 1.

Table 1.Classification of Particles into Groups Based on Morphology (Source: Pachauri et al., 2013)

Particle groups	Sub groups	Possible Phase/Minerals	Morphology of Particles
BIOGENIC AEROSOLS			
Biological Particles	Abundant C and O with minor elements (Na, K, Cl, Al, Fe, Ca, Mg and Si)		Variable morphology
GEOGENIC PARTICLES			
Quartz/ Silica	Si-O		Tubular shape
Aluminosilicates	Al-Si-O	Fly ash	Spherical shape
	Ca-Al-Si-O	Grossular	Irregular shape
	Na-Al-Si-O	Na-feldspar	Irregular shape
	K-Al-Si-O	K-feldspar	Irregular shape
	Ca-Al-Si-O	Ca-feldspar	Irregular shape
	Mg-Fe-Al-Si-O	Magnesium Iron aluminosilicate	Nearly spherical
	Ca-Mg-Al-Si-O	Ca Magnesium aluminosilicate	Irregular shape
Calcium rich particles	Ca-C-O		Nearly triangular
	Mg-Ca-C-O		Irregular shape
Fe/Ti oxide	Fe- Ti-O	Iron Titanium oxide	Nearly spherical
Chloride Particles	Ca-Cl	Calcium chloride	Triangular
	K-Cl	Potassium chloride	Irregular shape
ANTHROPOGENIC PARTICLES			
Industrial Particles	Metalliferous particles containing Cr (> 40%)		Irregular shape
	Fe rich particle (> 50%)		Irregular shape
	Ni rich particle (> 30%)		Irregular shape
Carbonaceous particles	C rich particle with minor amount of O	Organic particle	Individual carbonaceous spherules (spherical or irregular)
	C rich particle	Soot	Porous texture; Chain like aggregates

Polednik, (2013) studied the particle mass (PM) and number (PN) during winter and summer in three different secondary school classrooms, and they found out that particle concentration was appreciably influenced by emissions from residential coal combustion and particle spawning educational experiments. The study also showed that PM and PN recorded in summer and winter are higher indoor compared to outdoor.

Boman et al., (2010), used elemental composition of particulate matter samples to predict the likely sources of the components of PM samples that were collected at Gothenburg, Sweden. A cyclone that splits the $PM_{2.5}$ particles from the air stream and impacts them on polycarbonate filters was used for sample collection and subsequently this was characterized for particulate mass, black carbon (BC) and the elements chlorine (Cl), sulphur (S), potassium (K), calcium (Ca), Titanium (Ti), chromium (Cr), Manganese (Mn), iron (Fe), Nickel (Ni), copper (Cu), arsenic (As), bromine (Br), cadmium (Cd) and lead (Pb).was used and they concluded based on their finding that further study is required on the use of Total reflection X-ray fluorescence (TXRF) spectrometer to optimize its usage for the determination of the EU legally regulated elements As, Ni, Pb and Cd, but regardless of the finding, the AAQS limits for Cd and Pb in Gothenburg is not a difficult task.

Kim Oanh et al. (2010), studied the characteristics of PM samples emitted while diesel vehicles were in operation. Their aim was to develop source profile and emission factor for developing countries. Engel-Cox et al., (2013) summarized the fine particle monitoring models that combines ground-based and satellite-based data, and communications. Subsequently, they made recommendations on steps that regulatory bodies and scientists can take to increase and advance indigenous and universal indicators of PM air pollution. Also, they suggested that modern technologies and systems should be extended towards

expansion of air quality monitoring as well as involvement of non-experts in mass-obtained data collections, and they also believed that it is important to encourage the expansion and enhancement of universal multi- pollutant indicators of the health and economic consequences of air pollution in other to address air quality improvement globally.

Pipal et al., (2011) explained that SEM-EDX is a convenient method for identification of the source of emission of PM. In the study, SEM-EDX was used to identify the contrast with respect to shape and morphology as well as elemental composition of aerosols in PM, and to further relate them to the probable source as well as emission and transport of pollutants from different polluted areas. They used the SEM micrograph of PM_{10} and PM2.5 to show the size range of particles from the different sampling sites and the EDX spectra was used to estimate the different groups of elements for each particle from the different sites. Pachauri et al., 2013, used SEM-EDX for the characterization of individual coarse particles in Agra, India and they showed that this technique is appropriate for grouping aerosol particles based on their characteristics. They also used this technique to establish the likely sources (anthropogenic or natural) of the aerosols.

Satsangi and Yadav, (2013) carried out their study using SEM-EDX to emphasize and give detailed analysis of morphological composition of PM at discrete level. Singh et al. (2014) used SEM-EDX analysis to establish the variation in morphology and elemental composition of PM samples in suburban and urban cities in India. They were able to determine the source from where the particles were produced. The status of heavy metals in ambient air in a coal field was also studied by Mishra et al., 2013, to show the significance of PM as carriers of hazardous heavy metals. The study identified Cobalt,

Cadmium (Cd), Nickel (Ni), Manganese (Mn) and Lead (Pb) as the major heavy metals with the aid of Atomic Absorption Spectrophotometer (AAS). According to Yassin et al. (2012), Kuwait's PM pollution was estimated as the worst when compared with other countries of the world, and this is based on their study on the assessment of airborne PM in different residential environments in Kuwait.

Boman et al., (2013) assessed the composition of PM in Egypt, because of the importance of elemental composition of PM for the purpose of source apportionment and determination of their harmful effects, using energy dispersive X-ray fluorescence spectrometer (EDXRF). 16 elements were found including some trace metals although, some were found at levels lower than the detection limit of the instrument. The analysis showed temporal variation in the levels of PM and their likely sources of emissions, as well as the estimation of their human health effects.

Shaltout et al., (2014) developed a method for the determination of heavy metals in PM samples in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry without using modifier. They found out that the results obtained was similar to those obtained using TXRF and inductively coupled plasma mass spectrometry. Several other studies around the world have reviewed the sources, morphology and characteristics of airborne PM. Brunekreef and Holgate (2002), in their review study on air pollution and health discussed the evidences to show that certain air pollutants like PM have adverse health effects.

Davidson et al., (2005), in their review study on health effects of PM pollution on human health explained that health effects of PM is not dominated by a particular chemical species but they are due to a combination of species. Other factors aside PM such as socioeconomic

status and lifestyles were said to affect health risks, but according to them, it is difficult to account for these confusing non PM factors. They also stated that due to PM problems that relates to an array of societal concerns such as energy production and economic development, airborne PM is considered to also be responsible for other adverse effects asides human health problems. For this reason, they suggested that an integrated strategy which is interdisciplinary and puts holistic tradeoffs into consideration should be adopted in other to make progress on the reduction of the influences of PM.

Viana et al., (2008), studied the source apportionment (SA) of PM and identified four my types of sources of PM which are vehicular source that is tracked by C/Fe/Ba/Zn/Cu, crustal source (Al/Si/Ca/Fe), sea-salt source (Na/Cl/Mg), and a mixed industrial fuel-oil combustion ($V/Ni/SO_4^{-2}$) and a secondary aerosol ($SO_4^{-2}/NO_3^{-}/NH_4^{+}$). Biomass combustion and shipping emission sources were hardly identified. In 2010, Geiger and Cooper, outlined the health effects, exposure limits and regulations of airborne metal in PM. They based their estimates and regulations on the national ambient air concentration for rural, urban and industrial communities in the US. Mejía et al., (2011), studied the methods for exposure assessment and air pollution effects on school children using measurement of air quality at school level, link between measured air quality and children's exposure, relationship between children exposure and health, as well as source identification. Based on the study, they concluded that there is high connection between low socioeconomic status and proximity of schools to pollution sources.

Belis et al., (2013), identified secondary inorganic aerosol (SIA), traffic, resuspension of crustal/ mineral dust, biomass burning, point sources and sea/ road salt as the major sources of PM, and explained that SIA and traffic are the most important source categories for

abatement during a year. Ee et al., (2013), presented a summary of the of the sensitivity of teenagers to environmental pollution, international and local signs of harmful health effects on children and an appeal for help from pediatricians in urging the government to take legal actions for the realization of cleaner air to protect our child health. Engel-Cox et al., (2013), summarized PM monitoring models that combine ground-based and satellite-based data, and communications, then urges policymakers and scientists to take actions towards expanding and improving local and global indicators of PM air pollution.

Ahmady-Birgani et al., (2015), studied the mineralogy and physico-chemical properties of atmospheric particles collected at southwestern and northwestern Iran during ambient and dust events over a period of about 6 months. SEM-EDX was used to study particle morphology and elemental compositions, and while the SEM showed the various sizes and level of aggregation of the particles, the EDX showed the elemental composition of the samples. XRD was used for the identification of minerals such as quartz, gypsum, calcite and clay minerals that are contained in the sample. However, the study did not estimate the quantity of each element that are present, hence, the study did not relate with presence of the trace metals with the allowable limits by WHO, USEPA or EU. Farahat, 2016, studied air pollution in 6 countries over the Arabian Peninsula including Saudi Arabia, United Arab Emirate, Kuwait, Qatar, Bahrain, and Oman. He explained that the pollutants area are mainly particulates, greenhouse gases, nitrogen dioxide, and Sulphur dioxide, but their concentration varies from one country to the other. He reported that sandstorms have great impact on the distribution of the pollutants, and stated that emission from cement industry was highest in Saudi Arabia.

2.3 PM Studies in Saudi Arabia

In Saudi Arabia despite the increase in construction activities and the rise in the number of petroleum and petrochemical industries, occasioned by the oil boom over 3 decades ago (Al-Jarallah, 1984), only few studies have been carried out to assess the level of particulate matter in different environment in Saudi Arabia. Modaihsh and Mahjou, (2013), collected samples from 15 sampling sites. They reported that dust deposition especially in areas close to construction site were quite high. Silt constituted the dominant content of the dust samples. This was in agreement with Modaihsh (1997). The dust samples also contained high levels of pH, $CaCO_3$, trace metals and EC. The high level of the metal containing dust samples were attributed to natural sources and traditional sources such as motor vehicle emissions. Quartz and calcite were the major mineral component of the dust samples analyzed. Farahat et al., 2003, studied the characteristics and distribution of aerosols in four different regions of Saudi Arabia and found out that there was increase aerosol contribution at some period during the sampling time. They attributed the increase to a major dust storm that occurred during the period. In the study, they also reported that air pollution is higher in Eastern province compared to the 3 other areas that were studied.

While few studies have analyzed the level of particulate matter in different environment in Saudi Arabia, fewer literature have included the morphology and characteristics of airborne PM in it assessment. Amongst these studies were the determination of levels of lead in ambient PM from 6 different locations in Jeddah city (Abulfaraj et al., 1990), and the assessment of ambient air quality from PM samples collected in Jeddah city to estimate the concentration of lead after almost a decade of phasing out fuels containing lead (Aburas et al., 2011).

Also, as an effort towards determining the characteristics of particulate matter within the kingdom, Khodeir et al., (2013) used X–ray fluorescence (XRF) to analyze different samples collected over a long duration and from multiple sites to determine the elemental composition of $PM_{2.5}$ and PM_{10} in Jeddah province of Saudi Arabia. A model of the chemical composition data was also done with the aid of factor analysis while the source of the particulates was determined using Varimax orthogonal rotation. The main sources of PM_{10} were categorized into four; heavy fuel burning, re-suspended soil, industrial emission and marine aerosol. These particulates contained different level of nickel, iron, aluminum, silicon and vanadium. Polycarbonate filters fixed embedded in a cartridge and fixed in a cyclone were used as support to collect particulates from residential, industrial and traffic sites in Taif Saudi Arabia in 2011 (Shaltout et al., 2015). The samples were analyzed using energy dispersive X-ray fluorescence and electron paramagnetic resonance. Most of the elements analyzed for were below the limit sets by international and national air quality standards while others were below detection limits. Rushdi et al., (2013), reported the use of a mini-volume air sampler for sample collection and x-ray fluorescence to determine the elemental composition of heavy metals in dust particles collected in Riyadh between 2006 and 2007. The result obtained revealed higher concentration of PM_{10} compared to $PM_{2.5}$. The particulates also contained some heavy metals. Higher concentration of particulates was recorded in 2007 compared to 2006. The high level of particulates reported in 2007 were attributed to the increase in development activities such as cement, quarries and ceramic industries. Heavy metal concentration was also measured in a study on source apportionment and elemental composition of $PM_{2.5}$ and PM_{10} in Jeddah City, Saudi Arabia (Gatzeva-topalova et al., 2011)

However, in the Eastern province which is the recognized hub of most petroleum and petrochemical industries in the kingdom, very few studies have been carried out on airborne PM. Immediately after the Gulf war in early 90's, Mian and Sadiq studied the heavy metal concentration in airborne particulate matter in Dhahran, Eastern province of Saudi Arabia (Mian and Sadiq, 1993; Sadiq and Mian, 1994). Shaltout et al., 2013 evaluated the trace metal composition of atmospheric aerosols collected in Taif city of Saudi Arabia as well as the influence of these elements on air quality of the area. Thus, there is a need to conduct extensive study on the air quality of the residence area of this Eastern province to avail a current status in an accurate form not only for the academic literature but also for the knowledge of air quality and possible safety precautions. Importantly, the choice of method for sample collection of airborne PM is central to the quality of information to get from such a study, most especially that only little can presently be found in the literatures.

CHAPTER 3

METHODOLOGY

3.1. Study Area

3.1.1. Description of Sampling Area

Samples for this study were collected from the Eastern province of Saudi Arabia. (Figure 2). The region has a population estimated to be more than 4 million with a population growth rate of 2.9% per year. Eastern region is the Kingdom's of Saudi Arabia's largest region, located between latitudes 17.10, 29.10 and longitudes 44.81, 55.69 east of Greenwich Mean Time (GMT). The Eastern province extends from the Kuwaiti border to the endless dunes of the Empty Quarter, and also hosts the natural wonder of the world's largest oasis as well as immense wealth of huge reserves of oil and natural gas. The links to Gulf Cooperation Council neighbors (GCC): the kingdom of Bahrain, the peninsula of Qatar, the United Arab Emirates and Sultanate of Oman are provided by this region. The total area of the region is 710,000sq.km. The region functions as the backbone of the kingdom's economy, regarded as one of the largest reservoirs of crude oil in the world. The province also has Dammam industrial cities 1 and 2 as well as Jubail industrial cities 1 and 2. The region also has 3 ports namely King Abdul Aziz Port, Dammam, Jubail Commercial Port, and King Fahad Industrial Port in Jubail. The region along the gulf serves as a major link between the east and the West for centuries and has a vast coastline of about 560 km. Eastern province comprises of 12 cities namely Al ahsa, Abqaiq, Jubail, Ras Tanura, Qatif, Khobar, Dhahran, Dammam, Hafar Al- Batin, Khafji, Nariyah, and Qaryat al-Ulya. The capital of the region is Dammam metropolitan area. The Dammam metropolitan area is the largest metropolitan area in the Eastern Province of Saudi Arabia; it is formed by three

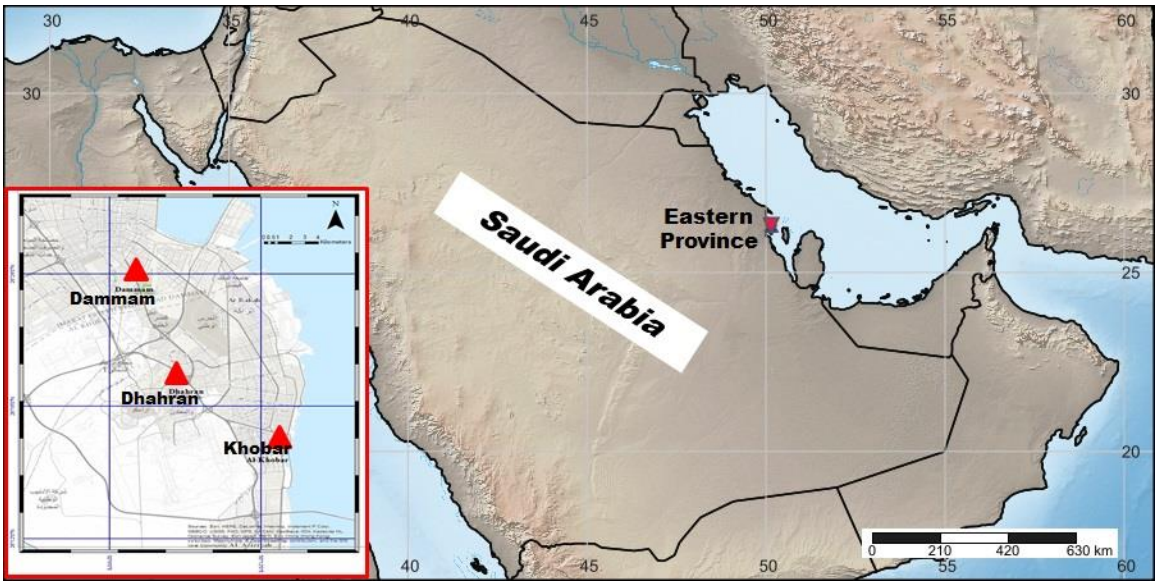


Figure 2. Map of Sampling Area

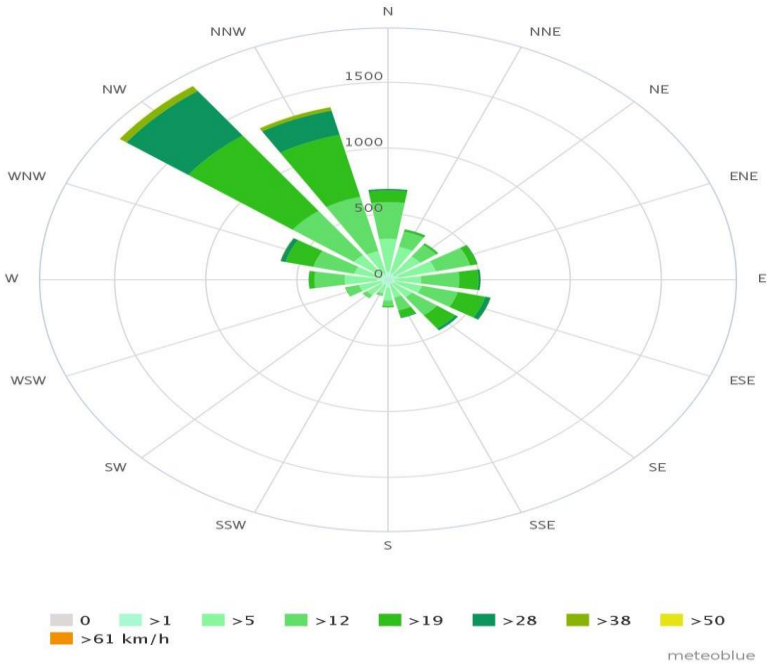


Figure 3. Wind Rose Diagram for the sampling Area

main neighboring cities: Dammam, Dhahran, and Khobar. These three cities are sometimes referred to as the "Triplet Cities". The Dammam-Dhahran-Khobar area is a major hub for shipping, oil, commerce and industry. Tankers take on oil at the terminal in Ras Tanura. The Dammam Area is also famous for the wide variety of recreational facilities it offers residents and visitors alike. Dammam metropolitan area is the 3rd largest metropolitan area in the kingdom and also includes Khobar and Dhahran. The wind rose image in Figure 3 shows that the wind is blowing from North West to South East.

3.1.2 Sampling Cities

Three (3) cities as shown in Figure 2, were used for sample collection and they include Dhahran, Khobar and Dammam.

Dhahran City

Dhahran is located on coordinate 26.2361° N, 50.0393° E and is 10km west of Khobar (26.2172° N, 50.1971° E) in the Eastern province of Saudi Arabia. Dhahran, with Dammam and Al Khobar, forms the Dammam Area. This city is known for housing the largest oil company in the world, Saudi ARAMCO. King Fahd University of Petroleum and Minerals (KFUPM) was chosen for the 3 sampling locations in this city because of its proximity and the population of the University community. Inside KFUPM, 3 locations were chosen and they were referred to as location 1, 2 and 3 respectively as shown in Figure 4. Location 1 is building 63 which houses the first ever Fabrication Laboratory (FABLAB) in the Eastern Province. The laboratory is typically a tech-advanced workshop to design, fabricate and assemble small parts into a single intact and functional component that works effectively to perform a certain job, and the resources are available to all the residents of the region

who are above the age of 15 of all genders and affiliations. This location is represented in Figure 4 as location 1. Location 2 is building 5 which is the first ever administrative building and one of the oldest building in the University. This area is also hosts the highest building in the university. Presently, the Building houses the Department of Mathematics and statistics. This location is represented in Figure 4 as Location 2. The third location in Dhahran is KFUPM building 805 and is represented in Figure 3 as Location 3. This building is the home of between 100 and 120 graduate student and it also shares boundary with the student cafeteria which serves the whole student population.

Khobar City

Al Khobar is situated in the Eastern Province of the Kingdom of Saudi Arabia, and on the coast of the Arabian Gulf, and it's among the largest cities in the Gulf Cooperation Council (GCC). Al Khobar has a large number of expatriates who usually come for jobs. The Half Moon Beach and Khobar Corniche are the major tourist attractions in Khobar.

People from the neighboring GCC states and Riyadh frequently visit the city to do activities such as fishing, scuba diving and other water sports. Khobar has a desert climate with very hot, humid summers and mildly cool dry winter. Two months – April and November – are transitional; sometimes the temperature exceeds 48 °C, with temperatures ranging from 37–50 °C during the day and 24–36 °C at night. The 3 locations that were selected in this city were chosen because of their proximity, availability of safe empty space to place the air sampling unit, nearness to a major event center such as mall, hospitals or workshop, and the availability of 220VAC power source.

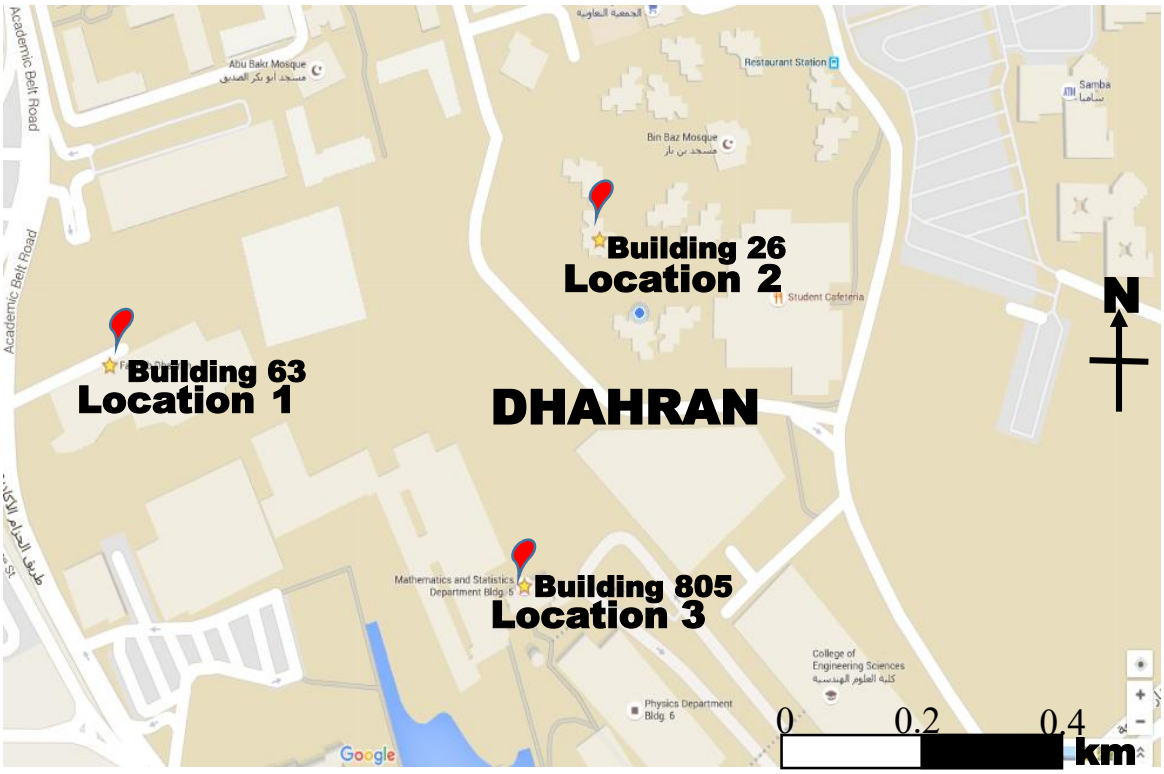


Figure 4.Map of Dhahran Sampling Sites

The three locations that satisfied these conditions were in Thuqbah. The first location is a residential apartment at Jizan St, Al Khobar with coordinates 26°15'35.59"N and 50°11'36.41". This location is between Thuqbah cemetery and Gulf Industrial Auto Workshops and it's represented as Location 1 in the Map of Al Khobar sampling locations shown in Figure 5. The 2nd location in Al-khobar is between street 22 and 23 in Thuqbah, Al Khobar. This location is unique for having major roads, several houses and a bank around it. Very close to this location is also coffee snack bars and a small supermarket. This location is represented in Figure 4 as Location 2 and its coordinates are 26°16'48.06"N and 50°11'42.12"E for X and Y coordinates respectively. The 3rd location in this city is situated at 2993 4th street, Thuqbah, Al-Khobar. It is situated around Venicia mall on King Khalid road and it has X and Y coordinates of 26°16'3.07"N and 50°11'37.85"E respectively. It is represented by location 3 in Figure 5.

Dammam City

Dammam which is larger than Dhahran or Khobar in the eastern region. Near Dammam are located the most important centers in the world for the production and refining of petroleum. The population of Dammam is greater than a million. The most important features of the city are King Fahd International Airport, King Fahd Park, National Museum, King Abdul Aziz Seaport, and Heritage Center Dammam. The 3 locations in Dammam are selected based on their proximity, safety of the sampling device and availability of power source in a house with an empty space to place the machine. The location includes 3 Street, Al-Qazaz with coordinates 26°26'2.70"N and 50° 5'41.44"E, 14 (A) Street, Al Badiyah with coordinates 26°25'51.04"N and 50° 5'16.74"E, and Al Anud with coordinates 26°26'46.60"N and 50° 4'21.68"E which are represented as location 1, location 2 and

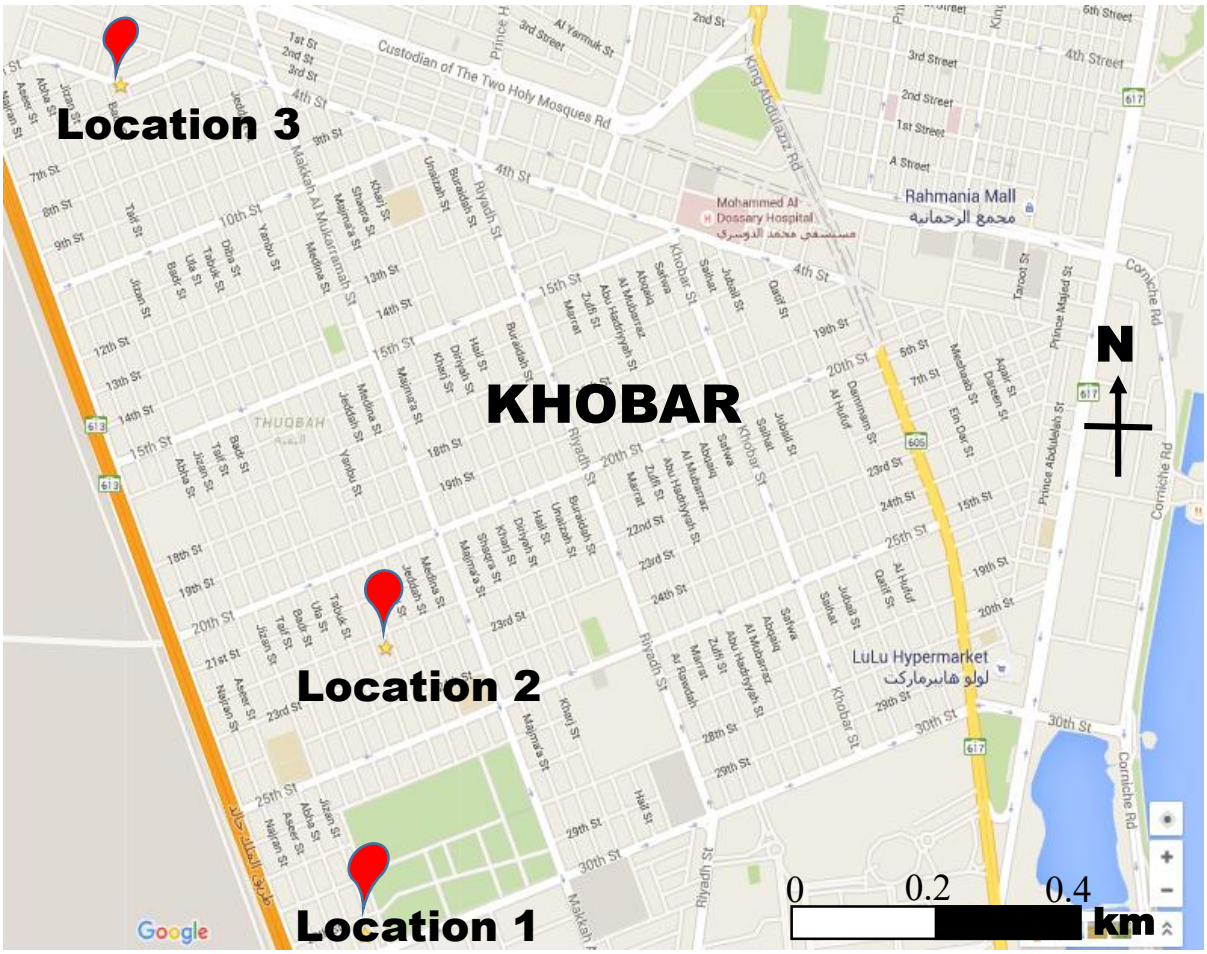


Figure 5. Map of Al-Khobar Sampling Sites

location 3 respectively. The map of Dammam showing the different locations is presented in Figure 6.

3.2 Sampling

3.2.1 Equipment for Sampling

The sampling equipment could be grouped into 2; those materials used for sample collection which could be categorized under the sampling unit and other materials used with the sampling unit such as membrane filter and the digital weighing balance

Sampling Unit

The sampling unit used for the collection is Ecotech HiVol-3000 sampler with PM_{10} size selective inlet. The Hi-Vol 3000 sampler incorporates advanced programming functions and electronic volumetric flow control to maintain a consistent flow and collect a representative sample of particulate matter. It carries out reliable sampling with volumetric flow control that is automatically corrected to standard reference temperature, programmable reference temperatures, industrial brushless motor.

Other material used with the sampling unit include; Mettler Toledo JL602GE analytical

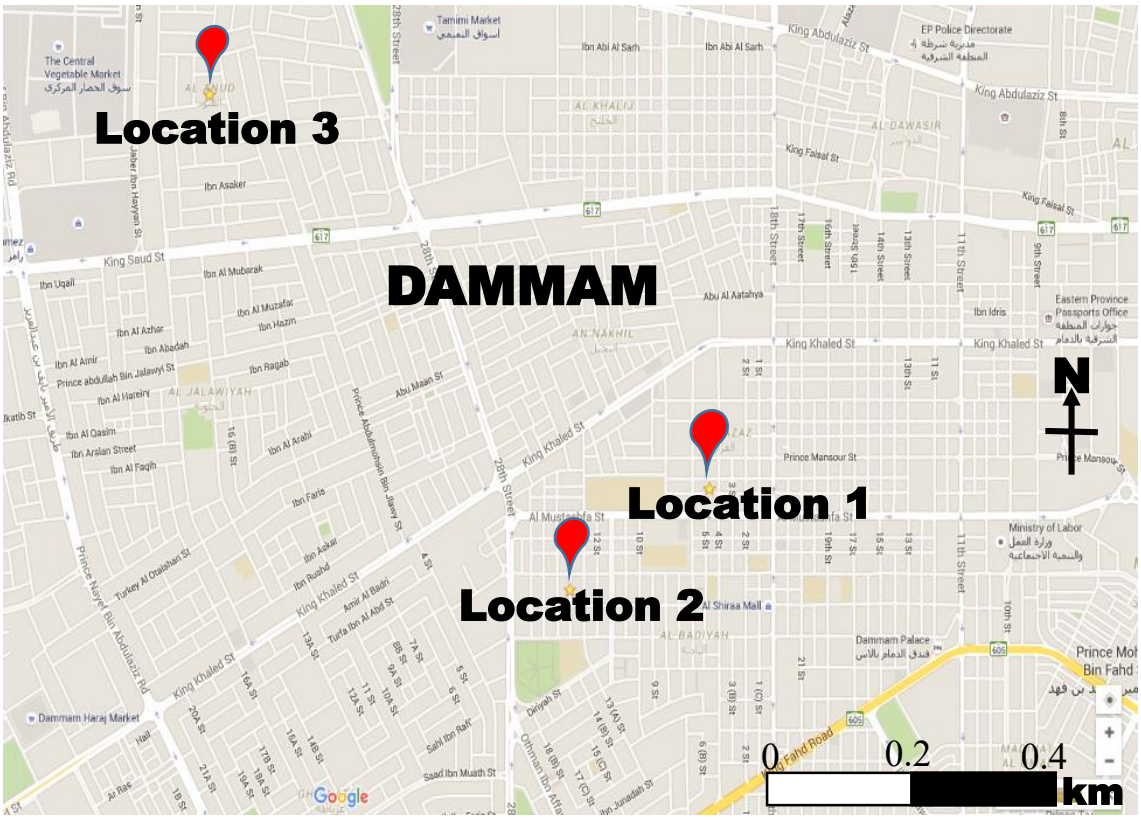


Figure 6. Map of Dammam Sampling Sites

balance which is an approved Class II digital scale for weighing samples lower than 1 gram, and Pall Flex Emfab filter type TX40HI20-WW which is manufactured by Pall Laboratories. Pallflex Emfab filters are made of borosilicate glass microfibers that are reinforced with woven glass cloth and bonded with Polytetrafluoroethylene (PTFE). They have low air resistance which makes them ideal for use in critical aerosol sampling tests. They can also withstand folding for weighing and transport. The Hi-volume sampling unit is shown in Figure 7 and the other materials used are shown in Figure 8.

3..2.2 PM Sample Collection Procedures

Particulate matter samples were collected from October – December 2015 as per the following steps:

1. Identifying a suitable site for the collection of the samples, seeking permission from the owner of the site.
2. Pre-weighing of the membrane filters each day before setting up the machine, transporting the sampling unit to the site.
3. Securing the sampling unit with rope to available beams or columns to prevent it from being blown away by strong wind, and then plugging the equipment.
4. Raising the size selective inlet dish, taking out of the membrane filter mesh, placing the pre-weighed filter inside the mesh, and returning the mesh to its position.
5. Recording the initial reading of the weight of the pre-weighed filter, total volume, corrected volume, and run time.

Figure 7. Air Sampling Unit

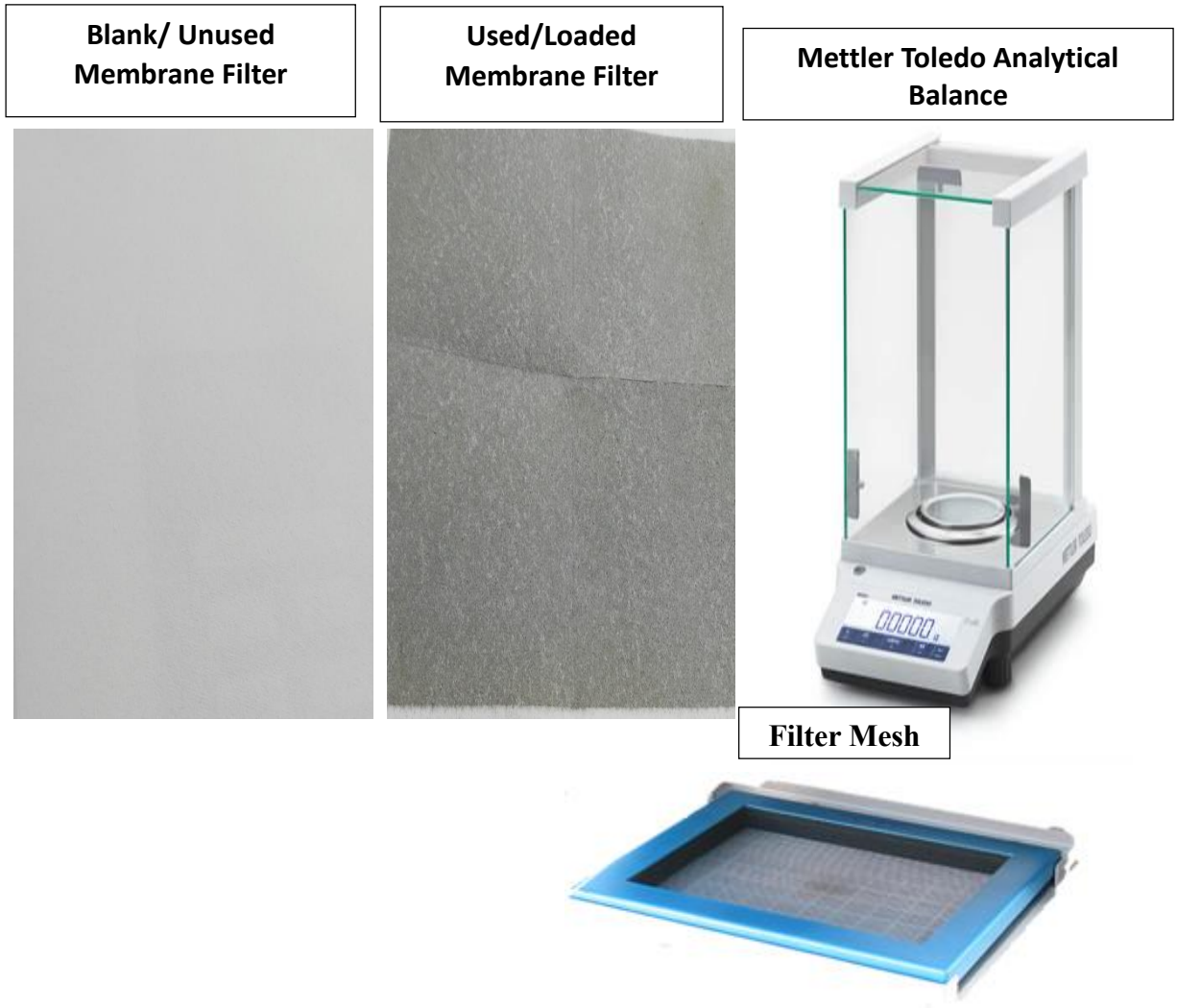


Figure 8. Other Materials used with the Air Sampling Unit

Then the sampling unit is set up for a 24-hour sampling period and the final reading is recorded the next day. After 24 hours, the particulate filled filters were removed from the sampler head and packed into zipper plastic bags to prevent contamination. The procedure was repeated for 7-days in each sampling location. For quality control and assurance, the sampling unit was pre-calibrated and the weighing of the filters was done in triplicates. The corrected volume was also used to obtain the concentration of the PM to ensure quality control and assurance.

3.2.3 Determination the PM Levels

The gravimetric analysis of the samples was done by obtaining the concentration of the PM_{10} samples in microgram per cubic meter ($\mu g/m^3$). The weight of the membrane filters was measured before and after the sample collection and then divided with the corrected volume that is recorded from the ECOTECH Hi-volume air-sampling device. This was then compared with PME, USEPA and WHO standards to know if the concentration was above or below the maximum allowable limits.

3.3 Sample Characterization Techniques

3.3.1 PM Morphology, Elemental and Mineralogical Characterization

Several methods have been adopted to characterize the constituents of particulate matter and they include scanning electron electron microscopy coupled with electron dispersive spectroscopy (SEM-EDX), X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray diffractometry (Rushdi et al., 2014; Shaltout et al., 2013). SEM is a method for sharp resolution superficial imaging used to study the

morphology of the PM samples (Chung et al., 2008; Pipal et al., 2011) collected on the filters in combination with EDX. Sample preparation for SEM-EDX involves punching of a 1mm2 area from the centre of the filter and then placing it on aluminium SEM stubs before then coating it with either gold (Fromme et al., 2008; Pachauri et al., 2013) or carbon (Singh et al., 2014). SEM-EDX analysis generally follows the procedure that was used by Pachauri et al. (2013) in his study where he set the accelerating voltage, beam current and X-ray detection line as 20 kV, 40-50 μA and ˜ 0.1% respectively. While SEM shows the shape and size of the PM, EDX gives the qualitative and quantitative elemental composition of the PM sample (Pipal et al., 2011). Other spectroscopic methods previously used includes XRF, ICPOES and XRD. XRF have been reportedly used in the characterization of particles by quantitatively determining the specific element concentration in relation to the standards. XRF is usually used to quantify elements with atomic number greater than 14 (Watson et al., 1999). XRF utilizes excitation source from X-ray tube while PIXE which is the other type commonly used, makes use of photons from cyclotrons. According the Watson et al. (1999), EDXRF is commonly used for airborne PM filter analysis because it's excellent sensitivity. Elements with atomic numbers greater than 14 in the atomic table have been quantitatively and qualitatively determined using XRF (Vermette and Landsberger, 1991; Shendell and Naeher, 2002; Pipal et al., 2011; Buczyńska et al., 2014). Although XRF can quantify trace element, ICPOES is more effective in quantitative and qualitative analysis of trace metals. ICPOES of different types have been used in various air pollution study to determine the levels of trace metals in the atmosphere (Kim Oanh et al., 2010; Kgabi, 2010; Ny and Lee, 2011). They are more reliable because they can detect any metal because of the lower detection limits compared

to other techniques (Shaltout et al., 2013). However, to understand the mineral composition of the airborne PM samples, XRD is the most suitable technique as it provides information on different minerals that exists in the in the samples (Fan et al. 2002; Satsangi and Yadav 2013; Hariharan et al., 2014).

3.3.2 PM Sample Selection for Analytical Studies

In order to avoid bias and for easy comparison of our samples, decision was made on the sampling days for analysis for each location. To arrive at this decision, we put into consideration that at least 33% of our total sample size must be analyzed in each location, hence we chose a total of 27 days as shown in Table 2. The corresponding dates were added after the sampling had been completed. The samples were labelled with respect to the city, location and day of sampling. For instance, sample collected from Dhahran, location 1 on the first day of sampling.

The selected samples were analyzed for the PM concentration; size and shape of the PM, elemental composition of the sample and the minerals contained in the sample and the procedure for each of the techniques are discussed in the sections below. Particulate matter samples collected were analyzed gravimetrically, chemically and mineralogically using various analytical techniques.

3.4.2.2 Morphological Characterization Technique for PM Samples

Morphological characterization technique used was Lyra3 FESEM coupled with EDX. The FESEM model used was Lyra3 series produced by TESCAN and it is a computer (PC) controlled SEM with Schottky field emission cathode, together with gallium Focused Ion

Table 2. Selected PM Sample for Characterization from each Site

Sampling City and Location	Sampling Days/ Dates		
	Sample 1	Sample 2	Sample 3
Dhahran Location 1	Day 2 (3/10/15)	Day 5 (6/10/15)	Day 1 (1/10/15)
Dhahran Location 2	Day 4 (12/10/15)	Day 7 (15/10/15)	Day 3 (11/10/15)
Dhahran Location 3	Day 6 (21/10/15)	Day 2 (17/10/15)	Day 5 (20/10/15)
Khobar Location 1	Day 1 (22/10/15)	Day 4 (25/10/15)	Day 7 (29/10/15)
Khobar Location 2	Day 3 (01/11/15)	Day 6 (04/11/15)	Day 2 (31/10/15)
Khobar Location 3	Day 5 (10/11/15)	Day 1 (06/11/15)	Day 4 (09/11/15)
Dammam Location 1	Day 7 (20/11/15)	Day 3 (16/11/15)	Day 6 (19/11/15)
Dammam Location 2	Day 2 (22/11/15)	Day 5 (14/12/15)	Day 1 (21/11/15)
Dammam Location 3	Day 4 (20/12/15)	Day 7 (23/12/15)	Day 3 (19/12/15)

Beam (FIB) column and possibly with Gas Injection System (GIS). This equipment has some exceptional optical properties, flicker-free digital image with super clarity, hi-tech user-friendly software for SEM/FIB/GIS control and image capturing using windows platform, standard formats of stored images, easy image management, processing and measurements, automatic set up of the system and as well as other automated operations are characteristic features of the equipment. The scanning speed was between 20 ns to 10 ms per pixel which is adjustable in steps or continuously. The magnification at 30 kV ranges from 1x – 10^6x with ion gun of Ga liquid metal ion source. Ion probe current ranges from 1 pA to 1 nA or 1 pA to 50 nA. The working distance (WD) of 9mm for SEM and WD of 12 mm for FIB and an angle of 55º. It is also planned to have high resolution at low beam voltages including system for negative voltage biasing of the sample stage and new in-beam detector that works either as SE detector (in BD mode) or BSE detector (in standard mode), as well as fully integrated third party EDX with take-off angle of 25º at SEM WD 9 (coincidence point). The image of the FESEM used for the study is presented in Figure 9.

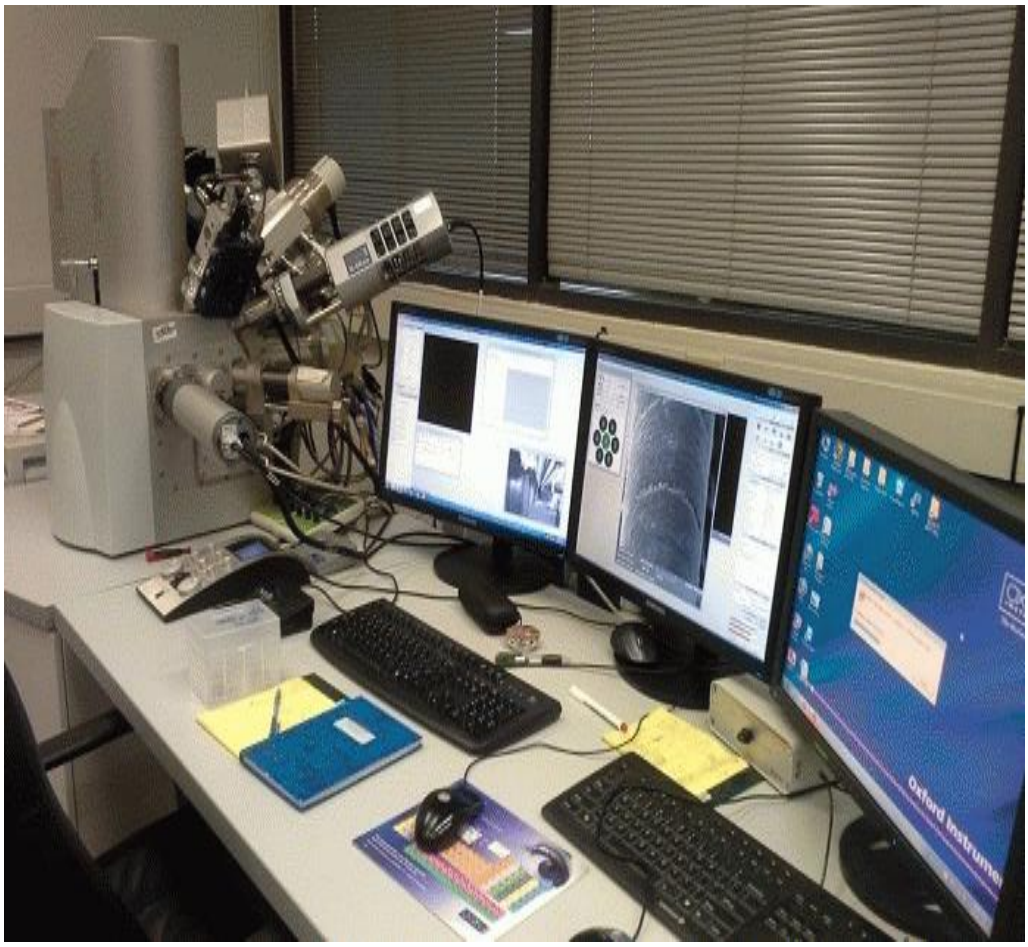


Figure 9. Lyra3 Field Emission Scanning Electron Microscope (FESEM)

3.4.2.3 Elemental Characterization Technique for PM Samples

Elemental characterization techniques used for this study were EDX and X-ray Fluorescence Spectrometer (XRF). The EDX is coupled with the Lyra3 FESEM and is discussed in the section above. The XRF model used for the determination of the elemental composition of the sample is JSX-3400RI, although it could not provide the composition of elements below sodium in the periodic table. The XRF analysis was done at the Geological Sciences laboratory at the college of Petroleum and Geosciences, KFUPM. It is furnished with highly sensitive, high resolution liquid nitrogen Si (Li) semiconductor detector. The model is a general purpose XRF instrument with outstanding cost performance ratio that utilizes a liquid-nitrogen-type detector. JSX-3400RII employs Si (Li) detector for heavy elements, and it can quantify trace elements at short time. The resolution of the detector of JSX-3400RII is high so it can separate the peak of the light elements such as Mg, Al and Si, very clearly. The equipment is suitable for quantitative analysis without having any standard substance, but by simply using the FP method (fundamental parameter method). The collimator is standardly equipped; it can be used to carry out analysis to check for minute foreign substances. JSX-3400RII has the pragmatic feature of the sum- peak as the standard and the qualitative analysis is easy. The thickness and composition of each layer in a multi-layer thin film such as the composite plating, the

Figure 10. JEOL JSX-3400RII X-Ray Fluorescence (XRF) Element Analyzer

alloy plating without reference samples and particles can be analyzed with the thin film FP method. Figure 10 shows the image of the JSX-3400RII that was used for this study.

3.3.2.4 Mineral Composition Technique for PM Samples

The mineral analysis was done using Rigaku MiniFlex600 XRD coupled with an oven as show in Figure 11. The machine was used for the analysis at the Centre of Excellence in Nano Technology (CENT), KFUPM Research Institute. The components of the instrument include X-ray generator, tube shield, goniometer, detector, counting control circuit. The X-ray generator uses tube output voltage and current of 30 kV and 15 mA respectively and these values are fixed. The high-voltage generation method adopted by this instrument is high-frequency Cockcroft-Walton method and it also has a stability of ± 0.05% for both tube voltage and tube current, with reference to ± 10% of input power variation.

3.3.2.5 Technique for Determining Trace Metal Levels in PM Sample

The trace metals analysis was also carried out at the Centre for Environment and Water, Research Institute of KFUPM using the PerkinElmer Optima 8000 inductively coupled plasma optical emission spectroscope (ICP-OES). It is a bench-top, dual-view ICP-OES with full-wavelength-range custom designed CCD array detector, with flexible and excellent analytical performance. Optima 8000 ICP-OES Spectrometer uses flat plate plasma technology for reduced argon consumption, plasma cam viewing camera with simplified method development which enables remote diagnostic capabilities for maximum uptime. It also has advanced optical system for superior detection limits at parts

Figure 11. Rigaku MiniFlex X-Ray Diffraction (XRD)

per trillion level, and a shear gas system that assists in elimination of interferences. There is also an adjustable, quick-change torch cassette which simplifies maintenance and optimizes performance.

3.4 Procedure of Analysis

3.4.1 Procedure for Determining the PM Concentration (Gravimetric Analysis)

The procedure for obtaining gravimetric data includes

- obtaining the difference between final corrected volume and initial corrected volume
- finding the difference between final weight of the membrane filter after sampling and value of the pre weighed filter using sensitive digital balance from Mettler was used for this purpose.
- The difference in weight of the filter is multiplied by 10^6.
- Then the weight is divided by change in corrected volume.
- Then, this gives us the concentration in microgram (µg).

3.4.2 Procedure for Determining Morphology of the PM samples

The equipment used for analysis of shape and size is Scanning Electron Microscope (SEM). The procedure is as follows

- The loaded membrane filters papers were cut in 1 mm^2 from the center of the one-quarter of each sample which is taken for the analysis.
- The samples were mounted on small stubs for gold coating using vacuum coating unit called Gold Sputter Coater.
- The gold was placed on the surface of each sample for a period of 60 seconds.

Figure 12. Optima 8000 Laser Ablation ICP-OES

- The fine coating was done to make the samples to be conductive electrically.
- Samples were placed in the SEM-EDX chamber.
- SEM images were taken at different magnification for each sample.

3.4.3 Procedure for Determining Elemental Composition of PM Samples

For the elemental composition analysis using EDX, the same sample used for morphological analysis in the SEM-EDX chamber was used to take elemental composition of the samples.

- The system was changed to backscattering mode and the accelerating voltage was also increased.
- EDX spectrum was taken at 4 different spots to obtain the percentage elemental composition for each spectra
- The average elemental composition for the 4 spectra was used to obtain the percentage elemental composition for each PM sample

X-ray Fluorescence (XRF) was also used for elemental analysis. For this analysis, the following steps were taken

- one-eighth of the loaded filter sample was taken.
- The samples were placed on a circular sample stub and loaded into XRF machine for analysis.
- The machine was set to vacuum condition
- The elemental composition was then obtained

3.4.4 Procedure for Determining the Mineral Composition of the PM Samples

The equipment used for mineralogical analysis is the X-ray Diffractometer (XRD). This involves the following steps.

- A $2mm^2$ sample was cut from the loaded filter and attached to a flat plastic holder.
- The oven was switched on before switching on the XRD machine to ensure that the temperature is maintained between 18-23ºC.
- The sample holder containing the loaded filter was then placed in the Rigaku MiniFlexII XRD.
- The XRD analysis condition was set as 0.02 step size, 2θ range of 2.5°-85º, scanning speed of 0.03º/min and the accelerating voltage used was 40kV.
- The analysis was run from the desktop
- Result was obtained showing different peaks and different positions
- The result was then matched with similar peaks in the databank of the XRD software.
- The results obtained were plotted with origin 8.6 data analysis and graphing software to determine the relationship between samples within the same site and from different sites.

3.4.5 Procedure for Determining the Trace Levels in the PM Samples

Trace metal level was obtained using Inductively Coupled Plasma optical emission spectroscope (ICP-OES). For this analysis, the following steps were taken

- One-quarter of the used/loaded filter was taken and weighed

- Then the filters were cut out into small pieces in a 100ml glass beaker and wet with some water.
- Aqua-regia solution of distilled HNO_3 and concentrated HCl were added in ratio 3:1 and some distilled water was added, and then stirred inside fume hood.
- The beaker is then placed on a heater to heat for 3-4 hours at about 130°C until it reaches near dryness.
- The beakers were then allowed to cool after heating
- Their contents were filtered with Whatmann filter paper (size 42)
- the volume of the filtrate was made up to 50ml.
- The acid digest (filtrate) was used for heavy metal determination using ICP-OES.

The digestion procedure is similar to that proposed by Sadiq and Mian (Mian and Sadiq, 1993). For each of the 9 samples analyzed for each sampling sites, 2 blanks were also prepared and analyzed in similar ways.

3.5 Data Analysis

The software used for data analysis includes

- **Excel**: This forms part of Microsoft Office. It features includes calculation, graphing tools, pivot tables, and a macro programming language called Visual Basic for Applications. For this study, it was used to prepare graphs, tables and calculation of results. This is the major analytical tool utilized for result presentation and analysis, and for designing graphs and tables used in this study.
- **Origin Pro 8.6.0**: This is a product from origin lab. It is essential for creating and designing a user's own type of graph especially when very large results are to be

presented graphically. The tools available on the user panel interface helps to ensure that the available tools, including the project explorer/manager are user-friendly, without compromising the available space to the user. This software was used in preparing XRD results graphically for easy comparison of results within cities and between cities.

- **Sigma Plot 11.0**: This is owned and managed by SYSTAT Software, it runs on Microsoft Windows and it can read multiple formats (such as Microsoft Excel spreadsheets), and can also perform mathematical transforms and statistical analyses. This was used for graphing of XRF results.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Concentration Levels of PM_{10}

The results presented in this section are the PM_{10} concentration in the different sampling location within Dhahran, Khobar and Dammam.

4.1.1 PM_{10} Concentration in Dhahran

Figure 13 shows the concentration of airborne particulate matter in Dhahran location 1, 2 and 3. The concentration of the particulate matter in location 1 ranges from 137.93 – 303.08 $\mu g/m^3$ with average concentration of 203.76 $\mu g/m^3$ and standard deviation of 55.55 $\mu g/m^3$. The average standard day-to-day gravimetric measurement in this location exceeded National Air Quality standard of USEPA (USEPA, 2014) and WHO (WHO, 2005b) but is lower than that of PME (PME Standard, 2014). The minimum PM_{10} concentration level recorded in this location is lower than USEPA and PME standards but higher than the WHO standard while the highest PM_{10} concentration was higher than USEPA and WHO standards but lower than PME standard.

The concentration of the PM_{10} in location 2 ranges from 66.98 – 290.36 $\mu g/m^3$ with average concentration of 181.23 $\mu g/m^3$ and standard deviation of 79.12 $\mu g/m^3$. The mean daily gravimetric measurement in this location exceeds National Air Quality standard of USEPA (USEPA, 2014) and WHO (WHO, 2005b) but is lower than that of PME (PME Standard, 2014). Meanwhile, it is worthy to note that the minimum PM_{10} concentration recorded in this location is slightly above the WHO standard while the maximum is lower than PME standard but higher than both USEPA and WHO standards.

The concentration of airborne particulate matter in location 3 ranges from 88.39 – 218.73 µg/m^3. The average daily concentration is 144 µg/m^3 and standard deviation is 43.38 µg/m^3. The mean daily concentration in this location is below National Air Quality standard of USEPA (USEPA, 2014) and PME (PME Standard, 2014) standard but is higher than the WHO (WHO, 2005b) standard. The gravimetric result in D shows that the overall average PM concentration (177 µg/m^3) in this area is lower to the PME standard but higher than USEPA and WHO standards. The minimum concentration of PM in this location is higher compared to WHO standard but lower than USEPA and PME standards while the maximum value recorded in this area is lower than PME standard but higher than WHO and USEPA standards.

4.1.1.1 Distribution and levels of PM_{10} in Dhahran

From Figure 13, we can compare the levels of PM_{10} in different locations within Dhahran. The overall mean PM_{10} concentration in Dhahran was around 177 µg/m^3, while the overall minimum and maximum PM_{10} concentration of 66.98 and 303.08 µg/m^3 were recorded from location 2 and location 1 respectively. The highest PM_{10} level was recorded on day 5 location 1 and this value is higher than both the USEPA and WHO standards but lower than the PME standard. The trend of airborne PM in all the 3 locations in Dhahran shows that there is variation in PM_{10} level recorded for the 7 days sampling period. This variation may be as a result of the difference in time of sample collection. It could also be attributed to difference in weather conditions which ranges from clear to humid, cloudy and sometimes hazy or dusty.

4.1.2 PM_{10} Concentration Levels in Khobar

Figure 14 shows the concentration of airborne particulate matter in Khobar location 1. The concentration of the particulate matter at this location ranges from 114.60 – 1575.46 $\mu g/m^3$ with average concentration of 442.67 $\mu g/m^3$ and standard deviation of 528.31 $\mu g/m^3$. The standard day-to-day gravimetric measurement in this location exceeded National Air Quality standard of USEPA (USEPA, 2014), WHO (WHO, 2005b) and that of PME (PME Standard, 2014). The high concentration recorded during this period could be attributed to days of heavy sand storm, hazy cloud and high temperature.

Very high PM_{10} concentration of more than 1500 $\mu g/m^3$ recorded on 22nd October 2015 in Khobar location 1 was due to heavy sand storm that occurred during the sampling period. The concentration of airborne particulate matter in Khobar Location 2 ranges from 93.65 – 555.34 $\mu g/m^3$ with average concentration of 295.98 $\mu g/m^3$ and standard deviation of 152.84 $\mu g/m^3$. The mean daily gravimetric measurement in this location surpassed National Air Quality standard of USEPA (USEPA, 2014) and WHO (WHO, 2005b) but is lower than that of PME (PME Standard, 2014). The maximum PM_{10} concentration in this location was 555.34 $\mu g/m^3$, and this was recorded on 4th November, 2015 which is the sampling day 6 in this location while the minimum PM_{10} concentration in this location was around 94 $\mu g/m^3$ and this was recorded on sampling day 1. The minimum PM_{10} concentration recorded in this location is lower than the USEPA and PME standards but higher than the WHO standard while the maximum level of PM_{10} concentration recorded in this area was higher than WHO and USEPA standards but lower than the PME standards. Airborne particulate matter concentration in Khobar location 3 is also represented in Figure 14. The concentration of the particulate matter in this location ranges from 126.29 – 926.33 $\mu g/m^3$.

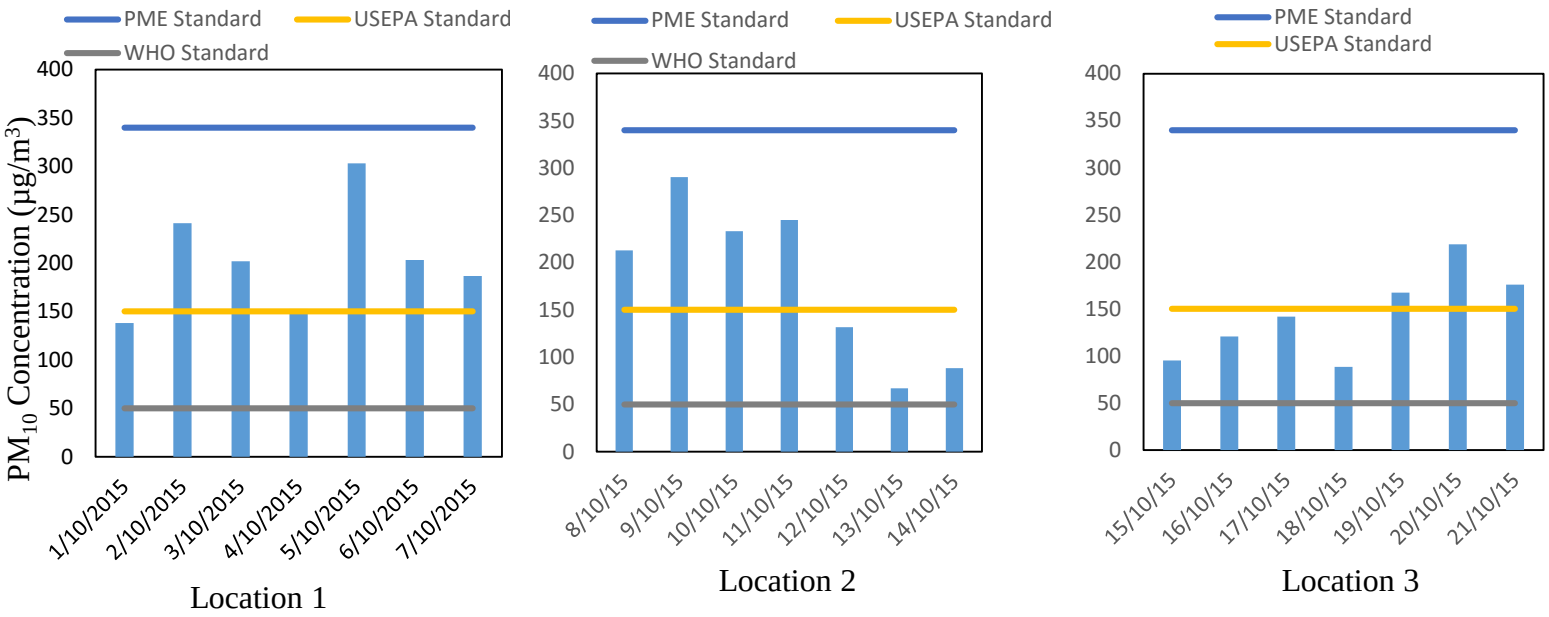


Figure 13. PM10 Concentration Levels in Dhahran

The average daily concentration is 400 µg/m^3 and standard deviation is 257.55 µg/m^3. The mean daily concentration in this location is above National Air Quality standard of USEPA (USEPA, 2014) and WHO (WHO, 2005b) standard but is lower than the PME (PME Standard, 2014) standard. The maximum PM_{10} level in this location was recorded on 12th November, 2015 which was sampling day 7 and the minimum was recorded on sampling day 1 which is 6th November, 2015 with values of 126.29 µg/m^3 and 926.32 µg/m^3 for minimum and maximum levels respectively.

4.1.2.1 Distribution and levels of PM_{10} in Khobar

Figure 14 presents the comparison between the PM_{10} concentration levels in the 3 locations within Khobar, Saudi Arabia. The average concentration of PM_{10} sample in this city is 379.85 µg/m^3. And the minimum and maximum levels of PM10 recorded in this city are 93.65 µg/m^3 and 1575.46 µg/m^3 respectively. The highest level of PM_{10} concentration was recorded on Day 1 in location 1 and the lowest was recorded on Day 1 in location 2. This could be attributed to a sharp and unpredictable weather condition that was observed during this period of sampling in the city. There was heavy sand storm, hazy cloud and very high temperature on some days during this period and at some other times during this period of sampling in this city (Khobar), it was thought that the summer period was over due to calm, clear and relatively humid weather condition. Figure 14 shows that there is dissimilar trend in the 3 locations within Khobar, hence, PM_{10} concentration level is affected by temporal variations. This shows that temporal and spatial variation as a factor, affects the concentration of particulate levels.

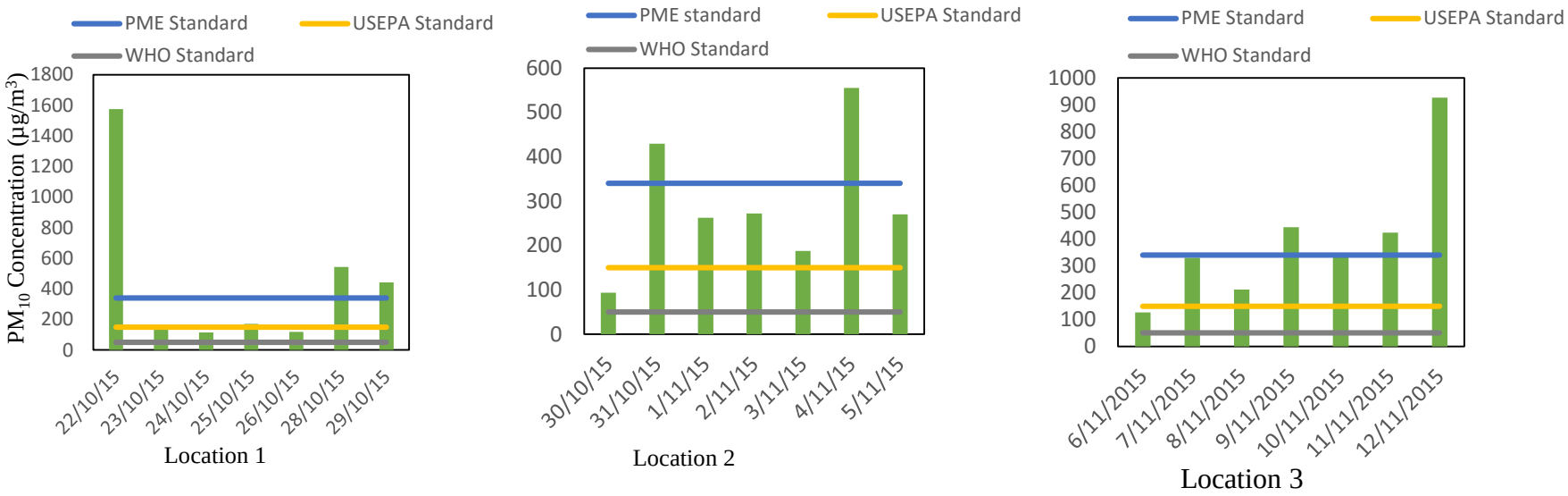


Figure 14. PM_{10} Concentration Levels in Khobar

4.1.3 PM_{10} Concentration Levels in Dammam

Figure 15 shows the concentration of airborne particulate matter in Dammam. The concentration of the particulate matter in this location ranges from 112.72 – 232.60 µg/m^3 with mean concentration of 151.49 µg/m^3 and standard deviation of 41.99 µg/m^3. The standard daily gravimetric measurement in this location was beyond the National Air Quality standard of USEPA (USEPA, 2014) and WHO (WHO, 2005) but is lower than that of PME (PME Standard, 2014). The maximum concentration of airborne particles was recorded on 18th November, 2015 and the minimum concentration of the particles was recorded on 14th November, 2015 which is sampling day 5 and sampling day 1 respectively. The difference in levels of PM_{10} in the different days of sampling in this location could be attributed to changing weather conditions such as sand storms and varied temperatures.

The concentration of the particulate matter in this location 2 ranges from 56.93 – 158.65µg/m^3 with average concentration of 118.34µg/m^3 and standard deviation of 35.61µg/m^3. The mean daily gravimetric measurement in this location surpassed National Air Quality standard of WHO (WHO, 2005b) but is lower than that of USEPA (USEPA, 2014) and PME (PME Standard, 2014). The average PM_{10} concentration is the lowest recorded in all the sampling locations used for this present study. The lowest level was recorded on sampling day 3 which is 23rd day of November, 2015 while the highest concentration was recorded on sampling day 5. The lower values obtained in this location when compared with other sampling locations could be attributed to a relatively calm and stable weather condition that was observed during this sampling period. Based on the PM_{10} level recorded in this location it could be assumed that this location portends less danger

to the inhabitants, however, this cannot be ascertained until the characterization of the particles are done.

The concentration of the particulate matter in this location 3 ranges from 84.19 – 158.34µg/m^3. The average daily concentration is 144µg/m^3 and standard deviation is 43.38µg/m^3. The mean daily concentration in this location is below

National Air Quality standard of USEPA (USEPA, 2014) and PME (PME Standard, 2014) standard but is lower than the WHO (WHO, 2005b) standard. The average PM_{10} concentration is among the lowest recorded in all the sampling locations used for this present study. The lowest level was recorded on sampling day 6 which is 22rd day of December, 2015 while the highest concentration was recorded on sampling day 5 which is 21/12/2015. The lower values obtained in this location when compared with other sampling locations could be attributed to a relatively calm and stable weather condition that was observed during this sampling period. The highest level of PM10 recorded from this location is lower compared to maximum concentrations that have been reported from previous studies (Engelbrecht et al., 2009; Ahmady-Birgani et al., 2015). The average PM_{10} concentration in this location is higher than what was obtained from a similar study that was carried out in Athens, Greece (Koutrakis, 2004). Based on the PM_{10} level recorded in this location it could be assumed that this location portends less danger to the inhabitants, however, this cannot be ascertained until the characterization of the particles are done.

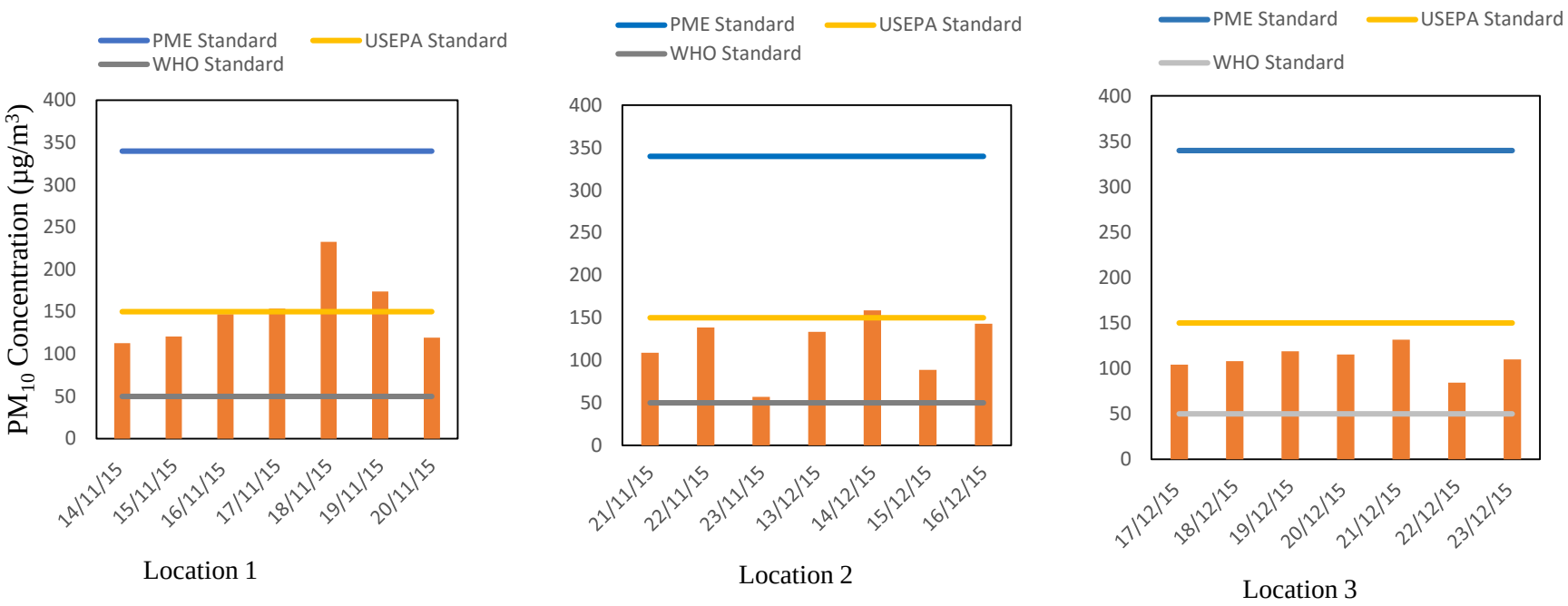


Figure 15. PM_{10} Concentration Levels in Dammam

4.1.3.1 Distribution and levels of PM_{10} in Dammam

The PM_{10} level in the 3 locations within Dammam is presented in Figure 15. The highest PM concentration level in the city was recorded on Day 1 location 1 while the lowest was recorded on day 3 in location 2. The lowest recorded value is higher than the WHO standard but lower than USEPA and PME standards while the highest level of PM concentration recorded in the city (Dammam) is higher than both USEPA and WHO standard but lower than PME. It is worthy to note that the lower concentration of particulate matter recorded in this city when compared to other cities that were used for this study may be attributed to a relatively lower temperature and calm weather conditioned that was observed during the period of sampling in this area. The trend shows that there is variable pattern of PM_{10} level in all the 3 locations with respect to change in time and locations, hence, this shows that temporal and spatial variation affects the level of concentration of PM.

4.2. Morphological Characteristics of Collected PM_{10}

The morphological analysis was used to establish the size and shapes of the particles as well as the chemical characteristics of the particles. Although chemical characterization was carried out with EDX, further elemental analysis was necessary with XRF since the latter considers a larger area of the membrane filter compared to EDX where spot analysis of a small area of the filter was carried out. In the morphological analysis result, shapes and sizes of the particles are presented and discussed using SEM images while the chemical composition in terms of the elemental components will be presented using EDX and XRF result. Study of the trace metal composition will be presented in the results and discussions.

The SEM results present the SEM micrographs showing the sizes and shapes of particles collected from the different locations from the different study cities. The image of the blank filter is presented in Figure 16 A, B, C and D where the letters indicate the SEM micrograph of the blank filter at 50 kx, 20 kx, 10 kx and 6 kx magnification with micron scale of 1 µm, 2 µm, 5 µm, and 10 µm respectively. Fibers of different shapes and size with different spaces in between them were seen on the blank filters, the morphology of the unused membrane filter was shown at a voltage of 20 kV. The images indicated that there are pore spaces as low as 1 µm for the PM samples to be collected. Figure 16 shows clearly that there are no residual particles on the blank filter before use and all particles after sampling will be PM_{10} collected from various sites.

4.2.1 Morphological Characteristics of PM Collected in Dhahran

Figures 17 reveals the morphology of the airborne particles collected from Dhahran and the letters E, F and G represents the different locations 1, 2 and 3 respectively while the micrograph represented by H is the image obtained when a particle was observed closely at a scale of 2 µm. Observation from micrograph 17E shows that the particles in Dhahran location 1 are dispersed with size of individual particle ranging from less than 2 µm while the aggregated particles is almost 6 µm. The particles have smooth and rough surfaces and their shapes are nearly angular, irregular, and nearly crystalline which suggests that the particles may be from biogenic or geologic materials which might have endured long term traffic induced abrasion or resuspension. This coincides with what has been reported by Satsangi and Yadav, 2013.

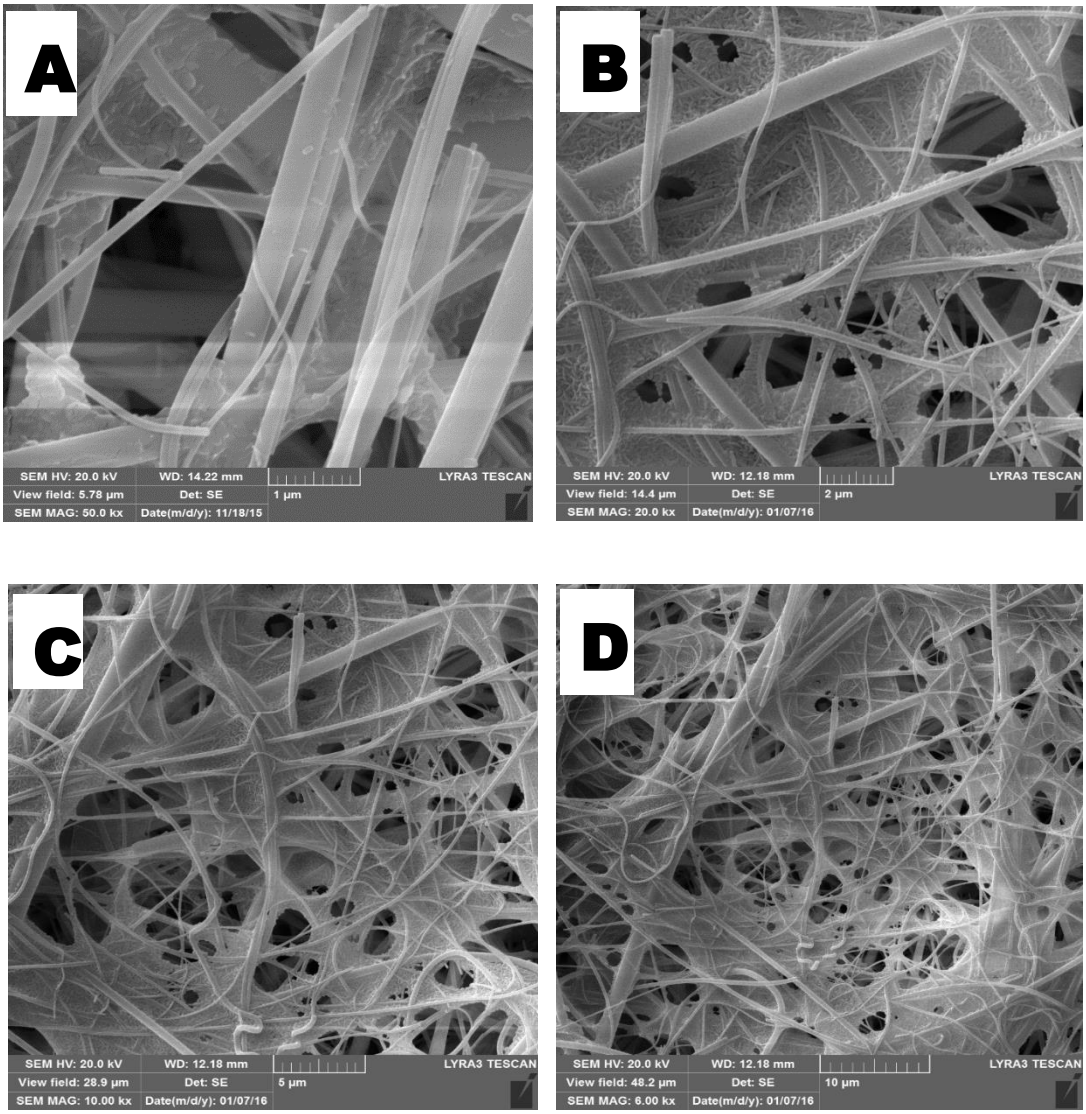
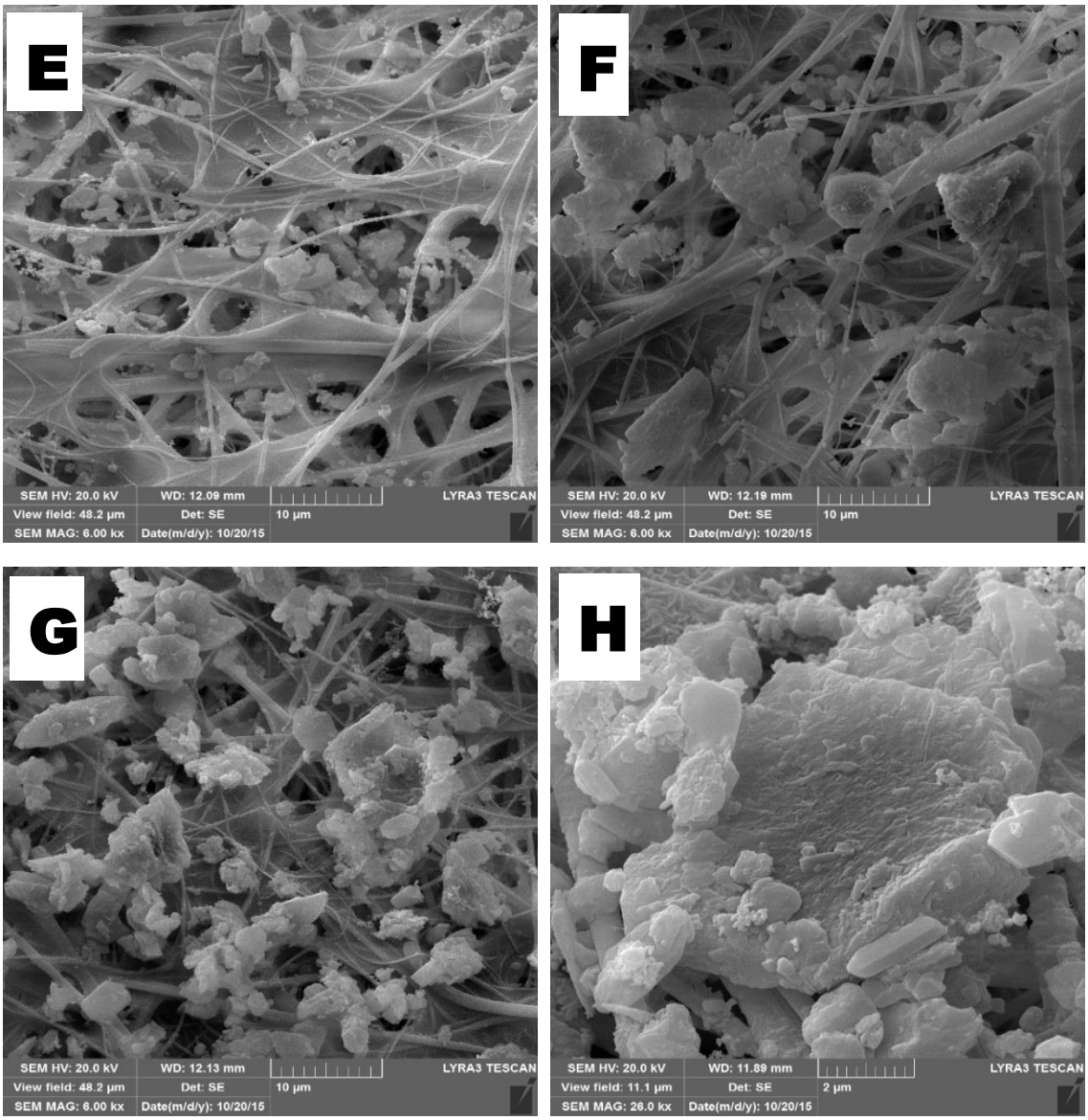


Figure 16. SEM Micrograph of Blank Filter at different Magnifications

The SEM micrograph F in Figure 17 is the image of particles collected from Dhahran location 2. The particles are large, angular, irregular and agglomerated with individual particles that as small as 1 μm. Both smooth and rough surfaces are found which indicates that the particles are from both biogenic and anthropogenic sources. Letter G represents the micrograph for samples collected at Dhahran location 3. The particles are group of agglomerated particles with irregular, spherical, and crystalline shapes. The final micrograph (H) represent the SEM image of particles from Dhahran at a lower scale. The image shows the likely source of the particles may be from resuspension of biogenic materials or geologic materials as reported in previous studies (Chung, Sharifi, and Swithenbank, 2008). This is still subject to elemental analysis to confirm the true source of the particles.

4.2.2 Morphological Characteristics of PM Collected in Khobar

Figures 18 shows the image of the airborne particles collected from Khobar. The letters I, J, K represents the images for each of the 3 locations in the city while the last letters L is used to show the image of a representative particle taken at a lower scale to show the larger characteristics of the particles. Figure 18 I shows the image of particles from Khobar location 1, the particles are similar in shape, irregular and plate-like and sizes ranging from 2 – 8 μm. This suggests that the particles may originate from similar source such as soils. The surfaces of the particles are smooth which may suggest that they are from crustal materials that have not undergone abrasion. This is similar to what was reported by Chung et al., 2008. Observation from micrograph 18J shows that the particles are dispersed with different sizes ranging from <2 μm up to 5 μm. The particles are rod-like, angular, agglomerated and irregular in shape. The particles have smooth and rough surfaces. This



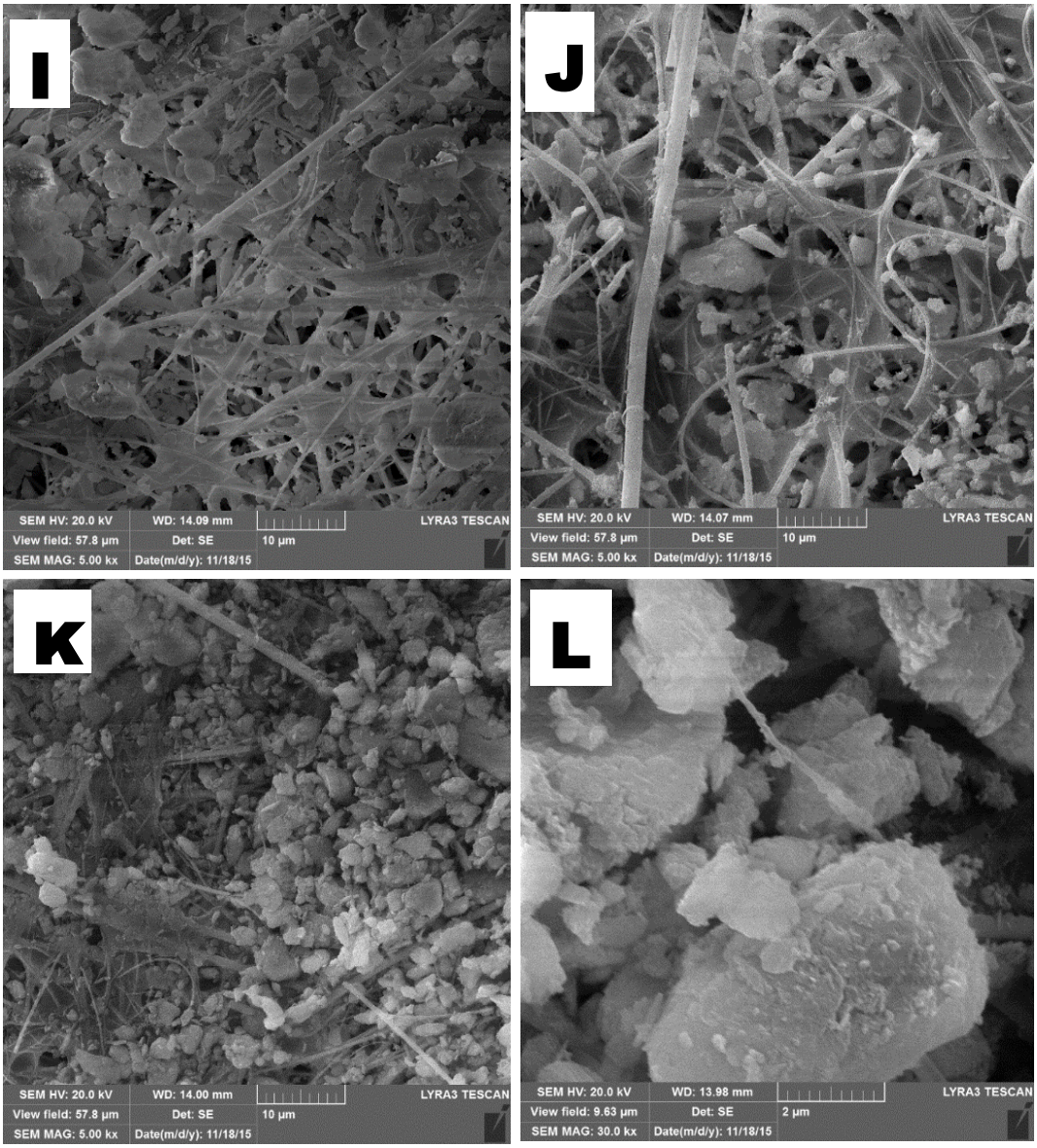
E: Location 1, F: Location 2, G: Location 3, H: Representative sample for Dhahran

Figure 17. Morphological Characteristics of PM Collected in Dhahran

suggests that the particles may originate from combustion or industrial activities or from soil and crustal materials. This coincides with what has been found in literature (Singh et al., 2014). The SEM micrograph K in Figure 17 shows the image of particles collected from Khobar location 3. The particles are clustered, rod-like, agglomerated and irregular. Individual particle sizes ranges from 1 µm to 3µm.

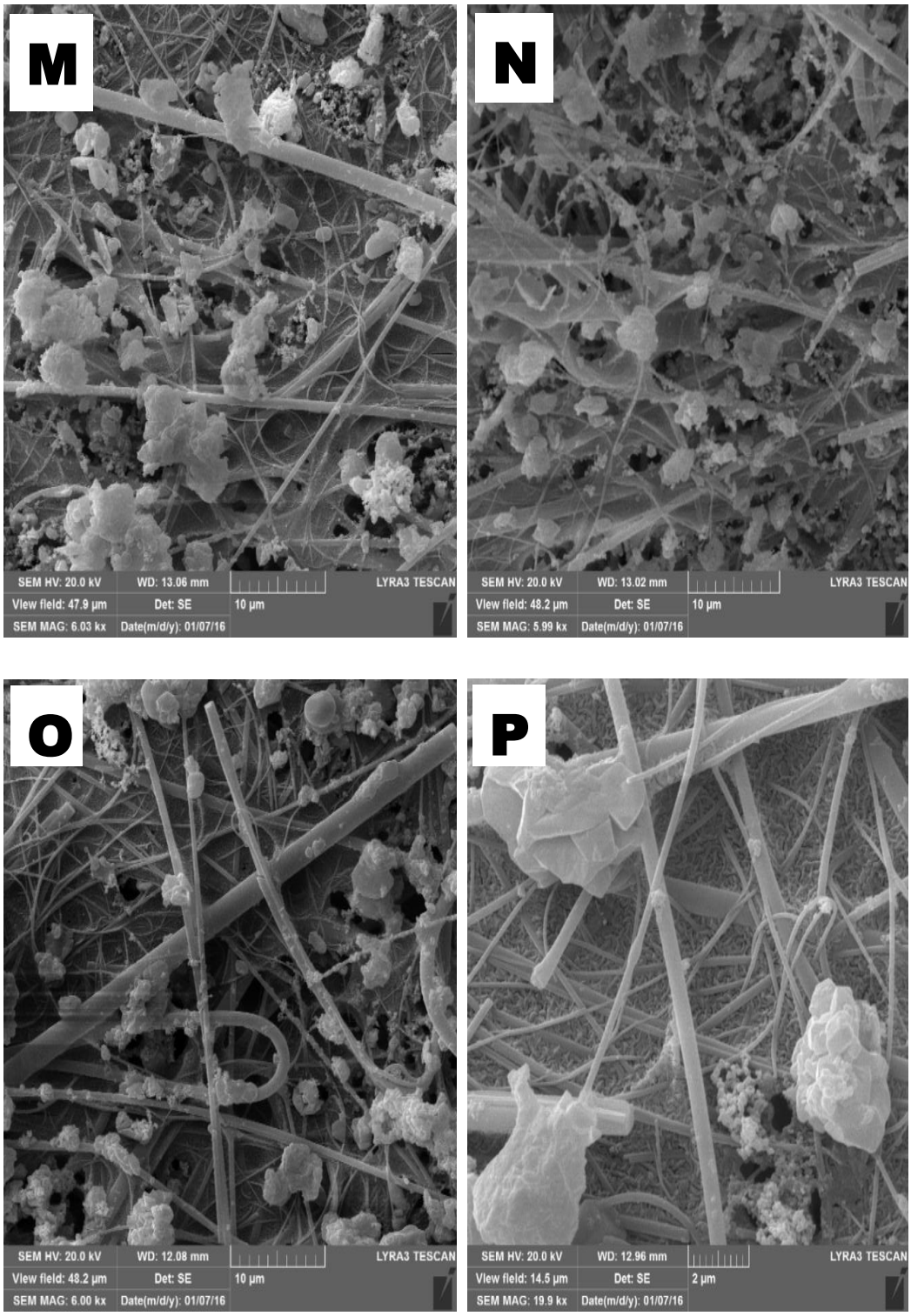
4.2.3 Morphological Characteristics of PM Collected in Dammam

Letters M, N, O in figure 19 represents the images for each of the 3 locations in the Dammam. While the last letter P is used to show the image of a representative particle taken at a lower scale in other to have a clearer view of the characteristics of the particles. Figure 19M shows the image of particles from Dammam location 1, the particles are not as much as found in the previously observed particles from other locations, they have different sizes, and shapes. The shapes of the particles are irregular and agglomerated. There are clustered particles that are at some different spots on the micrograph and their sizes ranges from 2 µm to more than 6 µm. Micrograph N shows that the particles collected from Dammam location 2, they are dispersed, irregular, spherical and agglomerated but with smaller sizes when compared with location 1. The sizes of the particles could be estimated to be between 1 µm and 4 µm. The particles have smooth and rough surfaces. Micrograph O represents the image of the particles collected from Dammam location 3, the particles are irregular, nearly spherical and agglomerated and their sizes are between 2 µm to 5 µm. The micrograph represented by N in Figure 19 is a typical particle from sample collected from Dammam, it is rod-like, spherical, irregular and agglomerated. This depicts that the samples may be from natural crustal materials and some anthropogenic activities.



I: Location 1, J: Location 2, K: Location 3, L: Representative sample for Khobar

Figure 18. Morphological Characteristics of PM Collected in Khobar



M: Location 1, N: Location 2, O: Location 3, P: Representative sample for Dammam

Figure 19. Morphological Characteristics of PM Collected in Dammam

4.2.4 Comparison of Morphological Characteristics of PM Collected in Dhahran, Khobar and Dammam Using SEM Micrographs

The micrographs present in Figure 20 shows the representative SEM images of the particulate matter collected from the different cities and that of blank filter before the samples were taken. It shows that the particles have different sizes and shapes which indicates that changes in location affects the processes which the particles undergone. As discussed previously, there are indications that suggest that the particles may originate from similar sources, but Figure 20 shows that the particles have changed their shapes and probably their forms due to their locations and the time or periods of collection. This result is not different from what was reported by previous studies (Pipal et al., 2011), and this shows that temporal and spatial variation may affect airborne particulate matter.

4.3 Elemental Composition of PM Samples

4.3.1 Elemental Composition of PM Samples Using EDX

4.3.1.1 Elemental Composition of PM Collected from Dhahran by EDX

Figure 21 shows the graph of elemental composition by percentage weight of the different elements contained in the PM collected from the 3 different locations. All the locations contain similar elements with different percentage weight except Titanium (Ti) which is not found in location 1. The presence of aluminum (Al), Silicon (Si), Potassium (K), Calcium (Ca) and Iron (Fe) in the samples shows the presence of aluminosilicates such as feldspar and clay mineral which could have originated from the crust or some may be from deterioration of buildings. The presence of Calcium (Ca), Carbon (C), Oxygen (O), and Sulphur (S) shows the presence of calcium sulphate which could have resulted from the reaction between calcium carbonate, from deterioration of buildings and dust from soils

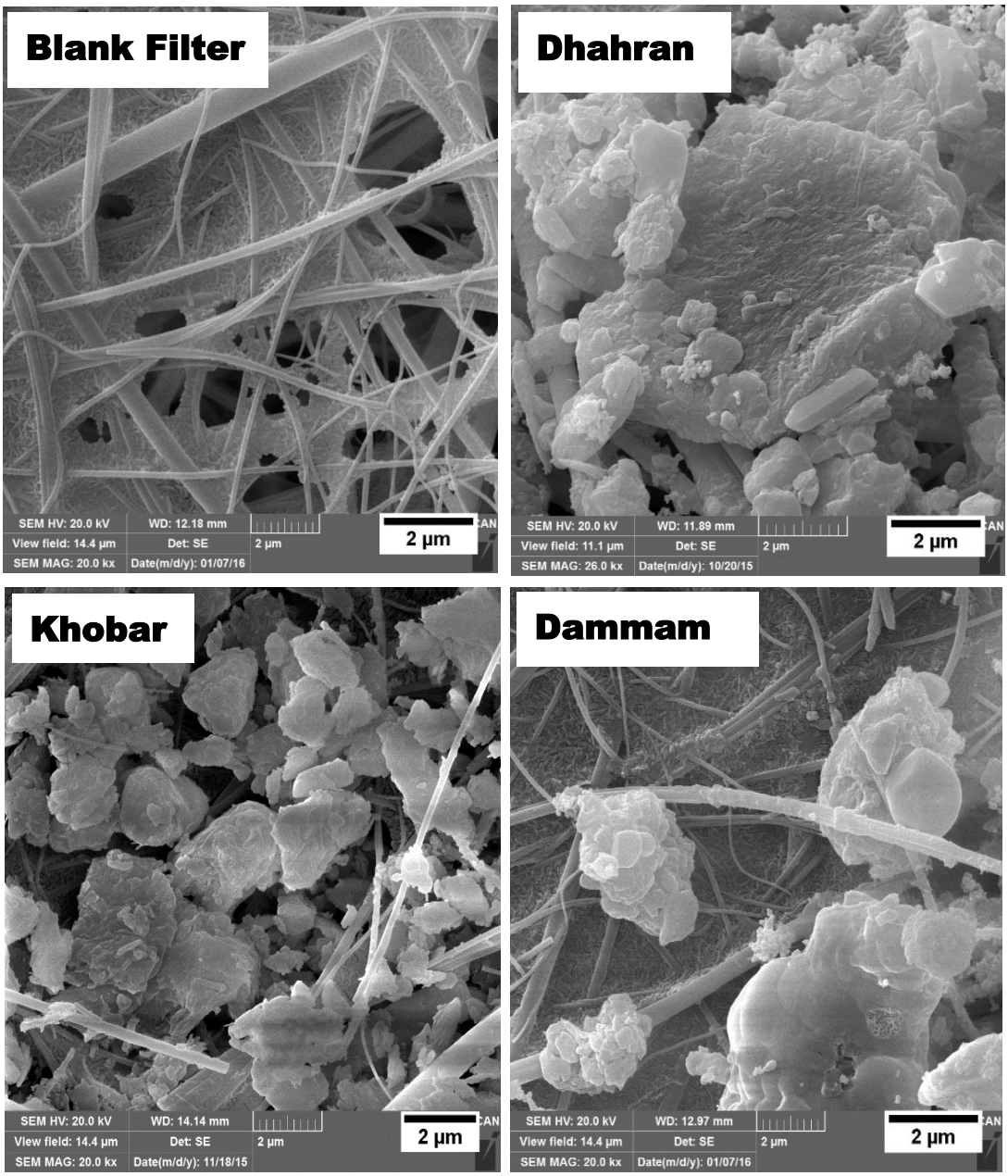


Figure 20. Comparison of PM Morphology from Dhahran, Khobar and Dammam at Magnification of 20.0 kx

and sand storm, and atmospheric Sulphur. This could be confirmed with the elongated or rod-like particle observed in the SEM micrograph. There is also presence of some metals such as Titanium (Ti), Iron (Fe) and Zinc (Zn) which confirms that the irregular particles observed in the micrograph could be from resuspension of dust from roads which results from wearing of vehicle tyres, soil dust and other crustal materials. A similar result was obtained from literatures (Roberto et al., 2013).

4.3.1.2 Elemental Composition of PM samples Collected from Khobar by EDX

Figure 22 presents the elemental composition of PM_{10} samples collected from the 3 different locations within Khobar, Saudi Arabia. It shows high percentage by weight of C, O, Si, Ca and F. Also, Na, Mg, Al, K, Fe and S are present in the samples from the 3 locations, meanwhile, Zn and Ti are absent in the samples from the 3 locations. While Cl is present only in sampling location 3, barium is present only in samples from locations 2 and 3.

The presence of C, O, Ca and S in the 3 locations indicates that calcium sulphate formed by reaction between atmospheric Sulphur and crustal dust is present in the samples, while the availability of Si. Al, Ca, Na and Fe may be an indication of the presence of aluminosilicates such as clay minerals or feldspar. This result is similar to what was reported in previous studies (Modaihsh, 1997; Rastogi and Sarin, 2006; Fromme et al., 2008; Engelbrecht et al., 2009b; Pachauri et al., 2013).

4.3.1.3 Elemental Composition of PM samples Collected from Dammam by EDX

The graph of the EDX analysis result obtained from samples that were collected from the 3 different locations in Dammam is presented in Figure 23. The result shows that C, O, F, Na, Al, Si, K, and Ca are available in different proportions in the samples. The EDX results suggests that the samples are mostly from calcium carbonate and aluminosilicates minerals which shows that their origins could be from dust particles or resuspensions. The result of this EDX analysis confirms what had been previously reported in literature (Pachauri et al., 2013; Roberto et al., 2013).

4.3.1.4 Comparison of Elemental Composition of PM samples from Dhahran, Khobar and Dammam

The EDX result in Table 3 and Figure 24 are used to compare the differences in levels of the different elements contained in the samples collected in all the different cities considered in this study. It reveals the presence of Carbon (C), Oxygen (O), Fluorine (F), Sodium (Na), Magnesium (Mg), Aluminum (Al), Silicon (Si), Potassium (K), Calcium (Ca), Iron (Fe), Zinc (Zn), Barium (Ba), Chlorine (Cl), Sulphur (S), and Titanium (Ti) are all present in Dhahran but only Zn and Ti are not found in the samples collected in Khobar. In Dammam however, C, O, F, Na, Al, Si, K, Ca and Zn are present in the samples. It can be observed that O has the highest percentage by weight in the 3 cities, followed by C in Khobar and Dammam. The most abundant element by weight in Dhahran after O is fluorine which could be attributed to high usage of air conditions during the period of this sampling. Si, Ca, C, and O are in high levels in all the 3 cities and this may indicate the presence of silica and calcite in the samples. The presence of Na, Mg, Al, Si, Ca and Fe in the different cities may show the presence of clay mineral in the samples collected. The percentage

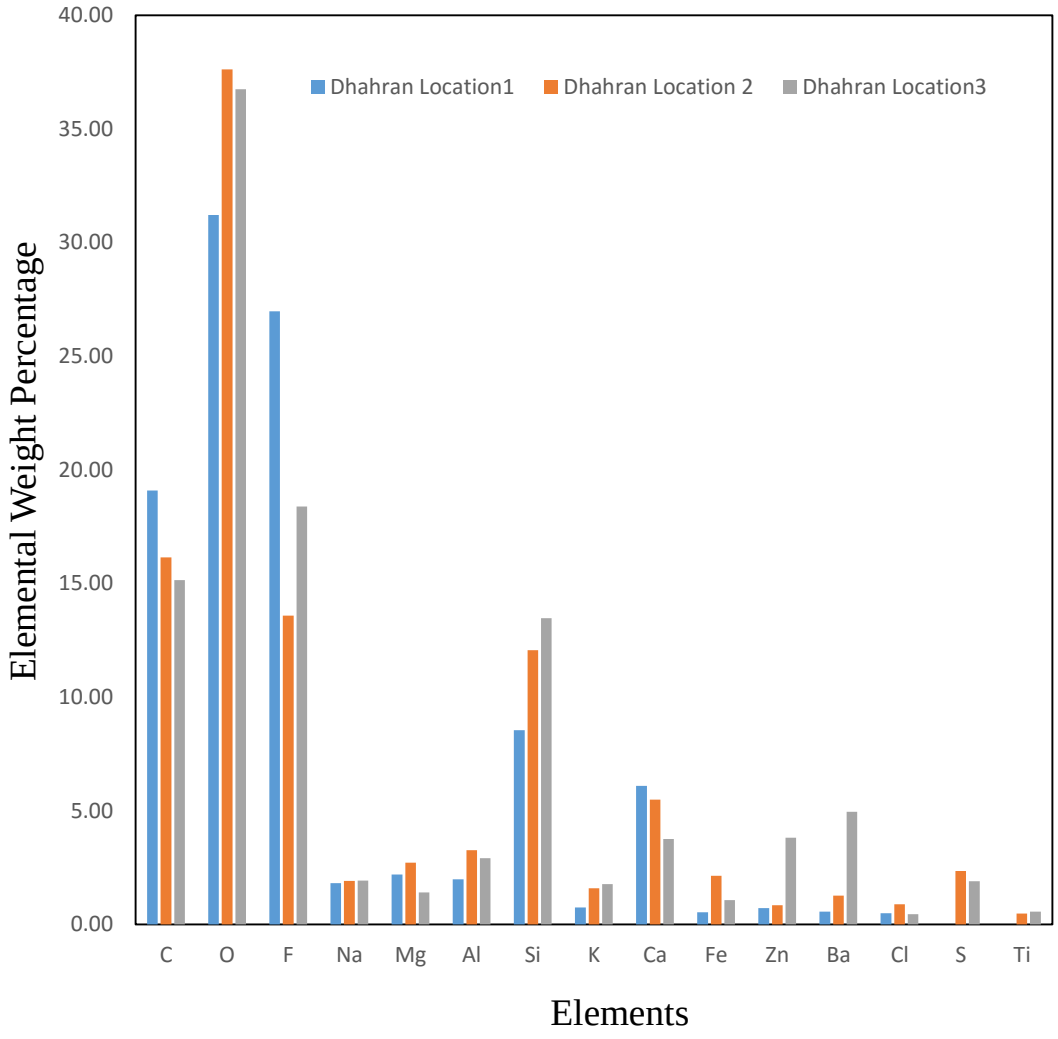


Figure 21. EDX Result Showing Elemental Composition of PM Samples Collected from Dhahran

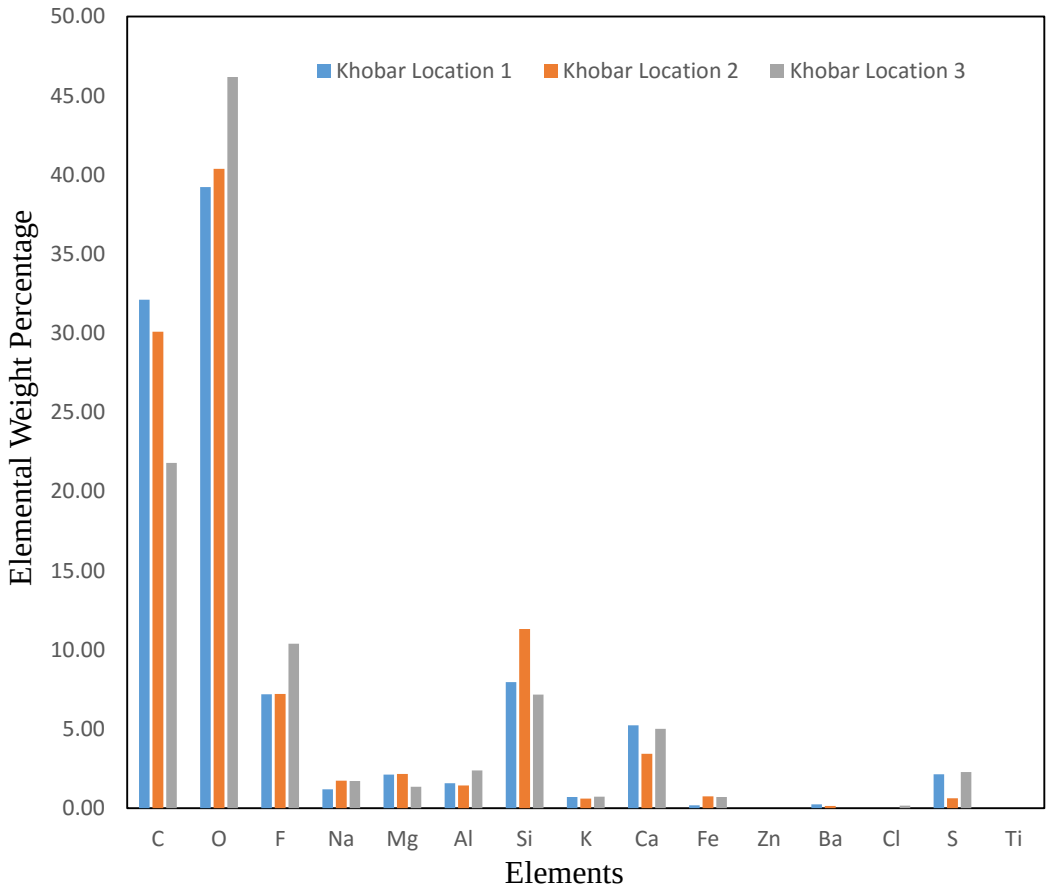


Figure 22. EDX Result Showing Elemental Composition of PM Samples Collected from Khobar

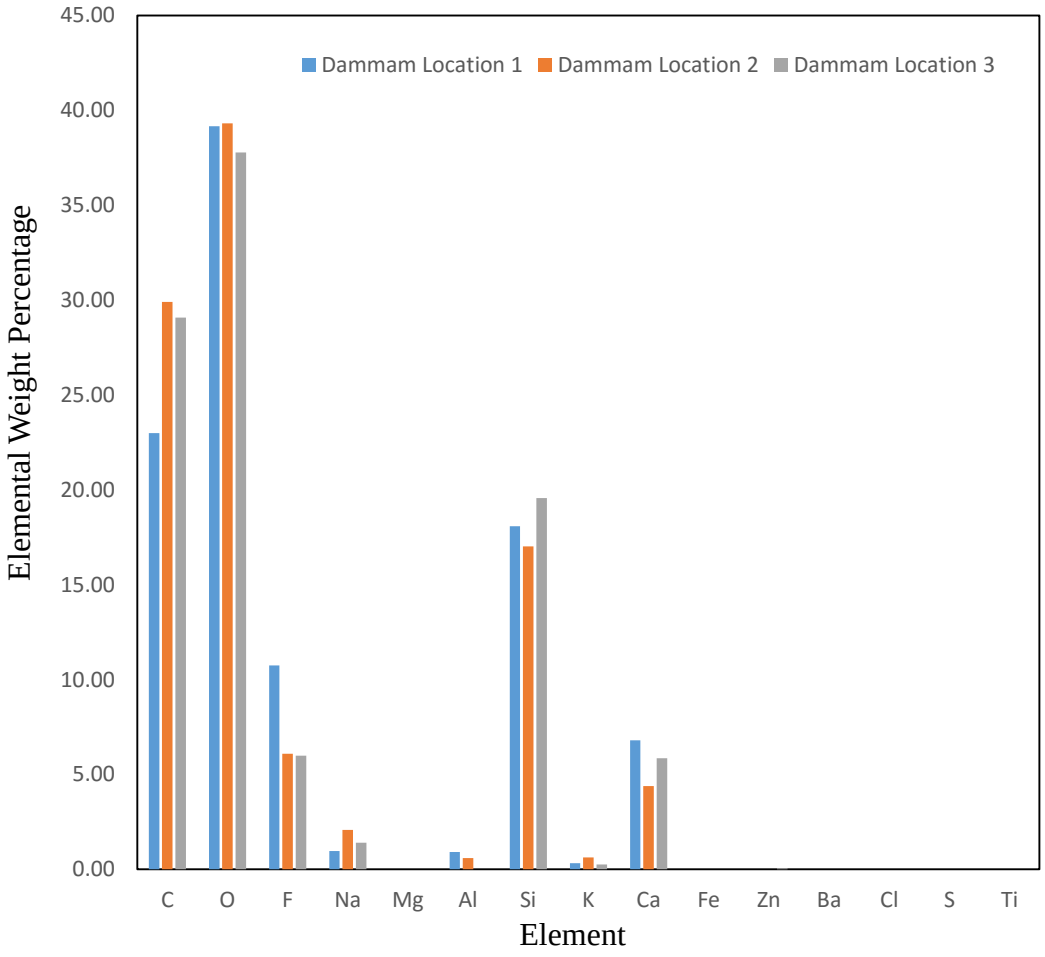


Figure 23. EDX Result Showing Elemental Composition of PM Samples Collected from Dammam

composition of Si and Ca is highest in Dammam while the percentage composition of C, O and S is highest in Khobar. Dhahran is the only city where Ti is found and the composition of Al, Ba, F, Na and Mg is highest in the samples collected in this city. This finding confirms that changes in time of sampling as well as location of sampling (temporal and spatial variation) only affects the percentage composition of individual elements but does not affect the type of elements present in the sample.

4.3.2 Elemental Composition of PM Samples Using XRF

Bearing in mind the limitations of using EDX to estimate the elemental composition of samples, it is expedient to explore other techniques such as XRF. This will help to ensure that a more representative samples are analyzed since the XRF uses a larger filter size as well as the whole area of the filter rather than spot analysis or small area analysis that was done in case of EDX. However, unlike EDX which can detect elements below Na in the periodic table, XRF will not detect elements with atomic number less than 11. Figures 24 – 26 shows the graph of XRF results from the 3 cities under study.

4.3.2.1 Elemental Composition of PM Samples Collected from Dhahran using XRF

Figure 25 shows the graph of XRF result obtained from the analysis of samples collected from Dhahran, Saudi Arabia. The elements present are Magnesium (Mg), Aluminum (Al), Silicon (Si), Sulphur (S), Chlorine (Cl), Potassium (K), Calcium (Ca), Iron (Fe), Zinc (Zn),

Table 3. Comparison of Elemental Composition of PM Samples from Dhahran, Khobar and Dammam using EDX

Elements	Dhahran (%)	Khobar (%)	Dammam (%)
C	16.79	28.01	27.33
O	35.19	41.94	38.76
F	19.65	8.27	7.61
Na	1.88	1.56	1.48
Mg	2.10	1.89	0.00
Al	2.72	1.81	0.50
Si	11.36	8.83	18.23
K	1.37	0.69	0.40
Ca	5.11	4.56	5.68
Fe	1.24	0.56	0.00
Zn	1.79	0.00	0.02
Ba	2.25	0.14	0.00
Cl	0.60	0.06	0.00
S	1.41	1.69	0.00
Ti	0.34	0.00	0.00

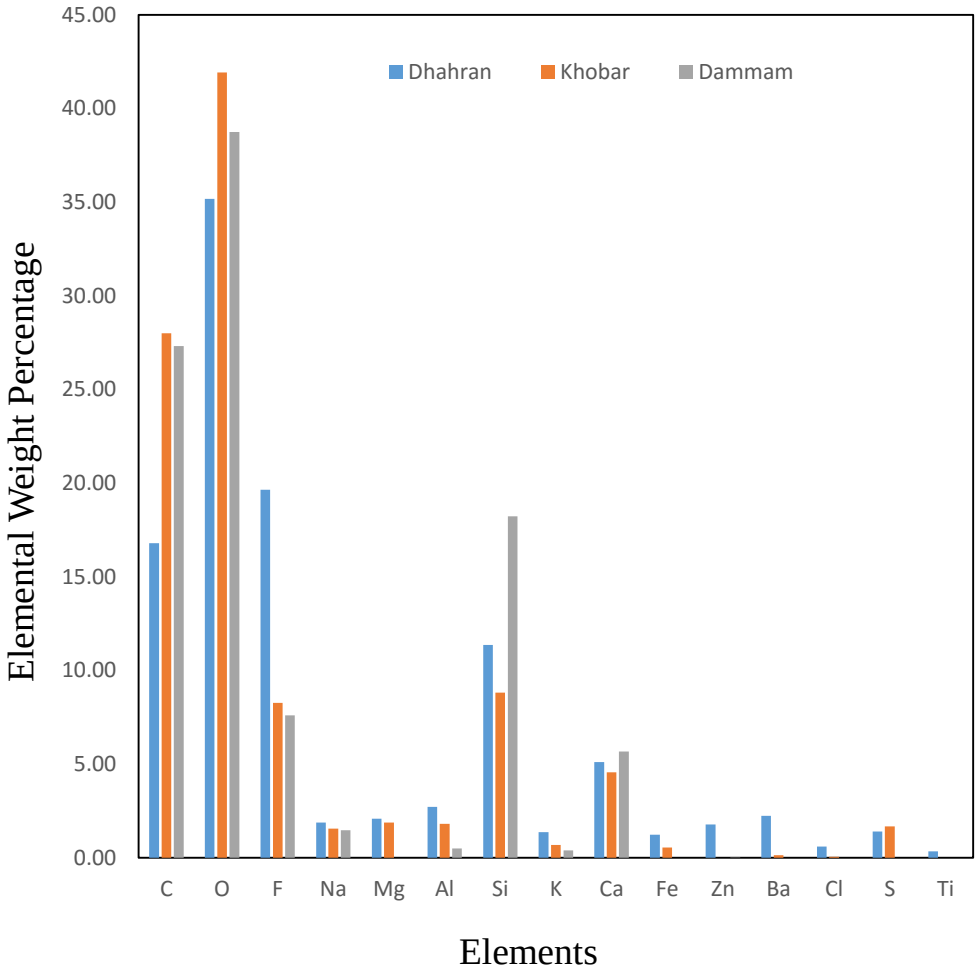


Figure 24. . Comparison of Elemental Composition of PM Samples from Dhahran, Khobar and Dammam using EDX

Strontium (Sr), Zirconium (Zr), Barium (Ba), Sodium (Na), Rhodium (Rh) and Nickel (Ni) found in the PM samples collected from this city. Except Rh, Sr, Zr and Ni that were found at very low percentage by weight of the samples in the 3 locations, other elements like Mg, Al, Si, S, Cl, K, Ca, Fe, Zn and Ba were found at higher percentages in all the sampling sites within Dhahran while Na is found only in sampling location 3. Particulates obtained from location 3 contains the highest amount of Si, Al, Ba, Na, Ni, K, S and Zn and lowest amount of Mg and Fe. The particles in location 2 and 1 have approximately equal amount of the element under study except for S that have higher percentage by weight in location 2. Na is absent in location 1 and 2, while Ni, Sr, Zr and Rh are available at very low percentage by weight of samples collected from Dhahran as presented in Figure 24.

4.3.2.2 Elemental Composition of PM Samples Collected from Khobar using XRF

Figure 26 shows the graph of elemental composition result for XRF analysis of samples taken from Khobar, Saudi Arabia. In Khobar, Si constitutes the highest percentage by weight in each location, followed by calcium and barium respectively as shown in Figure 26. Mg, Al, Si, Ca, Fe, Zn, K, Sr, Zr and Ba are present in all the 3 locations, but Na is present in only location 1 while Ni is not found in all the 3 locations. This shows that some trace metals are present in the area. Aside from the presence of trace metals in very small percentage by weight, the result of the XRF is similar to what was obtained from EDX analysis.

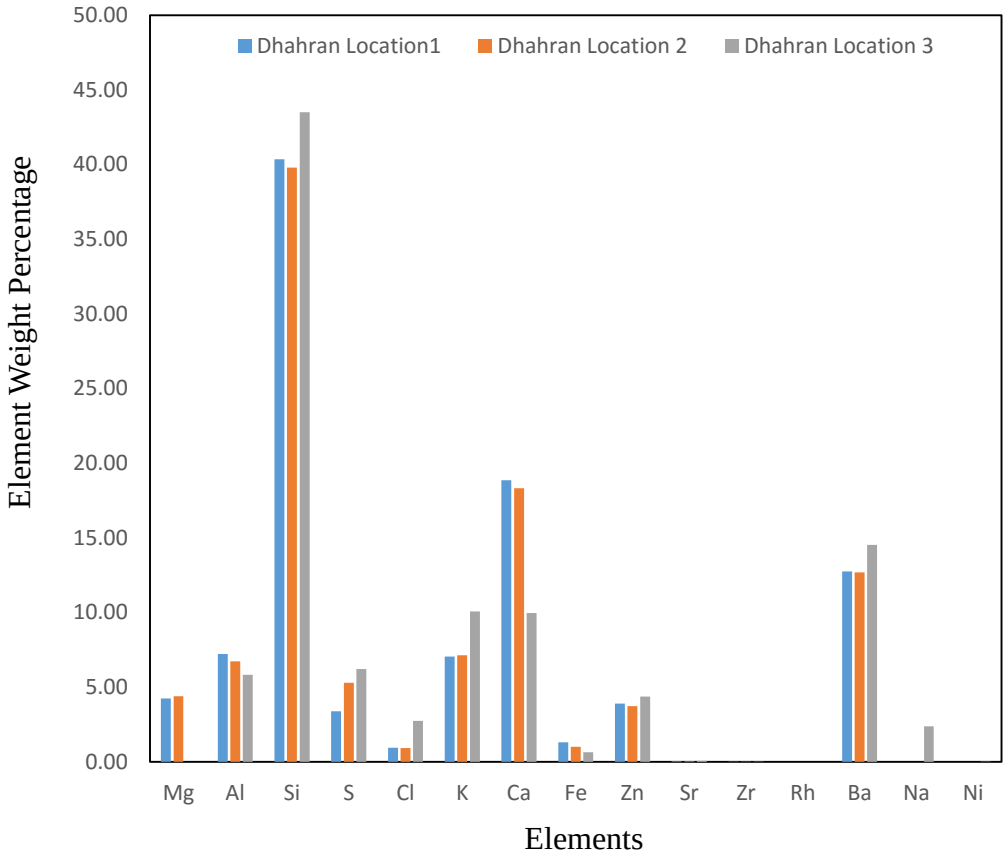


Figure 25. XRF Result for Dhahran

4.3.2.3 Elemental Composition of PM Samples Collected from Dammam using XRF

Figure 27 shows the result of XRF analysis in Dammam. Mg is present only in location 1, Na is only present in location 2, while Cl, Sr, Zr and Ni are not present in the samples collected in all locations in the city. Si has the highest percentage by weight. Barium is high in this area, and this could exist as barium carbonate which does not dissolve in human body, hence cause harmful effect (Agency for Toxic Substances and Disease Registry (ATSDR), 1995).

4.3.2.4 Comparison of Elemental Composition of PM Samples Collected from Dhahran, Khobar and Dammam using XRF analysis

XRF Results showing comparison between Dhahran, Khobar and Dammam is represented by the graph shown in Figure 28 and Table 4. It can be observed that all the results show similar trends, it shows high percentage by weight of Si, Ca, Zn and Ba in all the cities. This is indicative of possible hazards that people in this area are prone to, but it is important to obtain the mineralogical make-up as well as the concentration of the elements in the samples. The result obtained is similar to what was obtained from EDX analysis which showed that aluminosilicates compound may be present due to the availability of Al, Si, Ca, K, and Fe in the samples collected from the 3 cities. Also, presence of Ca, C, O and S suggests the presence of $CaSO_4$ formed by the reaction between crustal soil material from natural (biogenic) or anthropogenic sources with atmospheric Sulphur. And the presence of metals in the samples suggests the like sources of the particles may be from natural sources.

The result of this XRF analysis is similar to what has been reported from literature. It shows that change in time and space could only affect the processes and form of elements

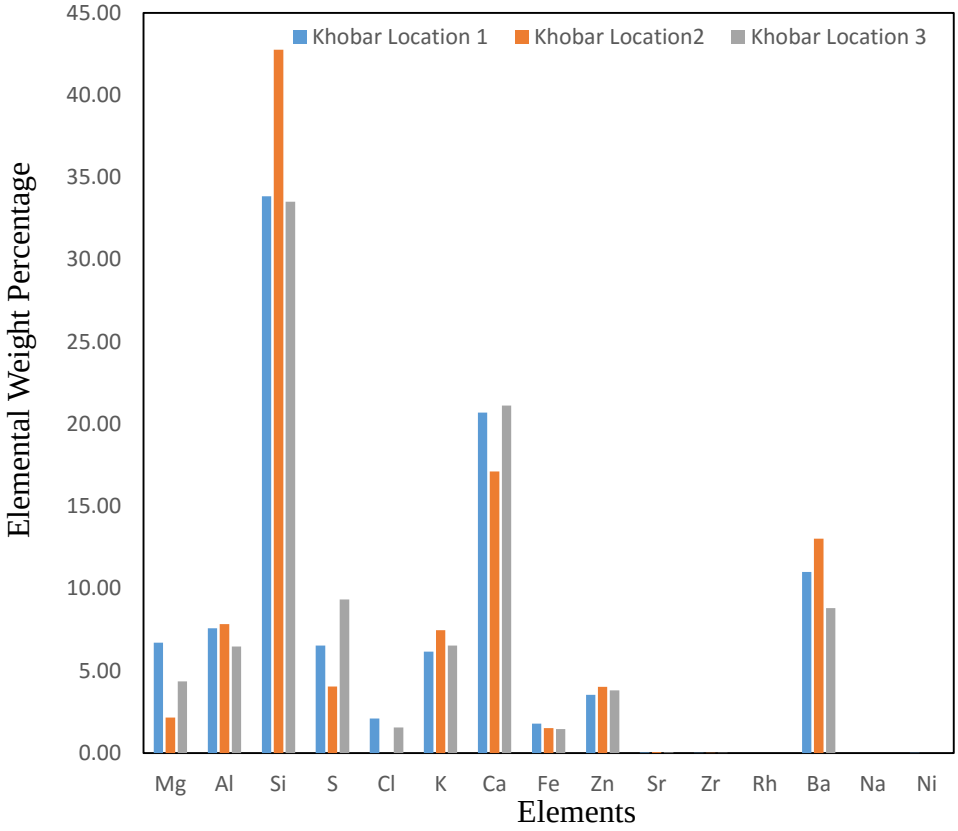


Figure 26. XRF Result for Khobar

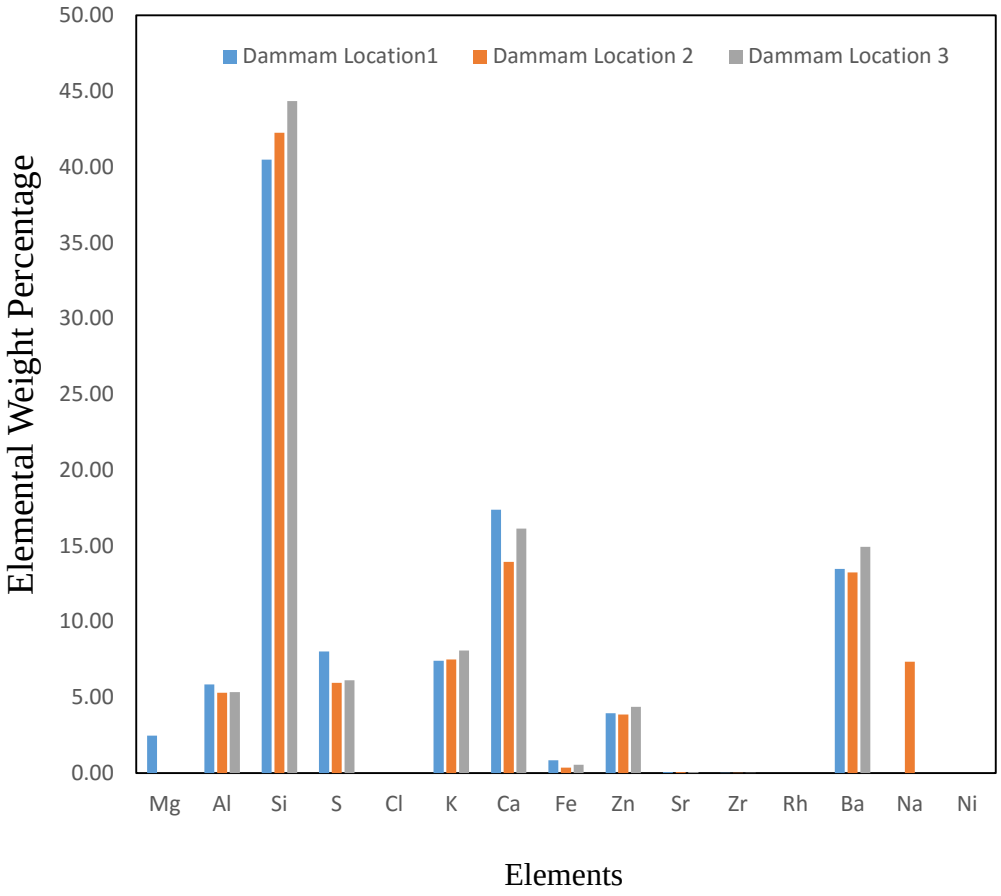


Figure 27. XRF Result for Dammam

Table 4**.** Comparison of Elemental Composition of PM Samples from Dhahran, Khobar and Dammam using XRF

Elements	**Dhahran (%)**			**Khobar (%)**			**Dammam (%)**		
	L1	L2	L3	L1	L2	L3	L1	L2	L3
Mg	4.24	4.39	0.00	6.71	2.15	4.35	2.48	0.00	0.00
Al	7.22	6.73	5.83	7.57	7.84	6.47	5.86	5.31	5.34
Si	40.36	39.80	43.51	33.85	42.75	33.51	40.49	42.24	44.35
S	3.39	5.28	6.21	6.53	4.05	9.33	8.03	5.96	6.12
Cl	0.93	0.91	2.74	2.10	0.00	1.56	0.00	0.00	0.00
K	7.04	7.13	10.06	6.16	7.47	6.54	7.42	7.50	8.10
Ca	18.85	18.31	9.97	20.69	17.12	21.13	17.37	13.95	16.14
Fe	1.30	0.99	0.62	1.79	1.52	1.46	0.84	0.37	0.56
Zn	3.89	3.73	4.37	3.53	4.03	3.80	3.95	3.86	4.38
Sr	0.04	0.04	0.05	0.04	0.05	0.04	0.06	0.06	0.07
Zr	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ba	12.74	12.68	14.52	11.00	13.02	8.81	13.48	13.25	14.93
Na	0.00	0.00	2.36	0.00	0.00	0.00	0.00	7.35	0.00
Ni	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00

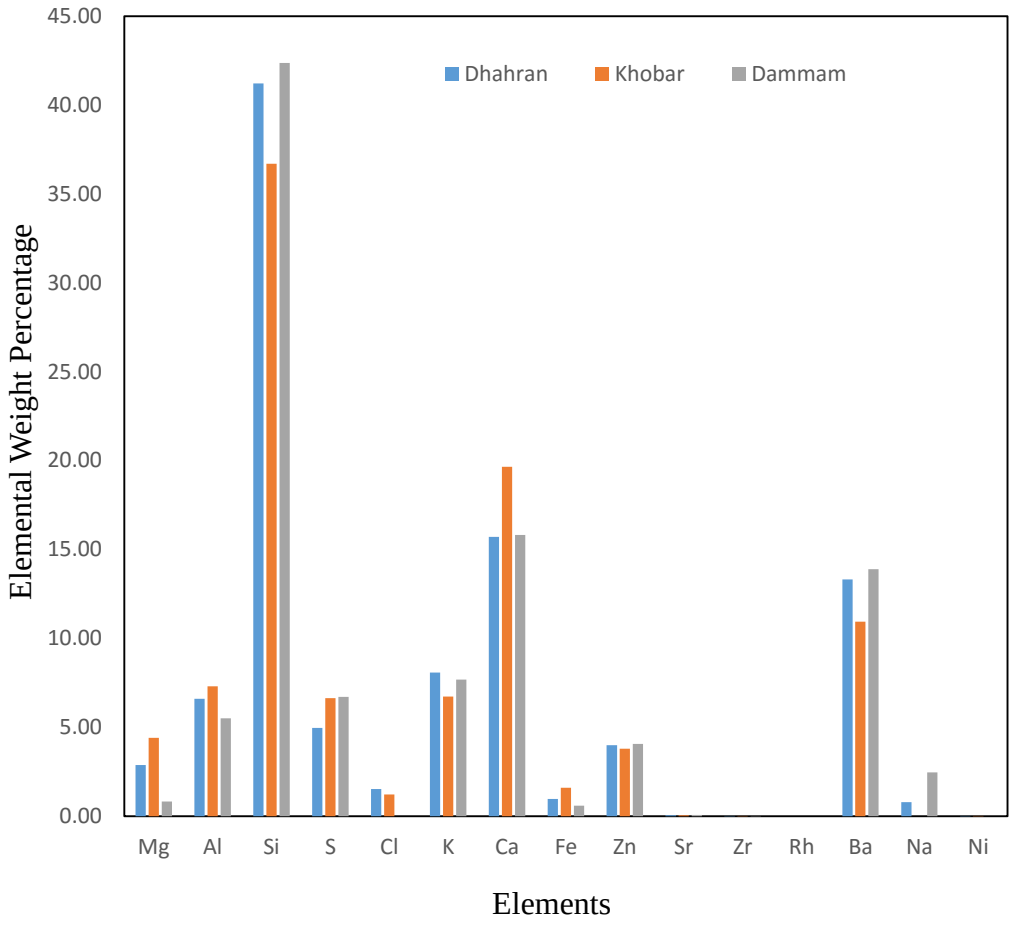


Figure 28. XRF Result Showing Comparison between Elemental Compositions of PM Samples from Dhahran, Khobar and Dammam

contained by PM samples but does not the affect the actual composition of the PM (Chung et al., 2008).

4.4 Mineralogical Characteristics of PM by XRD

4.4.1 Mineralogical Characteristics of PM from Dhahran by XRD

Figure 29 shows the mineralogical composition of the PM samples collected from Dhahran. It shows the bulk of the mineral to be of calcite (Calcite–Magnesian), and some montmorillonite clay mineral. From the result, it can be observed that all the 3 locations from this city have a similar XRD pattern but different intensities.

4.4.2 Mineralogical Characteristics of PM from Khobar by XRD

Figure 30 shows the XRD result for Khobar. Most of the peaks matches with calcite and few matches with montmorillonite (heated and oriented type). It reveals that the minerals found in the different locations within the city are similar based on peaks found on the same 2-theta positions. The major peak coincides with montmorillonite in all the samples analyzed.

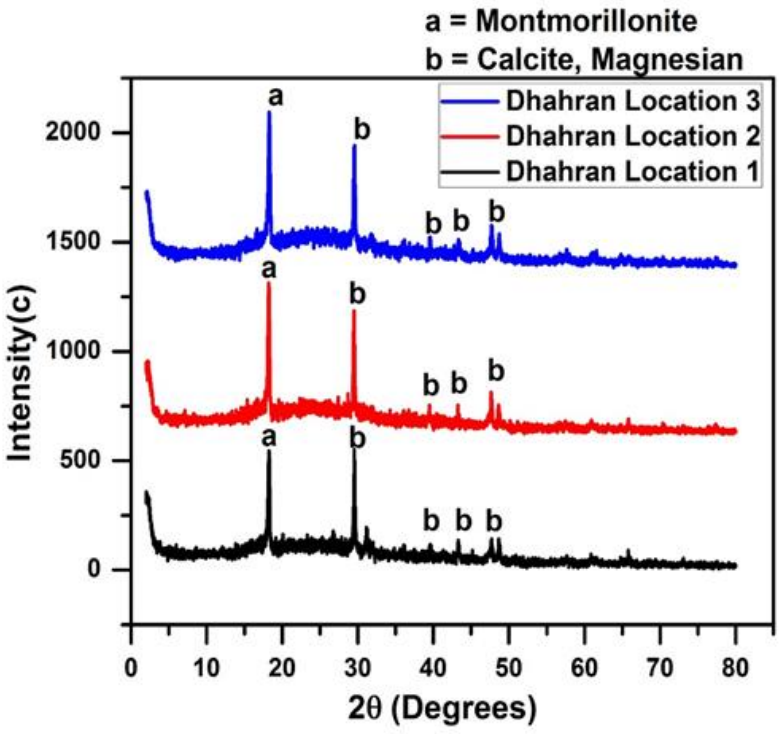


Figure 29. XRD Result for Dhahran

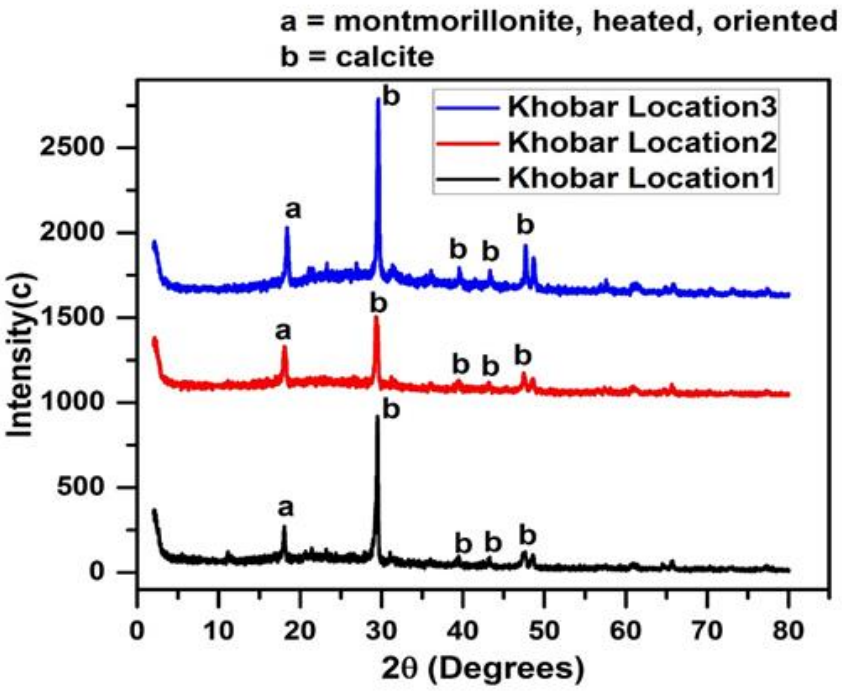


Figure 30. XRD Result for Khobar

4.4.3 Mineralogical Characteristics of PM from Dammam by XRD

XRD results from Dammam is shown in Figure 31, reveals the relationship between samples collected in the locations within the city. Samples from location 2 have the highest intensities compared to 1 and 3. Minerals found in the samples are calcites and montmorillonite, and this is because their peaks are found at the same position with what has been reported in literature (Bhattacharyya and Gupta, 2006; Hariharan et al., 2014). The mineralogical composition of PM shows no deviation from what has been reported from previous studies. Most studies on airborne PM shows that they contain both calcite and clay mineral which is montmorillonite in this present study (Satsangi and Yadav, 2013; Ahmady-Birgani et al., 2015).

From the XRD results for all the 3 cities it can be confirmed that the airborne PM in the 3 cities contained aluminosilicates compound which is montmorillonite that is a type of clay but not feldspar, and also confirms that the $CaSO_4$ suspected in the samples were formed by the reaction of calcite with Sulphur that is present in the atmosphere. The presence of similar minerals in the samples collected from the different cities confirms that the reaction of calcite with Sulphur that is present in the atmosphere. The presence of similar minerals in the samples collected from the different cities confirms that temporal and spatial variation does not really affect the type of mineral that constitutes airborne PM, it can only affect their physical forms such as size and shapes as well as their quantity. The mineralogical analysis confirms that the airborne PM sample originates mainly from crustal materials and the variation in their levels was due to variation in weather conditions at the different locations and times

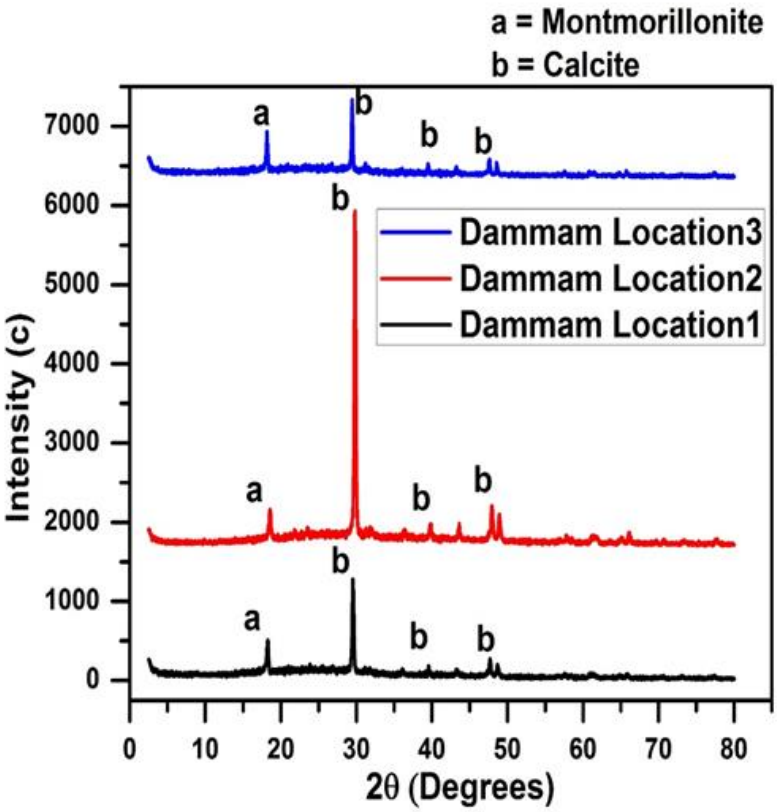


Figure 31. XRD Result for Dammam.

4.5 Trace Metal Levels in PM Samples

In other to understand the danger posed by the airborne PM in the different cities, it is important to estimate the concentration of the heavy metals which are present at trace levels in the samples. This was then being related to the standard set for each of the elements by various standard organizations or as reported by previous studies.

Fourteen (14) different elements of interest were selected from the ICPOES results and the elements includes arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), vanadium (V), zinc (Zn), titanium (Ti), selenium (Se), and lead (Pb). Arsenic (As) is present in the 3 cities at a concentration less than 0.01 $\mu g/m^3$ and this is lower than the threshold ambient air concentration for As (Raina et al, 2012; Shaltout et al., 2014).

Barium (Ba) has a high concentration in the 3 cities with the highest concentration recorded in Dammam with 10.13 $\mu g/m^3$. The concentrations in Dhahran and Khobar are 8.91$\mu g/m^3$ and 5.11 $\mu g/m^3$ respectively.

Cadmium (Cd) which is one of the most dangerous pollutant for organisms was found to be less than 0.005 $\mu g/m^3$ in the 3 cities. This is lower than the typical national ambient air concentration for Cd recorded in a typical urban and industrial area in the United States. Co was found in the 3 cities at a concentration lower than 0.001 $\mu g/m^3$ in Dhahran and Khobar but a concentration less than 0.002 $\mu g/m^3$ in Dammam. This is not regarded as a threat because it is not as high as the maximum allowable limit.

Chromium concentration is 0.06, 0.07 and 0.06 $\mu g/m^3$ in Dhahran, Khobar and Dammam respectively. The concentrations are higher than the allowable limit for both urban and

industrial areas in a typical ambient air recorded in the United States (Quiterio et al., 2004;Geiger and Cooper, 2010).

Copper was found at a concentration of 0.02, 0.03 and 0.01 $\mu g/m^3$ for Dhahran, Khobar and Dammam respectively. This is lower than the maximum allowable limit in the urban and industrial areas.

Manganese was found to have a concentration of 0.06$\mu g/m^3$ in Dhahran while it has a concentration of 0.11$\mu g/m^3$ and 0.01$\mu g/m^3$ in Khobar and Dammam respectively. The level of manganese in Dhahran and Khobar is very high compare to what had been reported in previous studies. Molybdenum is less than 0.03$\mu g/m^3$ in Dhahran and Khobar but it's less than 0.005$\mu g/m^3$ in Dammam. Nickel has a concentration of 0.02$\mu g/m^3$ in cities 1 and 2 while its Dammam is 0.01$\mu g/m^3$. The concentration of Ni in cities 1 and 2 is the maximum allowable limit in the ambient air according to EU and USEPA standards (Geiger and Cooper, 2010; European commission, 2014; Shaltout et al., 2014).

The level of vanadium recorded was 0.05$\mu g/m^3$, 0.07$\mu g/m^3$, and 0.06$\mu g/m^3$ for cities Dhahran, Khobar and Dammam respectively. Zinc has a very high level recorded in all the cities, and the highest concentration is recorded in Khobar with 12.64$\mu g/m^3$ while Dhahran and Dammam have concentration of 8.98$\mu g/m^3$ and 8.87$\mu g/m^3$ respectively.

Titanium level was 0.66$\mu g/m^3$, 0.99$\mu g/m^3$ 1.47$\mu g/m^3$ in cities Dhahran, Khobar and Dammam respectively. The threshold for titanium has not been reported in previous studies. Lead is not available in Dhahran and Khobar but it's present in a very low concentration of less than 0.001$\mu g/m^3$ in Dammam.

Table 5 Concentration of Trace Metals Carried by PM Samples from Dhahran, Khobar and Dammam Cities

Elements	Dhahran (µg/m^3)	Khobar (µg/m^3)	Dammam (µg/m^3)
As	<0.010	<0.010	<0.010
Ba	5.11	8.91	10.13
Cd	<0.005	<0.005	<0.005
Co	<0.001	<0.001	< 0.002
Cr	0.06	0.07	0.06
Cu	0.02	0.03	0.01
Mn	0.06	0.11	0.01
Mo	<0.003	<0.003	< 0.005
Ni	0.02	0.02	0.01
V	0.05	0.07	0.06
Zn	8.98	12.64	8.87
Ti	0.66	0.99	1.47
Se	<0.01	<0.01	< 0.004
Pb	NA	NA	<0.001

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Levels and concentration of airborne PM were carried out in three cities of the Eastern Province (Dhahran, Khobar and Dammam) Saudi Arabia.

The overall mean PM_{10} concentration in Dhahran was around 177 $\mu g/m^3$, while the overall minimum and maximum PM_{10} concentration of 66.98 and 303.08 $\mu g/m^3$, but in Khobar, the average concentration of PM_{10} sample is 379.85 $\mu g/m^3$. The minimum and maximum levels of PM_{10} recorded in these cities are 93.65 $\mu g/m^3$ and 1575.46 $\mu g/m^3$ respectively. In Dammam, the average PM_{10} level was 126.69 $\mu g/m^3$ while the minimum and maximum levels of PM_{10} recorded in this city was 56.93 $\mu g/m^3$ and 232.60 $\mu g/m^3$ respectively. This shows that PM_{10} concentration obtained from the gravimetric analysis is highest in Khobar and was above USEPA, WHO and EU.

The SEM images showed the presence of particles of various shapes and sizes which is as low as 1 micron. The SEM micrograph confirm that temporal and spatial variations affect the sizes and shapes of airborne PM collected from the same or different locations. SEM analysis of samples from Dhahran showed that the particle sizes range from 1 – 6 µm with angular, flaky, and irregular shapes that are either smooth or rough. In the SEM micrograph obtained from Khobar samples, the particle size ranges from 1 – 8 µm and their shapes ranges from irregular, spheroidal, rod-like, clustered and agglomerated. Based on the source classification by Roberto etal., (2013), particles from this city may have originated largely from aluminum silicates (such as clays) with high metal contents and calcium rich

materials. The airborne PM collected from Dammam have sizes as low as 1 μm and maximum of around 7 μm based on the SEM micrograph taken for this sample. The shape of the particles are spherical, irregular and agglomerated and this shows that samples may be from natural crustal materials and some anthropogenic activities. Comparison of different micrographs from the 3 cities showed that the particles have different sizes and shapes which indicates that changes in location affects the processes which the particles have undergone. The particles may originate from similar sources, but particles have changed their shapes and probably their forms due to their locations and the time or periods of collection. Based on the SEM analysis, it can be concluded that temporal and spatial variations affects the sizes and shapes of airborne particulate matter.

Elemental analysis from EDX and XRF shows that aluminosilicate compounds, some metals and calcium sulphate were contained in the airborne PM sample based on the elemental constituents and it also shows that temporal and spatial variation could only affect the form, shape and size in which the element is present in the in the airborne PM sample but not totally change the element. The presence of heavy metals at trace level confirms that airborne PM carries hazardous metal with them which makes them to pose more danger amongst other criteria pollutants. In general, the results obtained showed that Arsenic (As) does not exceed the allowable range in all the sampling location, Ba is at high level in all the 3 cities with the highest concentration recorded in Dammam. The result also indicates that Se, Co, Cu and Mo fall within the allowable range. The result also showed that Cd and Pb fall within the allowable range in the three cities, Cr has been found at a higher concentration in the three cities than the allowable limit.

In the case of Ti, there is no specific regulation on the limit of Ti in ambient air based on the previous studies, but Ti was found in high concentrations in the three cities with the highest level in Dammam. Manganese has a concentration below the allowable range in Dammam but a very high concentration in Khobar, Ni is lower in level than the allowable limit in Dammam but gives a warning sign in Dhahran and Khobar. V has a concentration above the maximum limit in Dhahran and Khobar with a warning sign in Dhahran, and based on the adopted standards, Zn is very high in the samples collected in the three locations with Khobar having the highest values.

The mineralogical analysis from the XRD result shows that in general, the airborne particulate samples in the study area contain mostly clay mineral and calcite and are purely from crustal materials.

5.2 Recommendations

In view of the obtained results, the following recommendations can be made:

- Concerted efforts should be made on national level to establish the airborne heavy metal guidelines for the Kingdom of Saudi Arabia.
- The assessment of airborne particulate matter should be continuous and efforts should be made to monitor and compare the levels and concentrations of trace elements in air with the levels and concentration in plants and soil.
- Year-long study should further be carried out on the levels to assess the seasonal variations of the PM concentration levels and identify their sources.
- Study should be extended to lower PM sizes such as $PM_{2.5}$ and $PM_{1.0}$
- Temporal and Spatial variation studies should be extensively conducted.

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