CHARACTERIZATION OF PM_{10} CONCENTRATION AND IDENTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) COMPOUND FROM URBAN AND RURAL SCHOOLS IN KELANTAN

HEMAMALINI A/P MANOGARAN

FACULTY OF EARTH SCIENCE

UNIVERSITY MALAYSIA KELANTAN

2017

CHARACTERIZATION OF PM_{10} CONCENTRATION AND IDENTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) COMPOUND FROM URBAN AND RURAL SCHOOLS IN KELANTAN

by

HEMAMALINI A/P MANOGARAN

A report submitted in fulfillment of the requirements for the degree of Bachelor of Applied Science (Sustainable Science) with Honours

FACULTY OF EARTH SCIENCE

UNIVERSITY MALAYSIA KELANTAN

2017

DECLARATION

I declare that this thesis entitled "Characterization of PM_{10} Concentration and Identification of Polycyclic Aromatic Hydrocarbon (PAH) Compound From Urban and Rural Schools in Kelantan" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : _____

Name : HEMAMALINI A/P MANOGARAN

Date : _____

ACKNOWLEDGEMENTS

Firstly I would like to express my gratitude to my supervisor, Dr Norrimi Rosaida Awang and my ex-supervisor, Madam Siti Hajar Binti Yaacob who has accepted me and guided me from beginning till the end of my final year project journey. Both of them had guided me and showed me the way to do my final year project from scratch to end with a lot of patience. I appreciate their style of letting their student to do things independently and learn from mistakes and all the time they spent for me toward the completion of my project.

I would also like to thank the other lecturers, Dr Nurul Syazana Abdul Halim, our SEL FYP course coordinator and Dr Irshad Ul Haq Bhat who never failed to give me advises to overcome my problems. Besides that, I would like to thank the principal from SMK Batu Melintang and SMK Kubang Kerian 1 for allowing us to place the air sampler in the school compound to collect our samples.

Furthermore, I would like to thank Faculty of Agro-Based Industries for guiding and allowing me to use their instruments like GCMS. I also would like to thank all the lab assistants for being supportive in order to accomplish my sample extractions.

Moreover, I am honored by University Malaysia Kelantan, especially the Faculty of Earth Sciences for allowing me to fulfill my final year project. Last but not least, I am very lucky to have a supportive family and friends who gave me countless support, motivations and inspirations to finish my final year project. The support I received from them has helped me a lot to complete this project successfully.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ace	Acenaphthene
Acy	Acenaphthylene
AD	Asian Dust
Ant	Anthracene
ATSDR	Agency for Toxic Substances & Disease Registry
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BghiP	Benzo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
Chry-d_{12}	Chrysene-d_{12}
Chry	Chrysene
CH_4	Methane gas
C_2H_4	Ethene
CO	Carbon monoxide
DCM	Dichloromethane
DEP	Diesel Exhaust Particles
DBA	Dibenzo[a,h]anthracene
DNA	Deoxyribonucleic acid
E	East
EU	European Union

Flt	Fluoranthene
Flu	Fluorene
GC-MS	Gas Chromatography-Mass Spectrophotometer
HMW	High Molecular Weight
Ind	Indeno(1,2,3-c,d)pyrene
LMW	Low Molecular Weight
LVAS	Low Volume Air Sampler
MSAT	Mobile Source Air Toxics
N	North
N_2	Nitrogen gas
Nap	Naphthalene
NO_X	Nitrogen oxide
O_3	Ozone
PAHs	Polycyclic aromatic hydrocarbons
Per	perylene-d_{12}
Phe-d_{10}	Phenanthrene-d_{10}
Phe	Phenanthrene
PM	Particulate matter
PM_{10}	Particulates with aerodynamic diameters <10 micron
$PM_{2.5}$	Particulates with aerodynamic diameters <2.5 micron
POPs	Persistent organic pollutants
Pyr-d_{10}	Pyrene-d_{10}
Pyr	Pyrene

QAQC	Quality Assurance and Quality Control
RMAQG	Recommended Malaysia Ambient Air Quality Guideline
RH	Relative Humidity
SIS	Surrogate Internal Standard
SO_2	Sulphur dioxide
SK	Sekolah Kebangsaan
SMK	Sekolah Menengah Kebangsaan
SPM	Suspended particulate matter
TEF	Toxic Equivalency Factor
UFP	Ultra-fine Particles
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF SYMBOLS

µL	Microliter
µg/m^3	Microgrammes per metre cube
min	minute(s)
mm	milimetre
µg/ml	Micrograms per mililiter
h	hour
min	minutes
m	metre
ml	Mililiter
m/z	Molecular/ atomic mass per charges
ng	Nanogrammes
ppm	Part per million
psi	pressure
rpm	revolution per minute

Characterization of PM_{10} Concentration and Identification of Polycyclic Aromatic Hydrocarbon (PAH) Compound from Urban and Rural Schools in Kelantan

ABSTRACT

Urban area with extensive transportation was associated with higher concentration of air pollutant than rural site. Particulate matter, PM_{10} was a major pollutant of concern as it can be adsorbed with toxic substances like heavy metals and organic compounds like polycyclic aromatic hydrocarbon compounds (PAH). Sampling was done in urban and rural schools of Kelantan from April, 2016 till June, 2016. The samples were then extracted through ultrasonification process and centrifuged before being concentrated to near dryness. 900 µL of n-hexane and 100 µL of pyrene $_{d\text{-}10}$ was added prior being analyzed using GC-MS. The result shows PM_{10} concentration in the range of three months in Kota Bharu ranged between 24.86 µg/m^3 and 99.55 µg/m^3 and for Jeli it ranged between 18.01 µg/m^3 and 86.05 µg/m^3 respectively. The mean concentration of PM_{10} for Kota Bahru was higher than Jeli with 52.57 µg/m^3 and 39.21 µg/m^3, respectively. But, result from Independent Sample t-Test shows no significant difference with p-value of 0.083. The PAH detected in both urban and rural sample, 1-methylnaphthalene was classified as Low Molecular Weight (LMW). Human activity and meteorological factors might cause fluctuation in the concentration of PM_{10}. We can conclude that the concentration of PM_{10} in urban site (SMK Kubang Kerian 1) is higher than rural site (SK Batu Melintang) but p-value was not significantly different with p-value of 0.083 due to fluctuational characteristics of PM_{10}. The 1-methylnaphthalene was PAH with low molecular weight can impose fewer risk to the school children.

Pencirian Konsentrasi Zarah Terampai PM_{10} dan Pengenalpastian Kompaun Polisiklik Aromatic Hidrokarbon (PAH) daripada Sekolah Bandar dan Luar Bandar di Kelantan

ABSTRAK

Kawasan bandar dengan kadar aktiviti manusia yang tinggi dianggap mempunyai kadar pencemaran udara yang tinggi. Zarah terampai PM_{10}, adalah antara pencemar yang penting kerana boleh dijerap dengan bahan karsinogenik seperti Polisiklik Aromatic Hidrokarbon (PAH). Penyampelan telah dijalankan di sekolah bandar dan luar bandar di Kelantan dari April 2016 sehingga Jun, 2016. Kesemua sampel telah diekstrak melalui proses ultrasonifikasi and melalui prosess penggemparan sebelum dipekatkan kepada takat kering. Ekstrak kemudiannya dicampurkan dengan n-hexana dan pyrena $_{d\text{-}10}$ sebelum dianalisa oleh GC-MS. Kepekatan zarah terampai, PM_{10} adalah diantara 24.86 μg/m^3 dan 99.55 μg/m^3 bagi Kota Bharu manakala bagi Jeli adalah diantara 18.01 μg/m^3 dan 86.05 μg/m^3. Purata kepekatan zarah terampai PM_{10}, bagi Kota Bharu adalah tinggi daripada Jeli iaitu 52.57 μg/m^3 dan 39.21 μg/m^3. Tetapi keputusan Sampel Bebas Ujian t tidak berbeza secara significan dengan 0.083. PAH yang telah dikenal pasti dalam kesemua sampel adalah *1-methylnaphthalene* iaitu sejenis polisiklik aromatic hidrokarbon dengan berat molekul rendah (LMW). Aktiviti manusia seperti pembakaran bahan api fosil (kenderaan motor dan industri) dan meteorologi telah mempengaruhi keputusan Sampel Bebas Ujian t. Sebagai kesimpulan, PM_{10} disekolah bandar (SMK Kubang Kerian 1) lebih tinggi daripada luar bandar (SK Batu Melintang) tetapi tidak significan kerana dipengaruhi oleh aktiviti manusia dan meteorologi. Manakala, 1-*methylnaphthalene* adalah PAH yang kurang berbahaya kepada pelajar sekolah kerana mempunyai berat molekul rendah.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Air pollution was associated with the existence of pollutants like sulphur dioxide (SO_2), particulate matter (PM), nitrogen oxides (NO_X) and ozone (O_3) in the air (Chen & Kan, 2008). These dangerous substances was proved to have the probability to exert an adverse effect to human health and environment (Turk & Kavraz, 2011). This was because air pollutants can cause acid rains, corrode buildings and urban heat island (Abdullah *et al*., 2012). These pollutants were regarded as the criteria air pollutants in urban areas and are influenced by the spatial and temporal variation. Increasing the understanding of both spatial and temporal variation in the concentration of air pollutant can help us evaluate and manage our air quality effectively.

The increased intervention of human with the natural environment had given rise to the increased production of atmospheric pollutants. Urbanization was the core development process which starts with the transformation of an area's natural landscape for various economic use was the major reason that affect the air quality (Abdullah *et al*., 2012). This due to the growth of transportation need, growing energy production and consumption and also the industrial processes which contributes to bad air quality (Rai *et al*., 2011).

Apart from anthropogenic activity, the concentration of air pollutants were also related with the intensity and duration of emission, the topographical variations, the uptake and assimilation of pollutant by urban vegetation, the chemical reactions among pollutants and finally the meteorological factors which induce chemical reaction and pollutant dispersion (Kim, 2010). However, among the pollutant that can be found in atmosphere, PM was said to be a critical pollutants that can affect health and act as foundation that damage the economy (Amarsaikhan *et al*., 2014).

Generally, particulate matters contain organic and inorganic chemical species adsorbed in it that could harm human health (Sienra *et al*., 2005). However, one such compound often found associated with particulate matter (PM) was polycyclic aromatic hydrocarbons (PAHs) along with other volatile carbonaceous compounds and toxic gases in air like methane (CH_4), hydrogen cyanide (HCN), ethane (C_2H_4) and carbon monoxide (CO). The study area involved was Kota Bharu and Jeli located in Kelantan. Kelantan covers a total area of 14, 922 km^2 or 4.4 % of Malaysia and divided into ten major districts namely Kota Bharu, Pasir Mas, Tumpat, Bachok, Kuala Krai, Machang, Tanah Merah, Jeli and Gua Musang (Ismail, 1996).

The Department of Statistics Malaysia (2005) defined urban area was gazetted area as well as the adjoined areas which has a combined population of 10,000 or greater, while rural area was an area with less than 10,000 people with forested area, water bodies and agriculture area. According to Jeli Land and Administration Office (2014), Jeli area was considered as a rural area as it has a total population below 10,000. In addition, Kota Bharu with the total population of 314, 964 were later regarded as an urban area and upgraded into Kota Bharu Municipality Council. Earlier in 1991 the total population in Kelantan was about 366,849 which

later had increased to 425,294 by the year 2010 (Fadzil *et al*., 2008). This shows that the rise in the total number of population could exert serious pressure for urbanization in Kota Bharu as well to meet the basic needs. It is expected in near future the possibility that the air quality in Kota Bharu may be worse due to high urbanization.

1.2 Problem statement

The problem of air pollution was strongly associated with the urbanization and industrialization of an area. According to Azmi *et al*. (2010) who conducted a study in three different air quality monitoring station in Klang Valley, the rural to urban migration had been the major factor for air quality deterioration. Study by Jamhari *et al*. (2014) in urban, industrial and sub-urban area in Malaysia shows concentration of PM_{10} was higher in the industrial and suburban area than the semi-urban area. This might be due to increase in human activity like transportation, residential and industrial in urban area than semi-urban area.

According to Silva Junior *et al*. (2009) the concentration of PM_{10} in the metropolitan area of Sao Paulo was higher during the weekdays than on weekends. Besides that, Azmi *et al*. (2010) also speculated that besides meteorological factors the difference in daily human activities either weekends or weekdays may influence the amount of particulate matter in the urban areas like Klang Valley. However, very scarce studies related with fluctuations of particulate matter (spatial and temporal) have been carried out in Malaysia apart from Shaadan *et al*. (2015), Dominick *et al*. (2012) and Azmi *et al*. (2010).

Particulate matter was a major concern as it can be adsorbed with organic and inorganic compound posing risk to human health. Studies by Salam *et al*. (2010) proved that suspended particulate matter can be associated with organic pollutants like PAHs adsorbed on it. This was supported by Bi *et al*. (2005) that particulate matters were a major pathway for harmful organic compounds like PAHs from the atmosphere. The priority PAHs listed by the US Environmental Protection Agency were naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenantherene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene due to their potential carcinogenic and mutagenic effects.

Study by Salam *et al*. (2010) in urban residential and sub-urban residential area in Japan shows dominance of 5- ring and 6- ring PAHs by about 70% total concentration. In Malaysia, studies by Jamhari *et al*. (2014) in urban, industrial and semi-urban area detected most of the PAHs ranging from 4 - 6 rings in the monsoon seasons. This shows that the types of PAHs could differ in different location due to the temporal fluctuation of PM_{10} concentration caused by human activity and meteorological factors. Exposure to PM_{10} and PAHs were reported to give adverse health effect to both children and adult.

However, children's are potential population at risk because of their high susceptibility apart from significant amount of time for development of health risks due to early life exposure (Ruchirawat *et al*., 2007). Some of the effects from the exposure of PAHs towards children were disturbance in cognitive development, affects childhood memory and respiration problems (Karimi *et al*., 2015). However, very scarce studies have been done in Kelantan particularly in Kota Bharu and Jeli to

study the PM_{10} and PAHs as many study focus on the urban areas like Kuala Lumpur, Klang Valley and Bangi. Besides that, PAHs studied in different area might be different as reported by Jamhari *et al*. (2014), Azmi *et al*. (2010) and Salam *et al*. (2010) due to different sources. This increased the need to compare rural area with an urban area to clarify factors that might affect the concentration of pollutants as well identifying the possible types of PAHs in both areas.

1.3 Objectives

The study aimed:

a) To determine the fluctuational characteristic of particulate matter (PM_{10}) in urban and rural school areas

b) To compare the concentration of particulate matter (PM_{10}) in urban and rural school areas.

c) To identify the common type of PAH in urban and rural school areas.

1.4 Significance of Study

This data obtained from study will aid for future research in understanding the behavior and concentration of pollutants in Malaysia. This research had speculated that there is link between both anthropogenic and meteorological activity in affecting the ambient air quality in rural and urban area in Malaysia. Therefore, based on these data more research can be conducted in Malaysia urban and rural area in future to determine the change in air quality. Besides that, this study can increase

the importance of air quality among school areas in rural and urban areas of Malaysia. Therefore, more research can be carried out in urban and rural school areas to determine the changes and risk of pollutions towards school students. This can be added as young children are more susceptible towards health risk in comparison with adults.

CHAPTER 2

LITERATURE REVIEW

2.1 Air Pollution and its Risks

Air pollution is becoming a major environmental issue due to rise of transportations (mobile sources), trans-boundary pollution from neighboring countries and the industrial activities (stationary sources) (Azid *et al*., 2011). The increase in demand to meet humans daily needs like transportations, factories and industries as well energy production have made the environment to be severely polluted. These can be seen when air pollution incidence were regarded as a serious problem which raised the concern for air quality and environment problem in rapidly expanding cities like Chicago, Mexico City, Lagos, Cairo, Tokyo and Athens during the period of 1970s till 1980 (Valavanidis *et al*., 2008).

Air pollution has serious effects towards respiratory and cardiovascular health that may lead to acute lung function, aggravation of asthma, increased pneumonia risks, low birth weight and death risk among newborns (Salam *et al*., 2011). Based on the 1997 haze phenomena in Malaysia, the sum of air pollution effects among secondary school children in Klang and Kuala Lumpur were estimated. The result from the study revealed that 50% from the secondary school children's have fall sick and seeks for medical treatments (Afroz *et al*., 2003). This shows to us that urban area with higher concentration of pollutants could increase the risk for children to develop health problems in future. Majority of Asian countries faced increase in

urbanization, industrialization and vehicular usage from the last decade. This was coupled with transboundary haze pollution and Asian Dust (AD) phenomenon which caused the concentration of particulate matter to increase in Asian cities (Tahir *et al*., 2013).

This makes impossible for human of all age ranges to avoid from being exposed towards these harmful substances because breathing is a continuous biological process. However, the exposure of pollutants in atmosphere could be controlled with proper emission control. This can be supported with a study conducted to test the effectiveness of emission control during the Asean Youth Games 2013 in Nanjing, China in the month of August. The result from the experiment showed a decrease in the percentage risk of exposure to the concentration of air pollutant for both children (23%) and adult (27%) (Li *et al*., 2016).

2.2 Presence of Particulate Matter in Ambient Air

High attentions were given in the past years toward fine particles in atmosphere due to the potential harmful effects they can pose towards human health. Aerosols are the solid or liquid particles in suspension found in atmosphere ranging from few nanometers to tens of micrometers. Atmospheric aerosols are an analytical matrix that contains water soluble inorganic compounds, organic carbon, elemental carbon and metal (Hassan *et al*., 2013). The particles in atmosphere can be divided based on their size as coarse particulate matter and fine particulate matter. Particle with size less than 2.5 μm ($PM_{2.5}$) was referred as fine particles while those with size 2.5 μm to 10 μm (PM_{10}) were regarded as coarse particles (Motallebi *et al*., 2003; Chow *et al*., 1994).

These aerosols can alter the balance of earth atmosphere by interfering with the absorption and scattering of solar radiation and as cloud condensation nuclei (Yadav *et al*., 2014). The increase in the amount of air particulates will also affect the natural processes like precipitation and change the global climate. This can be proved with studies in Japan which regard the suspended particulate matter (SPM) as the criteria air pollutant in urban areas related with the changing of climate (Salam *et al*., 2011). Besides that, PM may also affect the monsoon circulation by weakening the land-sea pressure and temperature gradients thereby reducing precipitation (Karar *et al*., 2006).

2.3 Sources of Particulate Matter, PM_{10} in Atmosphere

Atmospheric aerosols normally composed of the mixture from both primary pollutants which comes from the direct emission from the source and secondary pollutants which involves the transformation of gases to particles (Silva Junior *et al*., 2009; Yatkin & Bayram, 2007). Particulate matter can originate from natural sources like forest fires and biomass burning. In Klang valley, during summer monsoon season the PM_{10} concentration was reported to be high due to smoke from increased biomass burning coming from nearby sources (Juneng *et al*., 2011).

Besides that, PM can also arise from anthropogenic activities which include open burning (Afroz *et al*., 2003), dusts from roads (Wahid *et al*., 2014; Karar *et al*., 2006), construction sites (Dominick *et al*., 2012; Karar *et al*., 2006), combustion of fossil fuel (electric generation and internal combustion engines) (Afroz *et al*., 2003), motor vehicles (Wahid *et al*., 2014; Afroz *et al*., 2003; Lenschow *et al*., 2001),

biomass burning (Abas *et al*., 2004; Chow *el at*., 1992) and industrial activities (Rahman *et al*., 2015; Dominick *et al*., 2012; Karar *et al*., 2006; Afroz *et al*., 2003).

However, the main source of primary particles, PM_{10} in the urban environment was claimed to be from vehicle exhaust as well as fossil fuel burning in factories and power stations (Kelly & Fussel, 2012; Naser *et al*., 2008). In Malaysia, combustion of fuel by motorized vehicles were regarded as the major cause of air pollution among developed areas in Malaysia (Rahman *et al*., 2015). This statement can be proved when data collected from the past 5 year study in year 2003 showed that approximately 70-75% of air pollutants in Malaysia were estimated to originate from mobile sources (Afroz *et al*., 2003).

Besides that, diesel exhaust particles (DEP) are the major contributor of particulate matter in world's biggest cities as cars mostly equipped with diesel engines had raised the combustion of fossil fuels (Kelly & Fussel, 2012). Although the advancement in vehicles emission control technology had improved the increase in the number of vehicles over the years had led to more deterioration especially in urban environments. This makes motor vehicles emissions to be considered as the key determinants in the spatial and temporal variations of ambient air pollution concentration.

2.4 Time Series Analysis for Particulate Matter Variation in Atmosphere

Most studies regarding air particulates and other pollutants in atmosphere takes into account the spatial and temporal variation of particulates (hourly, daily, monthly and yearly) termed as the time series. This due to chances of the

concentration of pollutant throughout the study to be influenced by the local wind parameters namely direction, speed and other meteorological factors (solar radiation, temperature and humidity). Shaheen *et al*. (2005) also mentioned that there can be difference in the distribution of air particulates with the variations of meteorological conditions in many parts of the world. The early stage in the time series analysis was to draw a time series plot which provides a preliminary understanding of the behavior of the series with time (Saffarini & Odat, 2008).

For example, due to the temporal variation in ambient air we can have counterbalance of two process namely wind-blown emission/dust storms and dilution from strong winds. In Malaysia, the wind direction from the Southwest which originates from Sumatra between July and September was speculated to bring a high amount of particulate matter to the Klang Valley (Shaadan *et al*., 2015). Besides that, the local wind might influence the concentration of various pollutants in urban and industrial sites (Yadav *et al*., 2014). This can be supported with studies by Yadav *et al*. (2014), where the increase in local wind speed was associated with the increment of PM_{10} and $PM_{2.5}$ in Udaipur, India. However, the high rate of emission in an area with decreased wind speeds and frequent inversions in an area might result in high local pollution load (Hassan *et al*., 2013).

On top of that, the average aerosol concentrations could also be influenced by the variation of human activity during the weekends and weekdays. This can be supported by Kim (2010) where transportation and increment in land use holds the largest share of the spatial and temporal variation of pollution concentrations. According to studies by Hassan *et al*. (2013), the average aerosols concentrations were higher during the weekdays compared to the weekends in the summer and winter seasons. This reduction might be due to decrease in traffic density from

official days-off for government institutions, schools and colleges that possibly reduce exhaust particle emission and resuspension of street dust. Studies done by Motallebi *et al*. (2003) also noticed lower pollutant level on Sundays which might be due to lower car and truck traffic which reduces the road dust and emission of air particulates.

Besides that, even both meteorological factor as well as the difference in human activity during weekends and weekdays can influence PM_{10} concentration. This was proven by Shaadan *et al*. (2015) with studies done in Klang Valley, Selangor where Kuala Selangor was found to experience the most significant 'monsoonal effect' due to winds from the Sumatra during monsoon season while Petaling Jaya experienced the most significant weekend effect. Therefore, it can be summarized that the stations location and background, speed of wind with seasonal (monsoon) and weekend-weekdays variation also play an important role in influencing concentration of PM_{10}.

2.5 Effects of Particulate Matter towards Human Health

Classification of particulate matter according to their size differences was crucial to identify their penetration ability into human body. Normally, coarse particles can be filtered by the nose and the upper airway systems unlike the finer particles which can penetrate deeper into lungs (Ministry of Water, Land and Air Protection, 2003). Inhalation of particles with diameter less than 10 μm were strongly associated with the inflammation in the lungs. This was because the PM_{10} particles could reach until lower respiratory tract that induce pro-inflammatory cytokines after phagocytosis by alveolar macrophages (Kavitha *et al*., 2011). Recent research

regarding health problems and the exposure to PM with size 10 μm also supports the potential of lung function declination, increased respiratory symptoms, chronic pulmonary disease, premature death and heart disease (Wahid *et al*., 2014).

Besides that, one of the important contributor towards pulmonary inflammation among bus drivers was due to high exposure towards diesel exhaust particles (Kavitha *et al*., 2011). Long term exposures towards particulate matter was associated with asthma, lung cancer, cardiovascular disease and obstructive pulmonary disease and acute short term exposure might increase sudden mortality, hospital and emergency room visits and absenteeism from work and school (Ministry of Water, Land and Air Protection, 2003; American Journal of Respiratory and Critical Care Medicine, 2000). Therefore, WHO has established the exposure limit for PM_{10} towards human due to the harmful effect. According to WHO, the daily average limit set for 24 hour average of particulate matter was 50 $\mu g/m^3$ while the annual limit was 20 $\mu g/m^3$ (WHO, 2005).

2.6 The Association of PAHs with Particulate Matter

PAHs were reported to have tendency to associate with particulate matter in the air. This can be supported with the study on suspended particulate matter (SPM) in urban and suburban areas in Japan which proved that chemical composition of particulate matter may consist of organic contaminants like PAHs being adsorbed on it (Salam *et al*., 2011). Normally, the PAHs tend to be adsorbed onto fine particles first before being adsorbed onto coarse particles. The fine particles will undergo volatilization process and condensate onto the coarser particles (Bi *et al*., 2005).

Studies on SPM supports that the association of organic compounds especially PAHs onto particulate matter might increase serious health effects (Salam *et al*., 2011).

The association of PAHs into the particulate matter differs and varies according to the nature of the pollutant. This could be supported with the concentration of individual PAHs found in both $PM_{2.5}$ and PM_{10} aerosol sample with high molecular weight PAHs dominating the lower molecular weight PAHs (Naser *et al*., 2008). This supports that particulate matter was found to associate with the high molecular weight PAHs because they are less volatile compared to the low molecular weight PAHs.

2.7 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic (Poly-nuclear) aromatic hydrocarbon (PAHs) belongs to a class of complex organic compounds including carbon and hydrogen with at least two benzene rings fused to it (Jamhari *et al*., 2014; Azhari *et al*., 2011; Ravindra *et al*., 2008). PAHs which consists of large groups with more than 100 different compounds ranging from 2 to 7 benzene rings were classified among the persistent toxic pollutants (Mohanraj *et al*., 2011). PAHs are regarded as organic chemicals which is highly resistant to degradation that further increase adverse environmental effects (Maliszewska-Kordybach, 1999). Moreover, the resistance towards degradation caused PAHs to be discussed as POPs candidates and POPs Protocol (Aarhus Protocol) in the Convention on Long-Range Transboundary Air Pollution deciding that all PAHs as POPs (Lammel, 2015).

PAHs can be divided into two types namely the lower molecular weight (LMW) and high molecular weight (HMW) PAHs (Lamichhane *et al*., 2016). In

ambient air due to the lower vapour pressure PAHs can occur either in gas phase or atmospheric particulate depending on molar mass (Bian *et al*., 2016). Normally, PAHs with two or three benzene rings (LMW) were found to exist mostly in vapour form while the PAHs with more than five benzene rings was associated with particles (fine particles) (Mohanraj *et al*., 2012). While, PAHs with four-rings known as intermediate PAHs were found to exist in both vapour and particulate phase which depends with the atmospheric temperature (Srogi, 2007). According to Mohanraj *et al*. (2012) the higher molecular weight (HMW) PAHs will remain attached towards the fine particles because they have lower vapor pressures compared to the LMW PAHs. This can be supported with the heavier PAHs like B(a)P frequently found to be adsorbed towards air particles unlike the lighter PAHs namely phenanthrene which were mostly found in gas form (Ravindra *et al*., 2008).

The carcinogenicity of PAHs were said to increase with the addition of their ring number. The US Environmental Protection Agency had listed 16 PAHs as priority pollutants due to their toxicity and seven of it were categorized as carcinogenic chemicals (Jang *et al*., 2013). Among the compounds in the USEPA list of probable carcinogens were benzo[a]anthracene (BaA, four-ring), chrysene (Chry, four-ring), benzo[b]fluoranthene (BbF, five-ring), benzo[k]fluoranthene (BkF, five-ring), benzo[a]-pyrene (BaP, five-ring), dibenzo[a,h]anthracene (DhA, five-ring) and indeno[1,2,3-cd] pyrene (Ind, six-ring) (Callan *et al*., 2013).

According to Amarillo *et al*. (2014) the carcinogenic PAHs were frequently found to be associated with airborne particles compared to gaseous phase. This means that the HMW PAHs were classified as more carcinogenic due to their high tendency to be found associated with airborne particles. This was because the high molecular weight PAHs like benzo[a]pyrene was known in their ability to decrease

the cell viability and damage the DNA due to their potential as carcinogenic compound (Mohanraj *et al*., 2011). Besides that, the World Health Organization (WHO) also considered benzo[a]pyrene as compound with high potential to impose cancer to human compared to the other PAHs compound.

2.8 Sources of PAHs in Ambient Air

PAHs can be categorized into two sources of origin namely natural and anthropogenic sources. Natural source of PAHs mainly originates from biogenic and diagenetic sources while anthropogenic origin mostly comes from petrogenic and pyrogenic sources (Bahry, 2007; Boonyatumanond *et al*., 2007). It could be that most PAHs in urban areas were derived from the anthropogenic source than natural source due to higher combustion rate by humans. The main origin of PAHs can be classified into natural, industrial, commercial, (vehicular) mobile and residential sources (Amarillo *et al*., 2014).

2.8.1 Natural sources

PAHs in the natural environment are not only caused by the anthropogenic activities but also from the natural source. The example of activity that contributes to PAHs natural was natural oil spills, volcanic eruptions and sudden fires that happen in forests or prairies (Mahmoodi *et al*., 2012). In 1997, a huge forest fire incident happened in Indonesia had released a numerous amounts of particles from combustion. The study conducted during this period in Malaysia showed that the concentration of PAHs during the haze was three times higher compared to when

there is no haze. This can be supported with concentration of PAHs to vary between 12.5±14.8 ng/m^3 compared to the non-haze time period which was about 4.1±0.1 ng/ m^3 (Okuda *et al*., 2002).

2.8.2 Domestic sources

The common source of PAHs from the domestic source can originate from incomplete combustion during cooking and heating processes. This can be proved when PAHs was found in charcoal-broiled diets like barbeque or direct flamed foods (Jedrychowski *et al*., 2003). Some other potential substances which release PAHs from domestic sources can be classified into combustion of coal, tree woods, rubbishes and other carbon-based sources. World Health Organization had identified that about 70% of population in countries like China, India and some Southeastern part of Asia depends with fuels and wood for cooking in daily basis (Lee & Vu, 2010). This might increase the chances of PAHs to be released from the areas with high demand for fuels and wood. For example, in Sweden the B[a]P concentration from wood burning for domestic heating was reported to be 430 kg which was higher than the combined concentration of gasoline and diesel emissions which was 320 kg in total (Ravindra *et al*., 2008).

2.8.3 Mobile sources

Mobile source of PAHs were classified as an important source of PAHs in the urban environment due to extensive transportations (Abdel-Shafy & Mansour, 2016). Besides that, PAHs emissions could also reach about 90% in rural and suburban areas caused by mobile source emission compared to the stationary sources (Sharma

et al., 2007). According to Liu *et al*. (2010), major PAHs source in urban areas of Shenzen was originated from vehicle emission with the total of 50.0%, while other industrial source from coal and combustion contributed about 29.4% and 20.6% from total PAHs concentration. This was due to the rapid increase in vehicular traffic and the air pollutant dispersal in urban areas. The PAHs originating from mobile source were also proven to release a certain amount of toxics into the air. This can be seen when the USEPA cited 21 mobile source air toxics (MSATs) which included naphthalene and polycyclic aromatic substance (surrogated by seven PAHs) (He *et al*., 2010).

Study conducted in Bangkok also proved that the traffic police officers exposure to PAHs on the urban roadside was higher with mean level of 72.79 ng/m^3 in comparison to office workers with mean level of only 6.88 ng/m^3 (Suvarapu *et al*., 2012; Ruchirawat *et al*., 2007). This shows that higher number of transportation from the mobile source does increase the total concentration of PAHs in the urban areas. According to U.S Agency for Toxic Substances & Disease Registry (ATSDR), the value of PAHs in rural areas vary from 0.02 ng/m^3 to 1.2 ng/m^3 while for urban areas the values were higher ranging from 0.15 ng/m^3 to 19.3 ng/m^3 (Franco *et al*., 2008). Studies carried out in few cities in Europe also shows high levels of PAHs were found on samples collected from the busy urban roads in comparison to quiet roads with low traffic in urban areas (Ravindra *et al*., 2001).

Besides that, studies comparing urban traffic site and rural area of Dhanbad, India also proved that PAHs concentration found in the urban areas soil were 5.45 times higher than the concentration of PAHs found in rural soil from the same district due to increased emissions from vehicles (Suman *et al*., 2016). Another study performed in Ulsan, Korea also supports that mobile source accounts for 31.27% of

PAHs which was higher than the concentration found in oil combustion (19.78%), wood combustion (12.15%) and coal burning (8.64%) (Dong & Lee, 2009). This indicates that maybe the concentration of PAHs can vary due to the difference in the total number of sources and frequency of emission.

2.8.4 Industrial sources

PAHs could originate from anthropogenic sources through incomplete combustion process from different industries namely pitch and coal tar industries, gasification of coal, and aluminium production (Abdel-Shafy & Mansour, 2016), bitumen and asphalt manufacturing, petrochemical industries, power generation and incineration of municipal wastes (Rengarajan *et al*., 2015). Besides that, some PAHs were used in the manufacture of pesticides, pigmented products or as an intermediate to manufacture substances like plasticizers and drying agents (Franco *et al*., 2008).

Some examples of PAHs manufactured for commercial use were naphthalene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene (Ravindra *et al*., 2008). Studies carried out by Mu *et al*. (2013) also supports that the different stage in coke manufacture and combustion process from industries can release PAHs. Besides that, the total PAHs concentration in soil nearby an ex coke plant was about 6.27 up to 40.18 mg/kg by measurement of the dry weight (Mu *et al*., 2013). This shows that the industries can give rise to PAHs during both manufacturing or via usage of PAHs during production.

2.8.5 Agricultural sources

Normally, agricultural waste will be burned as a way the farmers clearing their lands for farming activity. The incomplete process of combustion in the fields tends to increase the chances of releasing PAHs to the atmosphere. PAHs derived from the agricultural sources were due to combustion of branches and twigs, stubbles, dry stalks of plants from open burning (Lee & Vu, 2010). Some PAHs mostly originate from the agricultural waste combustion were naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene which accounts for 80 – 90% in total (Lee & Vu, 2010). This shows that most of the area with major agriculture activity might be severely polluted by PAHs. This was proved when children's staying near to rice fields were frequently diagnosed with bronchial asthma especially when the rice fields are burned as a process of nutrient adding to the soil (Lai *et al*., 2009). This shows that the effects of PAHs originating from large scale agricultural fields have the tendency to affect health of humans.

2.9 Transport and Fate of PAHs in the Environment

Automobile as an important part in modern human life was also associated with transport of pollutants onto environmental media's like soil, water and air. The rapid multiplication of motor transport in comparison to the industrial activities also associated with the growth of pollutants like PAHs (Salam *et al*., 2011). Some other examples of pyrolysis were fossil fuels and other products which were burned in large broilers, kilns, furnace, open burning and combustion from vehicle engines like buses, trucks, lawn movers, ships, boats, locomotives and aircrafts (Golomb *et al*., 2001).

The wet deposition and dry deposition were the major route in which the PAHs from atmosphere could reach the terrestrial and aquatic environments (Bahry, 2007). Wet deposition happens when the particles are brought to surface by precipitating hydrometeors like rain drop and snows, while dry deposition occurs when the PAHs were brought onto land or water directly through wind blows (Golomb *et al*., 2001). During the wet deposition, the PAHs were either dissolved with rainwater or united as particles while for dry deposition the PAHs were associated with the dust particles in air (Ollivon *et al*., 2002).

In ambient air, PAHs can occur either in gas phase or atmospheric particulate depending with molar mass (Bian *et al*., 2016). The increase in the ring number cause the PAHs to be less volatile and tend to be deposited with atmospheric particles. Normally, PAHs ranging from higher molecular weight like benzo(a)anthracene to benzo(g,h,i)perylene were mostly found associated with atmospheric particles while the lighter PAHs like naphthalene (2 rings) to pyrene (4 rings) were found mostly in gas phase (Gocht *et al*., 2007). The PAHs have a long life time ranging from tens to hundreds of hours in air when it was in aqueous phase, while the lifetime of PAHs that undergo dry depositions were lower. This was because PAHs subjected to dry deposition will not be brought far from the emission source due to their short life in the atmosphere. Usually, PAHs that undergoes dry depositions can only be brought to a distance of few to tens of kilometers (Gocht *et al*., 2007).

After the PAHs have undergone either wet or dry deposition, they will be deposited on the top soils, vegetation, surface sea waters which will increase their accumulation on environmental media. The deposition of PAHs could also take place on soil after these organic compounds was subjected to natural weathering process

like photo-oxidation (Al-Turki, 2009). The large quantity and holding capacity of soil makes lithosphere as the main sink for deposition of environmental pollutants. This was proven as 90% of PAH from the environment in Great Britain was stored in soil (Ma & Zhou, 2011). Besides that, PAHs also tend to be accumulated in highly trafficked places like roads (streets) and parking lots and later transported via rain, storms and snowmelt into water bodies (Manzetti, 2013). However, due to their persistence and slow biodegradation process they also have higher tendency to be transferred into the lower compartments namely the ground water or deep seas (Lammel, 2015). Some examples of PAHs found to bio-accumulate in environment were benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene (Lammel, 2015).

2.10 Health Effect of PAHs to Human

In ambient air, exposure by PAHs towards human occurs mainly through inhalation of biomass burning, tobacco smokes, forest fires, volcanic eruptions and vehicular emission (Kaur *et al*., 2013). PAHs are an organic contaminant very closely related with carcinogenic and co-carcinogenic risk to human health (Bostrom *et al*., 2002; Mohanraj *et al*., 2012). PAHs can involve as both initiator and promoter and therefore was considered as complete carcinogens that may act at different stages in carcinogenic process (Bostrom *et al*., 2002). Besides that, their carcinogenicity, mutagenicity and teratogenicity have greater tendency to impose a great and lasting threat towards ecosystem safety and human health (Yu *et al*., 2014).

This was because PAHs can easily enter human body via food, water and skin contact due to their hydrophobic nature and transported into human body tissue that

contains fat. The increase in the ring number of PAHs could raise the tendency to be soluble in human fat tissue. This was because as the ring number increase, the PAHs becomes more fat-soluble and accumulate in fatty tissue of human. Therefore, the toxicity of PAHs can be said to increase with the molecular weight of PAHs. Besides that, PAHs with higher molecular weight also have higher tendency to be adsorbed with particulate matters compared to the lower molecular weight (He *et al*., 2010).

Lower Molecular Weight (LMW) PAHs except for naphthalene were mostly associated with relatively lower risk of toxicity than High Molecular Weight (HMW) PAHs with 5 or 6 aromatic rings (Lee & Vu, 2010). However, particles associated with PAHs can be accumulated into the tracheobronchial epithelium which could increase the concentration of PAHs via frequent exposures (Kaur *et al*., 2013). This was proven by Yu *et al*. (2015), as fine particulate matter with excessive content of high molecular weight PAHs (> 4 benzene rings) have greater penetration into lungs through inhalation.

Due to the absence of threshold value for dose-response relationship for PAHs no safe level been established for these compounds (Hui *et al*., 2008). More frequent exposure of human towards PAHs can lead to adverse health effects in the future. Some examples are gene mutation and cardiopulmonary mortality due to high risk of cell damage via prolonged exposure towards PAHs (Kim *et al*., 2013). This risk will be even higher for workers in transportation industry as they have high risk of respiratory and lung diseases caused by traffic air pollutant from daily exposure (Kavitha *et al*., 2011).

2.11 Health Effect of PAHs to Young Children

Children exposed with genotoxic environmental pollution have a high risk to develop cancer and other associated health risk in future (Jyethi *et al*., 2014; Tuntawiron *et al*., 2007). This due to their active behavior, higher ingestion rate and inhalation rates with respect to their body size compared to adults. The exposure of children with PAHs can be proven by studies done in United States where children's (aged 6 - 11 years) have elevated levels of urinary PAH metabolites compared to adolescents (aged 12 – 19) and adults (≥ 20 years) respectively (Abid *et al*., 2014).

According to Jung *et al*., (2015), high exposure to PAHs during prenatal and the age of 5-6 years was reported to trigger asthma among young children. Jyethi *et al*., (2014) also mentioned that children's staying in areas with known PAHs source was reported to face adverse health effects like lung function decline, infant growth retardation and neurodevelopment delay from prenatal exposure. Animal studies also showed that prenatal exposure to PAH might impair memory, affect learning ability and cause changes in behavior (Abid *et al*., 2014).

Besides that, the risk for cancer due to exposure with carcinogens during childhood was higher compared to exposure during mature age (Jyethi *et al*., 2014). DNA damage was known as the earliest phase for the development of cancer in human body. Based on the evidence from epidemiological and experimental reports also supports that PAHs could induce changes to DNA methylation and cause modification on the organisms gene expression that may lead to cancer in later life (Algeria-Torres *et al*., 2013). This was proven by Ruchirawat *et al*. (2007), as the DNA breaks for students in urban city, Bangkok was abruptly high with decreased

DNA repair capacity compared to children's in rural area based on the result by cytogenetic challenge assay which reflects higher chromosomal deletions per metaphase. A survey in suburban Yuncheng, Shanxi reported the annual lung cancer occurrence was higher than the national average that may affect children and people due to high localized risk (Zhang *et al*., 2009). Besides that, there is elevated risk of leukemia and central nervous system tumor among children staying close to highways and densely traveled roads. A study conducted in Sweden and United Kingdom also shows evidence that childhood cancer increase with exposure to motor vehicle exhaust (Tuntawiroon *et al*., 2007). Therefore, children living in capital cities were proved to have health risk than children living in rural areas.

CHAPTER 3

METHODOLOGY

3.1 Sampling Sites and Description

The study area chosen for sampling was Kota Bharu and Jeli in the state of Kelantan as shown in Table 3.1.

Table 3.1: Sampling location, duration and total number samples

Sampling location	Coordinate	Site	Sample collection (n)			Total (N)
			Month	Weekdays	Weekends	
Jeli (SK Batu Melintang)	N 05.70 E 101. 83	Rural area	April	3	0	N = 15
			May	7	0	
			June	5	0	
Kota Bharu (SMK Kubang Kerian 1)	N 06. 13 E 102. 310	Urban area	April	2	3	N = 15
			May	0	5	
			June	1	4	

Ambient air samples were collected using low volume air sampler (LVAS) from two sites namely urban school at Kubang Kerian (SMK Kubang Kerian 1) and rural school area at Batu Melintang (SK Batu Melintang) as shown in Figure 3.1 and Figure 3.2 respectively.

Figure 3.1: Sampling location in rural area at SK Batu Melintang, Batu Melintang, Jeli

(Source: Google Map, 2016)

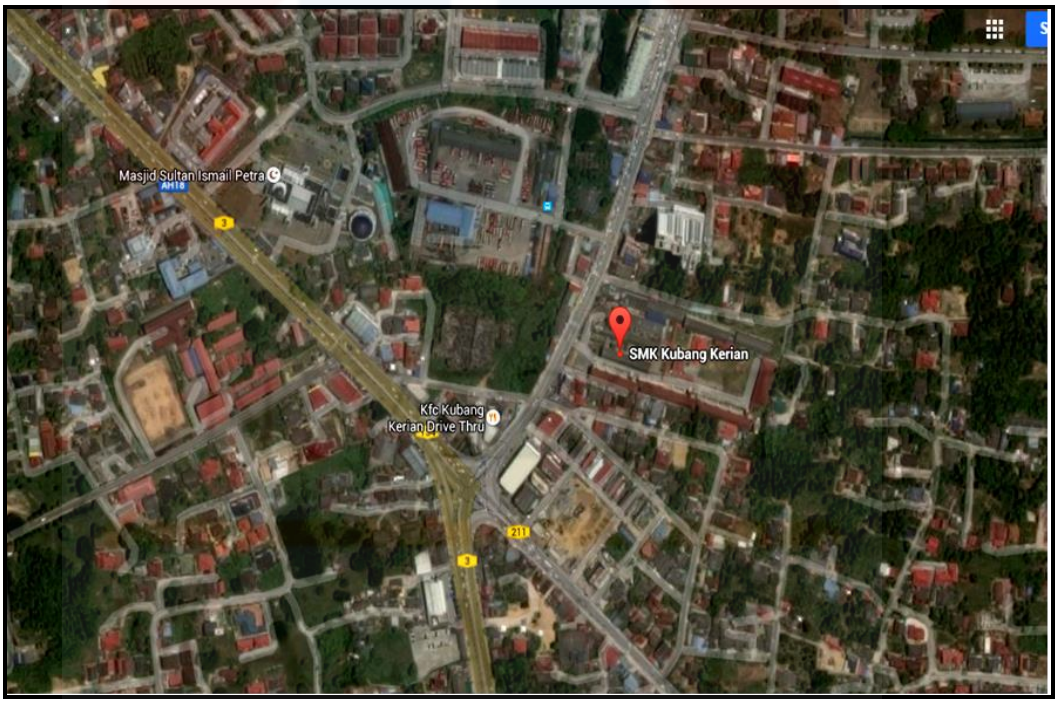


Figure 3.2: Sampling location at SMK Kubang Kerian 1, Kubang Kerian, Kota Bharu

(Source: Google Map, 2016)

Kota Bharu was one of the rapid growing towns in the state of Kelantan located in the east coast of Peninsular Malaysia. The total population of Kota Bharu is approximately 425,294 person and the city was the center for business, industrial and government establishment (Fadzil *et al*., 2008). Figure 3.1 shows the sampling location in Jeli district was SK Batu Melintang in Batu Melintang. It was located about 19 km from Jeli town consisting of 9,690 populations in total and was regarded as rural area (Jeli Land and Administration Office, 2014).

Kota Bharu experienced heavy traffic from transportation sector. Among the activity was manufacturing of automobile parts, industrial machineries, producers of chemicals, pharmaceuticals, printing, packaging and construction materials. The distance of SMK Kubang Kerian 1 to the major road was about 3 km. In comparison to the urban area, Jeli has lower industrial and commercial activities with relatively low density of road traffic. In comparison to Jeli, Kota Bharu was well developed with extensive roads and transportation and tall buildings together with rapid housing area construction. Besides that, both of these sampling sites were located near the roadside with active transportation activity.

3.2 Sample Collection

The aerosol samples were collected using low volume air sampler (LVAS) (Model LV-20P, Shibata, Japan) fitted with selective inlet that collects atmospheric particles at aerodynamic diameter < 10 μm only. The air sampler was operated for 24 hours (1 day) according to the standard set by USEPA for PM_{10} sample collection. The sampler was placed at a height of 1.5 m and the air flow rate of the sampler was set at 20 L/min. The glass fiber filters were baked in oven before sample collection to

remove organic contaminants at 300°C for 5 h (Jamhari *et al*., 2014). All fresh and exposed filter papers were placed in desiccator to absorb any moisture at 25 °C for 24 hours after baking (Lee *at al*., 2008). Based on Table 3.1, the sample for urban area was collected during the weekends and weekdays while for rural area it was collected from weekends only. This was due to constraint of sampling instrument, a total of 15 samples were collected from each location.

In Kelantan, the weekdays and weekends differs in which Sunday till Thursday was regarded as weekdays while Friday and Saturday was weekends. The variation in the concentration of PM_{10} during weekdays for rural area and for urban area during both weekdays and weekends was studied. The climate during sampling can be summarized as mixture of hot and rainy season from the end of April till May and June.

3.3 Sample Weighing and Storage

The glass fiber filter paper was weighed before sampling and after sampling using microbalance and placed in a desiccator maintained at 25° C (Omar *et al*., 2002; Bahry *et al*., 2009). The mass of particulate matter on the filter paper was determined by the gravimetric method using microbalance to an accuracy ±0.000001g. The gravimetric mass was measured at controlled humidity at 54.5 % relative humidity (RH) and temperature of 22.6 °C. The initial mass of the filter paper was then subtracted with the final mass of the filter paper after sampling. All the exposed filter papers were folded and re-wrapped in aluminum foil and were stored in chiller at 4 °C till the day of sample analysis. A total of 30 samples were collected which covered

a duration of three months which was April, May and June 2016 as shown in Table 3.1.

3.4 PAH Standard Solution Preparation

All the standard preparation and samples extraction methods were described by Salam *et al*. (2011). The surrogate and internal were prepared before the extraction process. The surrogate standard was phenanthrene-d_{10} and chrysene-d_{12} while pyrene-d_{10} was used as the internal standard. All the surrogate and internal standards were prepared for 1ppm (part per million) using n-hexane as solvent using the formula in Equation (3.1).

$$\mathbf{M_1V_1 = M_2M_2} \qquad (3.1)$$

Where, $\mathbf{M_1}$ = Concentration of standard (ppm)

$\mathbf{M_2}$ = Concentration of new standard (ppm)

$\mathbf{V_1}$ = Volume of standard needed (ml)

$\mathbf{V_2}$ = Volume of standard needed to be diluted (ml)

3.4.1 Mixture of Surrogate Internal Standard (SIS) Preparation

Each surrogate standard (phenanthrene-d_{10} and chrysene-d_{12}) were prepared using the formula mentioned above for 10 ppm. The surrogates were then mixed with hexane in 10 ml of volumetric flask to prepare a 1ppm standard solution of surrogate internal standard (SIS) mixture.

3.4.2 Internal Standard Preparation (IIS)

Pyrene-d_{10} which was in the form of solute was the internal standard and it was prepared for 1 ppm using the similar formula mentioned in Equation 3.1.

3.5 Sample Extraction

The filters of PM_{10} samples were cut into pieces and placed in a 30 ml extraction glass tube wrapped with aluminium foil. It was then extracted with 20 ml of dichloromethane (DCM) and 1 ml of 1 ppm mixture of surrogate standards (phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}) in ultrasonic bath for 20 minutes (three times). The extracts were transferred into centrifuge bottles after each ultrasonification process. The extracts were then mixed together in centrifuge tube and run at 3000 rpm for 10 minutes for insoluble particles to be screened out.

Only the clear supernatant was transferred to a round-bottomed flask of nitrogen evaporator and the remaining solution in the centrifuge bottles were filtered using the Millex syring driver (0.45 μm). The centrifuge bottles were cleaned thrice using 1-3 ml dichloromethane to ensure no remaining extracts in the bottles and the extracted sample were further concentrated till about 3-5 ml in the rotary evaporator system at 40°C in water bath. The round bottomed flask was cleaned for three times after rotary evaporation with 2-3 ml of dichloromethane to ensure there are no remaining extracts inside it.

The extracts were then further concentrated to near dryness at 35°C and 5 psi for 29-40 minutes in nitrogen evaporator. The final extracts were added to 0.9 ml of n-hexane before Milex syringe driver unit (0.20 μm) were used to filter and remove

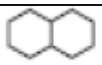
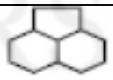
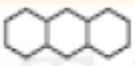
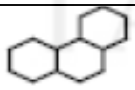
fine particles. The extracts were preserved at 4°C until the day of analysis. During analysis, the solutions were transferred into the 1.5 ml of target glass vial. Then, the same target glass vials were added with 100 µL of 1 µg/ml internal standard (Pyrene-d_{10}) solution to make exactly 1 ml of samples before the samples were analyzed by GC-MS.

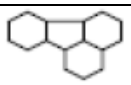
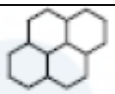
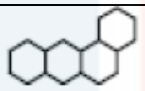
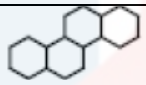
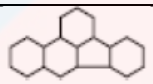
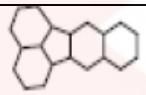
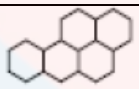
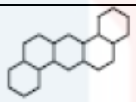
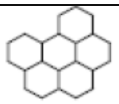
3.6 Sample Analysis

3.6.1 Target PAHs in Study

The target PAHs compound involved in this study was the 16 listed priority PAHs by the United States Environmental Protection Agency (EPA) reported by previous studies were shown in Table 3.2.

Table 3.2: US EPA 16 priority PAHs

PAH	**Abbreviation**	**Structural Formula**	**Molecular mass**	**Ring number**
Naphthalene $C_{10}H_8$	Nap		128	2
Acenaphthylene $C_{12}H_8$	Acy		154	3
Acenaphthene $C_{12}H_{10}$	Ace		152	3
Fluorene $C_{13}H_{10}$	Flu		166	3
Anthracene $C_{14}H_{10}$	Ant		178	3
Phenanthrene $C_{14}H_{10}$	Phe		178	3

Fluoranthene $C_{16}H_{10}$	Flt		202	4
Pyrene $C_{16}H_{10}$	Pyr		202	4
Benzo[a]anthracene $C_{18}H_{12}$	BaA		228	4
Chrysene $C_{18}H_{12}$	Chry		228	4
Benzo[b] fluoranthene $C_{20}H_{12}$	BbF		252	5
Benzo[k]fluoranthene $C_{20}H_{12}$	BkF		252	5
Benzo[a]-pyrene $C_{20}H_{12}$	BaP		253	5
Dibenzo[a,h]anthracene $C_{22}H_{14}$	DBA		278	5
Indeno[1,2,3-cd] pyrene $C_{22}H_{12}$	Ind		276	6
Benzo[g,h,i]perylene $C_{22}H_{12}$	BghiP		276	6

(Source: Lv. *et al*., 2016; Lee & Vu, 2010; Ravindra *et al*., 2008).

3.6.2 Analysis of PAHs Using Gas Chromatography Mass Spectrophotometer (GCMS)

PAHs were analyzed using GC-MS with 30 m fused silica capillary column, 0.25 mm internal diameter and 0.25 μm film thickness (Agilent Technologies). The GC temperature was held at 65°C for 2 minutes and raised to 280°C at 6°C/min. Sample was then held isothermally at 280°C for 20 minutes using helium as the

carrier gas. The samples of 1 μL were injected under SCAN mode for qualitative analysis of PAHs.

3.6.3 PAHs Identification

Type of PAH present in the sample were identified by comparing the structure displayed in the GCMS with their retention times as mentioned by (Bahry, 2009).

3.6.4 Quality Assurance and Quality Control (QAQC)

Quality control was conducted to ensure both sampling and measurement errors are minimized by conducting field blanks. The blank sample was run before the samples were analyzed to ensure there was no contamination. None of the target PAHs was detected in any sample when the procedural blank sample was run. All the glassware involved in this experiment was cleaned and rinsed with hexane and distilled water before baked in oven (5 h at 200°C) to reduce sample error due to contamination.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Descriptive Statistics of PM_{10} Concentrations

A total of 30 aerosol samples were collected from both Jeli and Kota Bharu for duration of three months. Samples were collected from both sampling sites from the month of April, May and June 2016 for Jeli and Kota Bharu with 24 hour averaging time. Table 4.1 shows the minimum, maximum, mean and standard deviation of PM_{10} concentration for both Jeli and Kota Bharu during sampling period.

Table 4.1: Descriptive analysis of PM_{10} concentration for Jeli and Kota Bharu

Variable	Statistics	Site		Avg time (h)	RMAQG	EU Commission
		Jeli	Kota Bharu			
PM_{10} concentration ($\mu g/m^3$)	**Min**	18.01	24.86	24	150	50
	Max	86.05	99.55			
	Mean	39.21	52.57			
	Std Deviation	19.64	21.02			

Based on Table 4.1 the average concentration of PM_{10} recorded at Kota Bharu (urban) and Jeli (rural) was 52.57 $\mu g/m^3$ (ranging from 24.86 - 99.55 $\mu g/m^3$) and 39.21 $\mu g/m^3$ (ranging from 18.01 - 86.05 $\mu g/m^3$). This shows that the mean of PM_{10} concentration for Kota Bharu was higher than Jeli during sampling durations. The minimum and maximum PM_{10} concentration does not show a huge difference

between rural and urban area. The average concentration of PM_{10} for both rural and urban area does not exceed the limit set by RMAQG. However, the average concentration of PM_{10} for urban area exceeded limit set by EU Commission. According to WHO (2015), generally air quality guidelines are intended for worldwide use to achieve air quality that protects public health in different contexts. However, the air quality standards are usually set by each country to protect the health of their citizens as well plays role in national risk management and environment policies. These national standards will vary according to the approach adopted for balancing health risks, technological feasibility, socio-political factors and economic consideration.

Table 4.1 also shows the concentration limit of PM_{10} for European Union to be lower than the limit set by Malaysia. The EU Commission limits was similar to the limits set by WHO which was lower than RMAQG because the European countries are highly urbanized which cause the population to be in high risk of adverse health effects (WHO, 2005). This can be supported with air pollution to be the top environmental risk factor for premature death in Europe (Air Quality in Europe, 2014). About 43,000 people die every year in Poland as the result of air pollutants (PM_{10} and $PM_{2.5}$) and were regarded as 'The China of Europe' alongside France, Finland, Czech Republic, Switzerland, Belgium, Hungary, Italy, Great Britain and Slovakia (Polish Iron Lungs, 2015).

Besides that, the particulate matters can also vary depending on local geography, meteorology and source of particulate matters. It was estimated that percentage of the urban population in Europe exposed to air pollutant concentrations mainly PM_{10} could reach above WHO reference levels to about 64 – 83 % in 2012 (European Environment Agency, 2014). The severity of pollutant exposure in urban

areas of Europe compared to Malaysia makes the permissible limit to be stricter than Malaysia. However, in the near future Malaysia might have to reduce their permissible limit to adapt with the rapid urbanizations change.

4.2 Monthly Variation of PM_{10} Concentration for Urban and Rural Area

Based on the result from sampling the daily average PM_{10} concentrations was used to analyze the monthly variations of PM_{10} for both urban and rural area. Figure 4.1 shows the monthly trend for PM_{10} concentration for Kota Bharu (urban) from the month of April, May and June 2016. The complete data for concentration of PM_{10} obtained from urban area was as in Table A1 (Appendix A). Based on Figure 4.1, it can be seen that there is clear fluctuation in the concentration of PM_{10} during the sampling periods. Result suggested that for the month of April the highest concentration of PM_{10} was on 24th of April with 99.55 μg/m^3 and the lowest was on 23rd of April with 51.01 μg/m^3. However, concentration of PM_{10} from all samples collected from April had exceeded the EU Commission limit but still below the RMAQG limit.

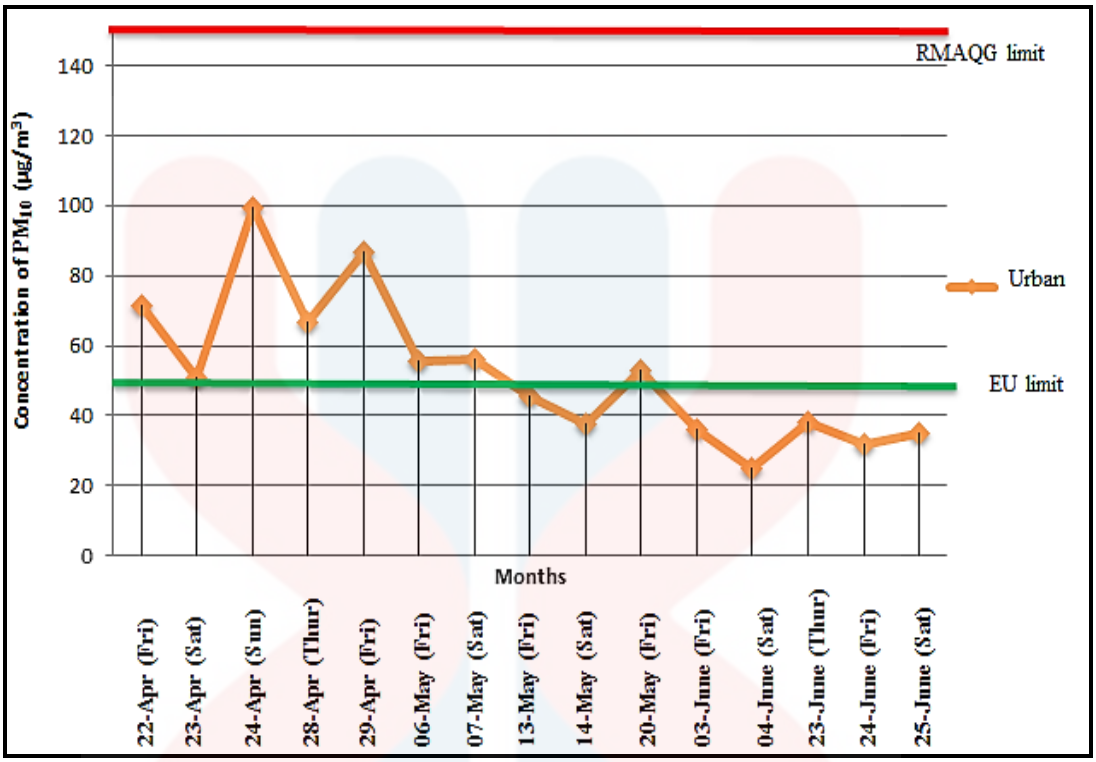


Figure 4.1: Monthly series of PM_{10} concentration for SMK Kubang Kerian 1

For the month of May the concentration of PM_{10} also shows fluctuation. Result showed that the highest concentration of PM_{10} was recorded on 7th of May which was 56.08 µg/m^3 and the lowest was recorded on 14th of May with 37.52 µg/m^3. The concentration of PM_{10} on 6th May, 7th May and 20th of May had exceeded the EU Commission limit but below RMAQG limit.

For the month of June, it can be seen that the concentration of PM_{10} also shows clear fluctuation. The highest concentration of PM_{10} was recorded on 23rd of June with 37.94 µg/m^3 and the lowest was measured on 4th of June with 24.86 µg/m^3. The concentration of PM_{10} for the samples in June was lower than limit set by both EU Commission and RMAQG for daily PM_{10} concentration. From result, the maximum concentration of PM_{10} from all three months in urban area was on 24th of April with 99.55 µg/m^3 and the minimum concentration was on 4th of June with 24.86 µg/m^3. Figure 4.2 shows the monthly trend for PM_{10} concentration for Jeli

(rural) from the month of April, May and June 2016. The complete data for concentration of PM_{10} obtained from rural area was as in Table A2 (Appendix A).

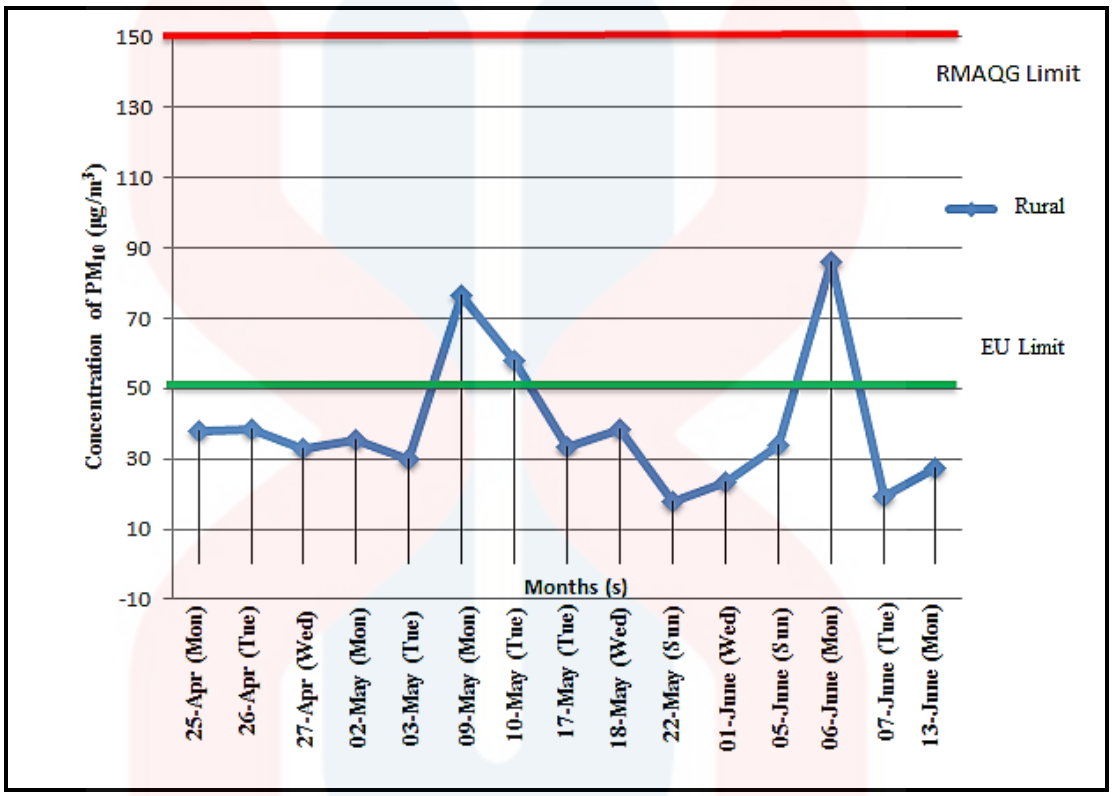


Figure 4.2: Monthly series of PM_{10} concentration for SK Batu Melintang

Based on the plotted monthly trend, there is clear fluctuation of PM_{10} concentration. For April, the highest concentration of PM_{10} for the month was measured on 26th of April which was 38.39 µg/m^3 and the lowest was on 27th of April with 32.78 µg/m^3. However, the concentration of PM_{10} for April does not exceed the limit set by RMAQG and EU. For May, high concentration of PM_{10} was recorded on 9th of May 76.63 µg/m^3 and lowest concentration was on 17th of May with 33.21 µg/m^3.

The PM_{10} concentration on 9th of May and 10th of May with 76.63 µg/m^3 and 57.99 µg/m^3 had exceeded the limit set by EU Commission but still lower than RMAQG. Finally, for June PM_{10} concentration was the highest for 6th of June with

86.05 μg/m^3 had exceed the European Union limit but still below RMAQG limit. The PM_{10} concentration on 7th of June with 19.42 μg/m^3 was the lowest for June. Based on the monthly trend, it can be concluded that the PM_{10} concentration for rural area was the highest in June and the lowest also from June.

4.3 Weekdays and Weekend Series of PM_{10} Concentration for Urban and Rural Area

The aerosol samples were collected on weekdays for rural area while for the urban area the samples were collected during both weekdays and weekends. The details on the number of samples collected for rural and urban site was as in Table 3.1. Figure 4.3 shows the comparison of PM_{10} concentration in urban area on weekends and weekdays. The graph shows fluctuations in the concentration of PM_{10} for urban area on weekends while for weekdays the PM_{10} concentration shows decreasing trend. On weekends, the highest concentration of PM_{10} was on 29th April (Friday) which was 86.53 μg/m^3 and the lowest concentration of PM_{10} was on 4th June (Saturday) with 24.86 μg/m^3.

Based on the graph, the concentration of PM_{10} decreased from April, May to June. This can be proved when PM_{10} concentration only exceeded the limit of EU for April only while for May and June it was below the limit for RMAQG and EU. For the weekdays, the graph shows a decreasing trend where the highest PM_{10} concentration was on 24th April (Sunday) which was 99.55 μg/m^3. The lowest PM_{10} concentration was on 23rd June (Thursday) which was 37.94 μg/m^3.

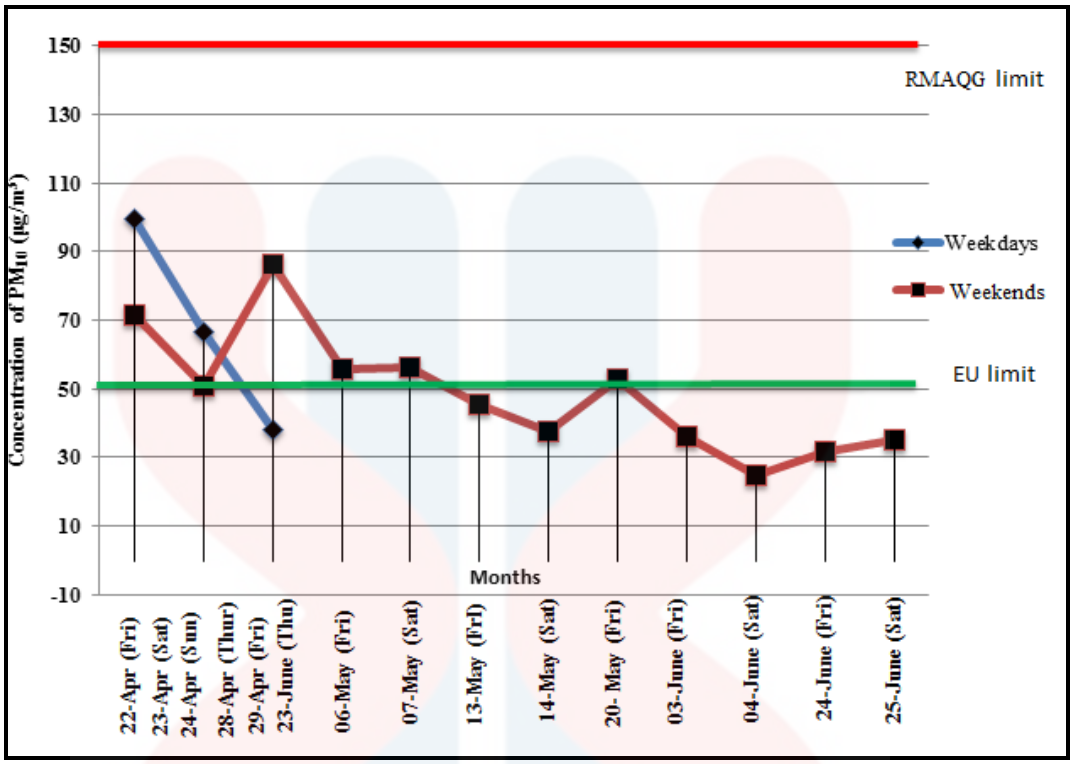


Figure 4.3: PM_{10} concentration for weekdays and weekends in urban area

Figure 4.4 shows the comparison of PM_{10} concentration in rural area on weekdays. Based on Figure 4.4 the concentration of PM_{10} for rural area shows clear fluctuation during the sampling period. The concentration of PM_{10} on weekdays shows two extreme values on 9th of May (Monday) and 6th of June (Monday) with 76.63 µg/m^3 and 86.05 µg/m^3 respectively. The lowest concentration of PM_{10} recorded was for 22nd of May (Sunday) with 18.01 µg/m^3.

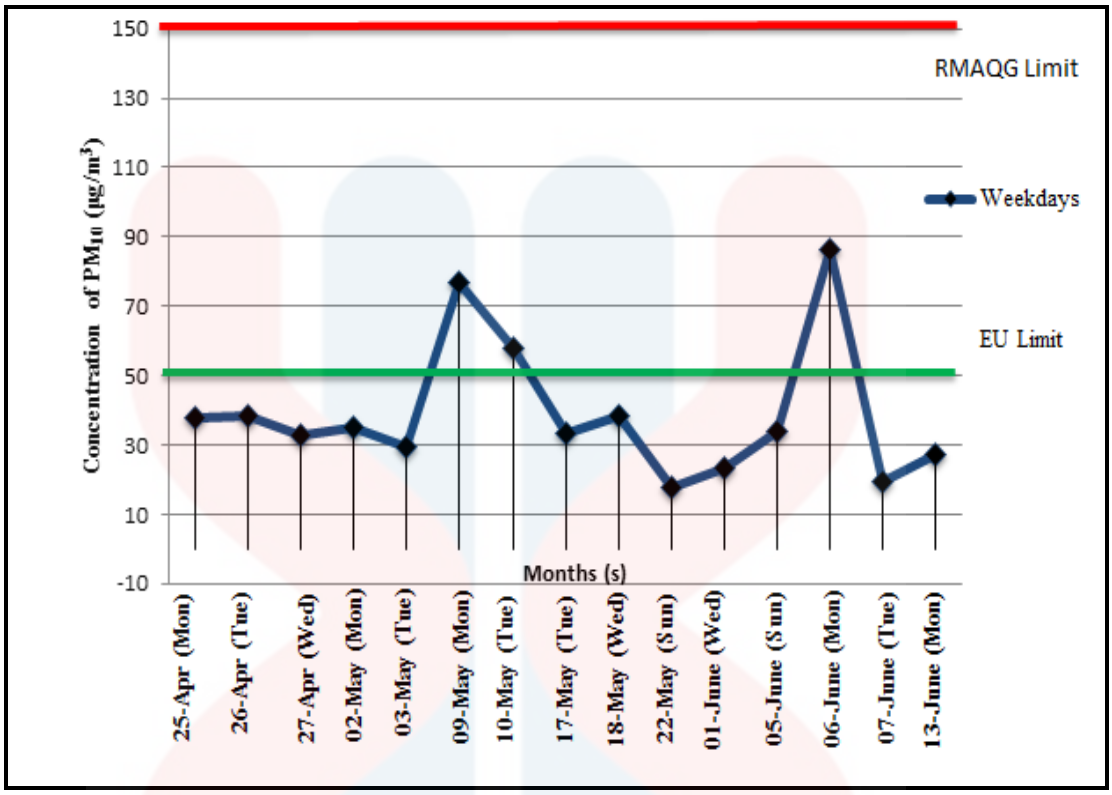


Figure 4.4: PM_{10} concentration for weekdays in rural area

4.4 Comparison of Particulate Matter (PM_{10}) Concentration between Urban and Rural Area

The sources of PM_{10} in Malaysia mostly arise from natural sources (forest fires or biomass burning), industrial activity, power station operation, fossil fuel burning and transportations. Therefore, traffic and meteorological factors are the most related variables to explain the fluctuations of PM_{10} concentration in the study area. The average concentration of PM_{10} in urban area was higher than Jeli which was 52.57 µg/m^3 (ranging from 24.86 - 99.55 µg/m^3) and 39.21 µg/m^3 (ranging from 18.01 - 86.05 µg/m^3) as shown in Table 4.1.

The higher number of vehicles, industries and street dust was expected to contribute to higher average of suspended particulate matter in Kota Bharu compared to Jeli. This was due to asphalt debris and resuspension of paved and unpaved road

dust associated with traffic flows can increase the concentration of PM_{10}. A study from urban environment in Munich also supports that urban areas can have more fine and ultrafine particles due to high number of mobile vehicles particularly diesel engines (Schnelle-Kreis *et al*., 2001). Besides that, different urban areas might have distinct emission source which could influence the contribution of PM_{10} as recorded by Bahry *et al*. (2009).

In his studies done in selected locations in Peninsular Malaysia namely Alor Setar, Bukit Kledang, Bayan Lepas, Kuala Terengganu, Melaka, Petaling Jaya, Seberang Perai, Senai and Tanah Rata, the highest concentration of suspended particulate matter was recorded from Seberang Perai which housed the national electricity power plant holding high potential to release pollutants. An Independent Samples T-test was conducted to test the difference in mean between both sampling sites. Table A10 shows there is no significant difference in the mean between both locations, Jeli and Kota Bharu with p-value of 0.083. This was because of the fluctuation of PM_{10} concentration for all the months in both urban and rural area as shown in Figure 4.1 and Figure 4.2. This fluctuation might be due to atmospheric factors like precipitation, wind speed or human activity like heavy transportation.

Therefore, the monthly comparison was done to analyze the fluctuation of PM_{10} concentration. Figure 4.5 shows the comparison of monthly average concentration of PM_{10} for both urban and rural area. Based on Figure 4.3, for urban area the average concentration of PM_{10} decreased from 75.01 $\mu g/m^3$, 49.47 $\mu g/m^3$ and 33.23 $\mu g/m^3$ from April, May and June. The average concentration of PM_{10} for rural area showed inconsistent trend as the concentration increased from 36.27 $\mu g/m^3$ to 41.33 $\mu g/m$ and decreased to 38.01 $\mu g/m^3$.

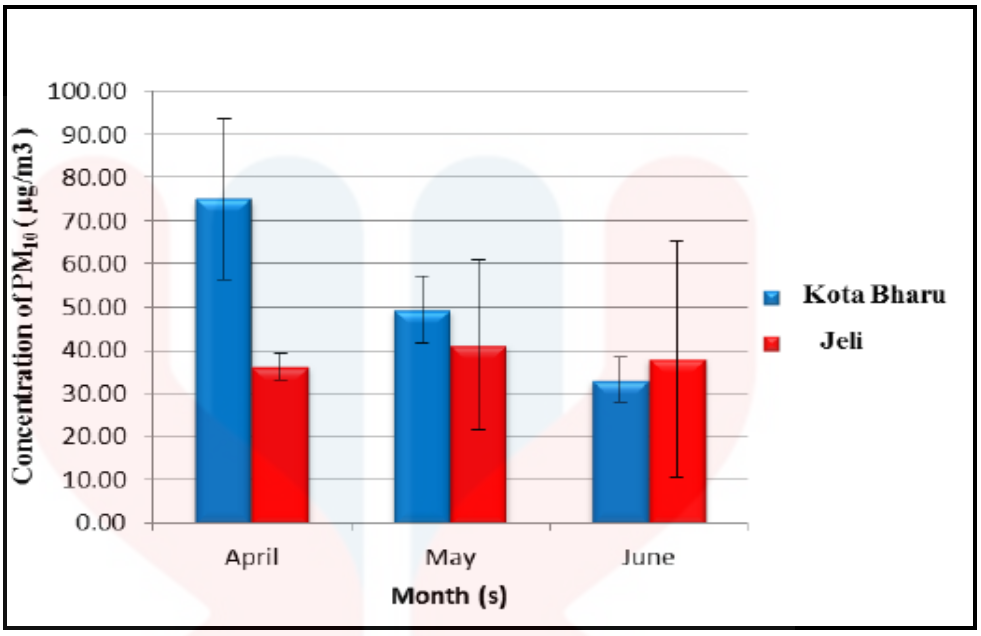


Figure 4.5: Monthly PM_{10} concentration comparison between urban and rural site

Figure 4.5 also shows average concentration of PM_{10} from urban site for April and May was higher than urban site. This can be supported with studies performed by Jamhari *et al*. (2014) in urban, semi-urban and industrial areas in Malaysia, concluding that urban site contributed to highest concentration of PM_{10} compared to semi-urban and industrial areas.

However, based on Figure 4.5 the average concentration of PM_{10} for June was higher in rural site than in urban site. In the past, urban areas were believed to be more polluted while the rural areas were less polluted or free from pollution. Today, air pollution has become widespread as it does not recognize geographic or political boundaries. According to Majra (2011) most of the rural areas all over the world in particular the developing countries might be more polluted than some urban areas. This was because rural areas are prone to pollution via both indoor and outdoor air pollution. Rural areas suffer from pollution through both natural and anthropogenic source. Human activities like burning solid fuel, tobacco smoking as well agriculture,

mining and cement making was proved to produce high level of outdoor air pollution (Majra, 2011).

According to Jandacka (2015), studies done in 'non-urban area' near open area close to highway in Slovakia showed three factors were involved in the formation of PM_{10} via multivariate statistical analysis in the study area. The factors include local combustion and non-exhaust traffic source (tyres) (23%), exhaust traffic source (diesel fuel, lubricating oil and earth crust) (44%) and road dusts (33%). The sampling site in rural area which was SK Batu Melintang was a roadside school where transportation might be the highest contributor of particulate matter.

Besides that, meteorological factors like winds do help in the dispersal and dilution of pollutants. However, according to Majra (2011) topography dominated by mountains and tall buildings will weaken the wind speed and cause pollutants to start concentrating in the breathing zone. This was also supported by Yadav *et al*. (2014) in which local wind was also a factor in the increase or decrease of PM_{10} concentration.

This can be associated with the rural sampling site in Batu Melintang which consist of high mountains namely Gunung Stong and densely forested area. The mountains and dense forests might be reason to decrease wind movement and accumulate air particulates leads to higher air particulates in rural area for the month of June. Furthermore, rural areas also need to bear the air pollution generated from urban area which moves with the wind. The higher concentration of PM_{10} could also be caused by winds that carry particulates from urban areas and deposit in the rural area. This can be supported with studies by Majra (2011) where dust and sand blown

by westerly winds usually picks up pollution from heavily industrialized countries like northeast of China, Shenyang and deposit them in South Korea and Japan.

4.5 Factors Affecting the Temporal Variation of PM_{10} Concentration

An Independent Sample T-test was used to test the difference in means between urban and rural area according to the respective months. Table 4.2 shows the comparison of PM_{10} concentration for the month of April for both sites. According to Table 4.2 the mean for PM_{10} concentration for Jeli was 36.27 $\mu g/m^3$ (ranging from 32.78 $\mu g/m^3$ to 38.39 $\mu g/m^3$) and 75.01 $\mu g/m^3$ (ranging from 51.01 $\mu g/m^3$ to 99.55 $\mu g/m^3$) respectively.

Table 4.2: Summary of PM_{10} concentration in April for Jeli and Kota Bharu

Variable	Month	Statistics	Site	
			Jeli	Kota Bharu
PM_{10} concentration ($\mu g/m^3$)	**April**	**Min**	32.78	51.01
		Max	38.39	99.55
		Mean	36.27	75.01
		Std Deviation	3.05	18.69
		p-value (0.05)	0.014	

Before the Independent Samples t-Test was conducted statistical analysis was done to detect for 'anomaly' or outliers in both of data set collected. The result proved there are no outliers detected for both urban and rural data and further analysis was done. An Independent Samples t-Test result as in Table A4 (Appendix A) shows there is significant difference in the mean of PM_{10} concentration for both locations (p<0.05). As discussed in Chapter 2, studies done in Klang Valley by

Shaadan *et al*. (2015) mentioned that wind speed along monsoon seasons and weekend-weekdays variation plays an influential role in affecting the concentration of PM_{10}.

Besides that, the difference in traffic flows during the weekends and weekdays might cause the concentration of PM_{10} to be different in urban and rural sites. Figure 4.1 shows for urban area on April, the highest concentration of PM_{10} was on 24th of April with 99.55 μg/m^3. The weekends and weekdays comparison of PM_{10} concentration as in Figure 4.3 shows that the air particulate was higher on 24th of April (Sunday) which was a weekday. This might be due to heavy transportation that release dust from exhaust engines as many people travel to go for work on weekdays. This can be supported with studies done by Hassan *et al*. (2013) where the concentration of PM_{10} will be higher on weekdays compared to during the weekends in urban areas.

Besides that, urban winds are thought to be lowered by both friction and urban canopy barriers due to uneven surface area and varying height of the buildings (The British Geographer, 2016). Hence, the lower speed of wind might cause particulate matters to be retained in the urban site and raise the concentration of PM_{10}. The lowest concentration of PM_{10} was on 23rd of April (Saturday) with 51.01 μg/m^3 during the weekends as shown in Table A1. This might be due to rainfall that carried the air particulates via wet deposition which reduced the amount of air particulates. Wet deposition happens when the particles are brought to surface by precipitating hydrometeors like rain drop and snows (Golomb *et al*., 2001).

For rural area, the highest concentration of PM_{10} was the highest on 26th of April (Tuesday) with 38.39 μg/m^3 and the lowest was on 27th of April (Wednesday)

with 32.78 μg/m^3. Figure 4.4 shows that both samples was collected during the weekdays where transportations are higher as people pass the area to work in city like Tanah Merah and Kota Bharu. The concentration of PM_{10} was also lower compared to urban area in April. This might be due to less transportation in rural area compared to the hectic urban area. Besides that, rainfall could also have carried the particulates to the ground via wet deposition. The average concentration of PM_{10} was below the value suggested by RMAQG for both sites. However, the mean of PM_{10} concentration for Kota Bharu exceeded the limit set by the European Commission with 50 μg/m^3 (European Commission, 2016).

Table 4.3 shows for May, the mean PM_{10} concentration for Jeli was 41.33 μg/m^3 (ranging from 18.01 μg/m^3 to 76.63 μg/m^3) and 49.47μg/m^3 (ranging from 37.54 μg/m^3 to 56.08 μg/m^3) respectively.

Table 4.3: Summary of PM_{10} concentration in May for Jeli and Kota Bharu

Variable	**Month**	**Statistics**	**Site**	
			Jeli	**Kota Bharu**
PM_{10} concentration (μg/m^3)	**May**	**Min**	18.01	37.52
		Max	76.63	56.08
		Mean	41.33	49.47
		Std Deviation	19.64	7.92
		p-value (0.05)	0.405	

The result of Independent Samples t-Test as in Table A6 (Appendix A) shows there is no significant difference in the mean of PM_{10} concentration for both locations (p<0.05). This was due to the fluctuation of PM_{10} concentration for urban

area as shown in Figure 4.1. For urban area, the concentration of PM_{10} was highest on 7th of May (Saturday) with 56.08 μg/m^3 while the lowest was on 14th of May (Saturday) with 37.52 μg/m^3. Figure 4.3 shows that the sample on 7th of May was collected from the weekends. However, the higher concentration of PM_{10} might be due to heavy transportations and other human activities (combustion and industrial) during the weekends. However, the concentration of PM_{10} was lowered again on 14th of May (Saturday) which might be due higher wind speed that carried the air particulates to the ground. Besides that, there is possibility that during that weekend there was less human activity (transport, combustion and industries) in the urban area. This might cause the PM_{10} concentration to decrease from 7th, 13th and 14th of May.

The concentration of PM_{10} also shows fluctuation in the rural area as shown in Figure 4.4. For the rural area, the concentration of PM_{10} was highest on 9th of May (Monday) with 76.63 μg/m^3 and the lowest on 22nd of May (Sunday) with 18.01 μg/m^3 as shown in Table A2. The higher concentration of PM_{10} on 9th of May (Monday) could be due to heavy transportation activity as the sample was from weekdays. This can be supported with data provided by Malaysian Meteorological Department (2016) for the Kota Bharu station. The weather for that day was sunny with no rainfall was observed. Besides that, higher wind speed can also increase the quantity of air particulates in the study area. This can be supported with studies by Shaheen *et al*. (2005) where the coarse particles and giant particles can be carried by high wind speeds under sunny condition. This might cause more air particulates to be present in the air and raise the concentration of PM_{10}. The concentration of PM_{10} showed slowly decreased from 76.63 μg/m^3 to 33.21 μg/m^3 for May.

By referring to Figure 4.4, the sample was collected during the weekdays where many people travel to work from the rural area to other neighboring cities. The lowest concentration of PM_{10} was on 22nd of May (Sunday) with 18.01 μg/m^3. Based on data by Kota Bharu weather monitoring station, it had rained heavily during that week with rainfall depth of 143 mm. The rainfall depth was among the highest observed from both urban and rural sites during the sample collection month. The heavy downpour that occurs during that week might have decreased the overall concentration of PM_{10} via wet deposition process. However, the average concentration of PM_{10} for May was below the value suggested by RMAQG for both sites. However, the mean of PM_{10} concentration for urban site was close to reach the limit set by EU commission.

Table 4.4 shows for June, the mean for PM_{10} concentration for Jeli was 38.01 μg/m^3 (ranging from 19.42 μg/m^3 to 86.05 μg/m^3) and 33.23 μg/m^3 (ranging from 24.86 μg/m^3 to 37.94 μg/m^3) respectively.

Table 4.4: Summary of PM_{10} concentration in June for Jeli and Kota Bharu

Variable	**Month**	**Statistics**	**Site**	
			Jeli	**Kota Bharu**
PM_{10} concentration (μg/m^3)	**June**	**Min**	19.42	24.86
		Max	86.05	37.94
		Mean	38.01	33.23
		Std Deviation	27.40	5.09
		p-value (0.05)	0.711	

An Independent Samples t-Test was conducted to test the difference in mean between both sampling sites. Table A8 (Appendix A) shows there is no significant

difference in the mean of PM_{10} concentration for both locations (p<0.05). This could be due to the fluctuation of PM_{10} concentration for urban area as shown in Figure 4.1. For urban site, the highest concentration of PM_{10} was on 23rd of June (Thursday) with 37.94 μg/m^3 and the lowest was on 4th of June (Saturday) with 24.86 μg/m^3. The concentration of PM_{10} on 23rd of June (Thursday) was the highest might be because the sample was collected during weekdays. Besides that, a day before sampling which was on 22nd June (Wednesday) it was public holiday for Hari Nuzul Al Quran in Kelantan. This might cause many people to travel to their hometown, go out for shopping or vacations due to public holidays in Kelantan. Moreover, the accumulated PM_{10} from the heavy transportation during that week might raise the PM_{10} concentration as less rainfall was observed for the week based on the meteorological data.

The concentration of PM_{10} was lowered on 4th of June (Saturday) although sample was collected from weekend which might be due to high wind speeds which reduced the PM_{10} concentration. This can be supported using the meteorological data where no rainfall and high wind speed was observed few days before the sampling period. For rural site, the highest concentration of PM_{10} was on 6th June (Monday) with 86.05 μg/m^3 while the lowest concentration of PM_{10} was on 7th June (Tuesday). The concentration of PM_{10} was high on 6th June (Monday) due to heavy transport and higher wind speed that might raise the concentration of PM_{10}.

Based on the data from meteorological station, although it had rained for that day but the concentration of PM_{10} was higher. This could be due to higher wind speed that carried the particulates before it had rained in the evening. The particulates might also be accumulated due to the increased emission of PM_{10} during the past few days as no rain was observed. However, the average concentration of

PM_{10} was below the value suggested by RMAQG. The mean of PM_{10} concentration for both sites did not exceed the limit set by the EU Commission.

Therefore, we can conclude that the average concentration of PM_{10} was higher in urban area than rural area based on Table 4.1. However, the result from the Independent Samples t-Test conducted as in Table A10 (Appendix A) shows there is no significant difference in the average concentration of PM_{10} from both sampling sites. This might be due to the temporal fluctuation of the PM_{10} concentration during the different sampling months which had affected the result of Independent Samples t- Test. The fluctuation in the concentration of PM_{10} in all three months could be due to factors as mentioned by Shaadan *et al*. (2015) which are high human activity from heavy transportation, industries, agriculture and meteorological factors like wind speed, rainfall and topography of sampling site.

4.6 Summary of PAH Found in Urban and Rural Area Sample

A total of 12 aerosol samples was analyzed to detect the presence of polycyclic aromatic hydrocarbons in which six samples was from urban site and other six was from rural area. The detected PAH from rural and urban site was as in Table 4.5. The concentration of PM_{10} in urban area ranged between 24.86 - 99.55 $\mu g/m^3$. However, only two samples with one maximum and one minimum concentration of PM_{10} in the month was chosen for PAHs analysis due to instrument constraint. This was carried out to compare the possible PAHs with respect to the concentration of PM_{10}. Table 4.5 shows the sample date and type of PAH found in the urban and rural area after analysis.

Table 4.5: PAH found in urban and rural area from analyzed samples

No	Site	Sample date	Concentration of PM_{10} ($\mu g/m^3$)	Weather	PAHs detected	Ring number
1	Urban	22nd April 2016 (Friday)	51.01	Sunny	1-methyl naphthalene	2
2	Urban	24th April 2016 (Sunday)	99.55	Sunny	Not detected	-
3	Urban	14th May2016 (Saturday)	37.52	Sunny	Not detected	-
4	Urban	7th May 2016 (Saturday)	56.08	Sunny	1-methyl naphthalene	2
5	Urban	4th June 2016 (Saturday)	24.86	Sunny	Not detected	-
6	Urban	23rd June 2016 (Thursday)	37.94	Rainy	Not detected	-
7	Rural	27th April 2016 (Wednesday)	32.78	Sunny	1-methyl naphthalene	2
8	Rural	26th April 2016 (Tuesday)	38.39	Sunny	Not detected	-
9	Rural	22nd May 2016 (Sunday)	18.01	Sunny	Not detected	-
10	Rural	09th May 2016 (Monday)	76.63	Sunny	Not detected	-
11	Rural	07th June 2016 (Tuesday)	19.42	Rainy	Not detected	-
12	Rural	06th June 2016 (Monday)	86.05	Rainy	Not detected	-

Based on Table 4.5, for April the PAH detected was 1-methylnaphthalene as shown by Figure C1 (Appendix C) from sample dated 22nd of April (Friday). However, the other sample from 24th of April (Sunday) shows no PAH was detected.

For May, the sample on 7th of May (Saturday) shows one PAH was detected which was 1-methylnaphthalene as shown by Figure C2 (Appendix C). While the other sample on 14th of May (Saturday) shows no PAHs were detected. However, both samples analyzed from June shows there are no PAHs detected. For rural area in April the PAH detected was 1-methylnaphthalene from 27th of April (Wednesday) as shown in Appendix C (Figure C3). The remaining analyzed samples from May and June shows none of the PAHs were detected.

4.7 Comparison of PAH Between Rural and Urban Area

Based on Table 4.5, the only PAH detected in the sample from urban and rural area was similar as both site detected 1- methylnaphthalene. But, in normal periods LMW PAHs (2 – 3 rings) like 1-methylnaphthalene was harder to detect as they are mostly found to be associated with vapour phase than particulate phase. Therefore, the LMW PAHs were normally being ignored in the analysis of PAHs (Suvarapu *et al*., 2012). However, 1-methylnaphthalene was detected in the sample from urban and rural area as it was a common pollutant released from combustion of fossil fuels, wood, exhaust smokes and industrial discharge (ATSDR, 2005).

Based on Table 4.5, the urban site have PAH detected in both April and May compared to rural area where PAH was detected only in April. For urban site, PAHs was detected in sample from 22nd April (Friday). This can be supported with heavy transportation in urban area as 1-methylnaphthalene mostly originates from fossil fuel combustion. During sampling, the weather was observed to be sunny which makes the volatile PAHs like 1-methylnaphthalene to be present in the sample. According to Mohanraj *et al*. (2012) that PAHs with two or three benzene rings were

most likely to exist in vapour form. This was because the hot weather might increase the rate of volatilization of PAHs with two to three rings. For May, PAH was detected in sample from 7th May (Saturday).

According to data from the weather monitoring station, the sunny weather makes the volatile 1-methylnaphthalene to be detected. Besides that, the sample was collected during the weekends where most people might travel out to buy groceries or shopping. This could increase the amount of car travelling on the road in the urban site. For rural site, the PAH was detected only in April while for May and June no PAH was detected. For April, PAH was detected in sample from 27th April (Wednesday) only. This could be due to more transportation which caused the amount of 1-methylnaphthalene to be higher in the sample. In June, no PAHs was detected which might be due to the rainfall observed during the sampling days that reduce the amount of PAHs in atmosphere.

The other PAHs were not detected from the GCMS analysis because the PAHs might not present in the sample. This might be due to the higher molecular weight PAHs are more abundant in atmospheric particles and the lower molecular weight particles was found to be more dominant in street dusts (Omar *et al.*, 2002). The location of air sample placed to collect PM_{10} was also not high to capture atmospheric air particulates. Therefore, the source of particulate matter might be mixture from the street dust and some atmospheric particles dispersed due to heavy transportation as both sampling sites were located near roadside. Thus, the sample might not contain higher atmospheric particles which could adhere a higher molecular weight PAHs (4 – 6 rings). Besides that, heavy wind might blow the heavier particles far from the sampling location as heavier particles have higher tendency to be carried by the wind.

4.8 Factors Affecting the Presence of PAHs in Aerosol Samples

Meteorological factors like air temperature, wind direction, wind speed, air mass trajectory and precipitation rates are important factors that affect the distribution and deposition of PAH from atmosphere (Suvarapu *et al*., 2012; Park *et al*., 2001). This can be seen in Figure 4.1 and 4.2 which shows the fluctuation in the concentration of PM_{10} due to meteorological factors and human activities (heavy transportation and industries). This might be the reason PAHs were not detected from the month of June from both study area due to more rainy days during sampling. Moreover, heavy rainfalls and higher wind speeds might results in more air particles to be blown away or dissolved. More rainfall favors the wet deposition of PAHs in which the PAHs are likely to be incorporated with rainwater and dissolved (Ollivon *et al*., 2002).

Therefore, it can be concluded that the concentration of PM_{10} possess relation with PAHs detection on samples. This was the detected PAHs are all from the sample with lower concentration of PM_{10}. The presence of LMW PAHs like 1-methylnaphthalene detected in the urban and rural samples shows that the volatilization rate at sampling sites was low as mentioned by Jamhari *et al*. (2014). This might also be affected with the meteorological factors like temperature, wind speed and precipitation in study area. Frequent rain and other meteorological factors during sampling from the end of April till the end of June in both Jeli and Kubang Kerian might have effect to the result of study. The location of the air sampler being placed also plays a major role in the type of PAH to be detected.

According to Jamhari *et al*. (2014), total PAHs was found to be effected when the air sampler was placed at rooftop of a three-storey building due to meteorological

factors such as wind and rainfall. Although, the study did not found any of the PAHs listed in the US EPA priority PAHs, the presence of 1-methylnaphthalene proves that heavy transportation could give rise to PAHs in environment. Naphthalene with two rings is classified as a probable carcinogen released from combustions of fuels and gasoline in automobile vehicles (Jia & Batterman, 2010). This was because previously 1-methylnaphthalene had been cited by USEPA as one of the 21 mobile source air toxics (MSAT's) (He *et al*., 2010). According to Andersson and Achten (2015), there are many other PAHs considerably higher toxicity not included in the traditional list of US EPA. This established list was used though human knowledge and analytical potential had increased due to less study done regarding the frequency and toxicity of other types of PAHs.

Generally, the urban site (SMK Kubang Kerian 1) and rural site (SK Batu Melintang) was not affected with PAHs listed by US EPA. The absence of HMW PAHs shows that the school students were less likely to be affected with adverse health effects during the time they spent in the school compound. This was because HMW PAHs are mostly associated with adverse effects due to their carcinogenicity, toxicity and mutagenicity (Jedrychowski *et al*., 2003).

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

As a conclusion, the average concentration of PM_{10} for Kota Bahru was higher than for Jeli which was 52.57 $\mu g/m^3$ and 39.21 $\mu g/m^3$ respectively. However, result from the Independent Sample T- test shows that the mean concentration of PM_{10} between both sites was not significantly different with the p-value of 0.083. This was due to the fluctuation in the concentration of PM_{10} from three different months affects the result of Independent Samples t- Test. The result from Independent Samples t-Test for April was significant, however for May and June the result was not significant. This was due to fluctuation of PM_{10} concentration by meteorological factors and human activity in the study area.

The PAH detected from the sample from urban and rural area was 1-methylnaphthalene a type of LMW PAHs. None of the US EPA 16 priority PAHs was detected in the samples. Besides that, most PAHs were detected from sample with lower concentration of PM_{10} as both human activity and the meteorological factors have effect to the association of PAH with PM_{10}. We can conclude that the urban site (SMK Kubang Kerian 1) and rural site (SK Batu Melintang) was not affected with US EPA 16 priority PAHs shows that the school students were less likely to be affected with adverse health effects.

5.2 Recommendations

For future study, the aerosol samples can be collected from urban and rural sites during both weekends and weekdays. This will allow us to have a better comparison and understanding on the real factors that might affect the fluctuation characteristic of air particulates. Besides that, the sample collection duration can be prolonged to more than three months to increase data on PM_{10} concentration. This will allow researchers to have more data to analyze the fluctuation characteristic of PM_{10} in urban and rural sites. Moreover, sampling could be done by selecting more than one location to represent both rural and urban area. By increasing the location of study allows a better understanding of the characteristics of air pollutants.

REFERENCES

Abas, M. R., Oros, D. R., & Simoneit, B. R. T. (2004). Biomass burning as the main source of organic aerosol particulate matter in Malaysia during haze episodes. *Chemosphere, 55*, 1089-1095.

Abdel-Shafy, H. I., & Mansour, M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum, 25*, 107-123.

Abdullah, A. M., Samah, M. A. A., & Jun, T. Y. (2012). An overview of the air pollution trend in Klang Valley, Malaysia. *Open Environmental Science, 6*, 13-19.

Abid, Z., Roy, A., Herbstman, J. B., & Ettinger, A. S. (2014). Urinary polycyclic aromatic hydrocarbons metabolites and attention/deficit hyperactivity disorder, learning disability, and special education in U. S children aged 6 to 15. *Journal of Environmental and Public Health*, 10.

Afroz, R., Hassan, M. N., & Ibrahim, N. A. (2003). Review of air pollution and health impacts in Malaysia. *Environmental Research, 92*, 71-77.

Agency for Toxic Substances and Disease Registry (ATSDR) (2005). US Department of Health and Human Services, 1 – 172.

Air Quality in Europe. (2014). European Environment Agency, 5 - 80. Retrieved from: http://www.eea.europa.eu/publications/air-quality-in-europe-2014/download

Al-Turki, A. I. (2009). Microbial polycyclic aromatic hydrocarbons degradation in the soil. *Research Journal of Environmental Toxicology, 3*(1), 1-8.

Algeria-Torres, J. A., Barreta, F., Batres-Esquivel, L. E., Carrizales-Yanez, L., Peres-Maldonado, I. N., Baccarelli, A., & Bertazzi, P. A. (2013). Epigenetic markers of exposure to polycyclic aromatic hydrocarbons in Mexican brickmakers: a pilot study. *Chemosphere, 91*, 475-480.

Amarillo, A. C., Tavera Busso, I., & Carreras, H. (2014). Exposure to polycyclic aromatic hydrocarbons in urban environments : health risk assessments by age groups. *Environmental Pollution, 195*, 157-162.

Amarsaikhan, D., Battsengel, V., Nergui, B., Ganzorig, M., & Bolor, G. (2014). A study on air pollution in Ulaanbaatar City, Mongolia. *Journal of Geoscience and Environment Protection, 2*, 123-128.

American Journal of Respiratory and Critical Care Medicine. (2000). What constitutes an adverse health effect of air pollution. Retrieved from : http://www.atsjournals.org/doi/abs/10.1164/ajrccm.161.2.ats4-00#readcube-epdf

Andersson, J. T., & Achten, C. (2015). Time to say goodbye to the 16 EPA PAHs. Towards an up-to-date use of PACs for environmental purposes. *Polycyclic Aromatic Hydrocarbon Compounds, 35*, 330-354.

Azhari, A., Dalimin, M. N., & Wee, S. T. (2011). *Polycyclic aromatic hydrocarbons (PAHs) pollution from vehicle emission in the environment of highway roadside in Johor, Malaysia*. Paper presented at the International Conference on Biotechnology and Environment Management, Singapore.

Azid, A., Juahir, H., Toriman, M. E., Endut, A., Kamarudin, M. K. A., Rahman, M. N. A., Noraini, C. H. C., Saudi, A. S. M & Yunus, K. (2011). Source Apportionment of Air Pollution : A case study in Malaysia. *Jurnal Teknologi, 72*(1), 83-88.

Azmi, S. Z., Latif, M. T., Ismail, A. S., Juneng, L & Jemain, A. A. (2010). Trend and status of air quality at three different monitoring stations in the Klang Valley, Malaysia. *Air Quality, Atmosphere & Health, 3*, 53-64.

Bahry, P. S. (2007). *Characterization of polycyclic aromatic hydrocarbons in atmospheric aerosols collected from selected locations in Peninsular Malaysia.* Unpublished MSc Thesis, Universiti Putra Malaysia.

Bahry, P. S., Zakaria, M. P., Bin Abdullah, A. M., Abdullah, D. K., Sakari, M., Chandru, K., & Shahbazi, A. (2009). Forensic characterization of polycyclic aromatic hydrocarbons and hopanes in aerosols from Peninsular Malaysia. *Environmental Forensics, 10*, 240-252.

Bi, X., Sheng, G., Peng, P., Chen, Y & Fu, J. (2005). Siz distribution of *n*- alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhao, China. *Atmospheric Environment, 39*, 477-487.

Bian, Q., Alharbi, B., Collett Jr, J., Kreidenweis, S., & Pasha, M. J. (2016). Measurements and source apportionment of particle-associated polycyclic aromatic hydrcarbons in ambient air in Riyadh, Saudi Arabia. *Atmospheric Environment, 137*, 186-198.

Boonyatumanond, R., Murakami, M., Wattayakorn, G., Togo, A., & Takada, H. (2007). Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Science of the Total Environment, 384*, 420-432.

Bostrom, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johannson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., & Westerholm, R. (2002). Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environmental Health Perspectives, 110*, pp. 451-488.

Callan, M. S., Lopez, J. M., Iturmendi, A., & Mastral, A. M. (2013). Nature and sources of particle associated polycyclic aromatic hydrocarbons (PAH) in the atmospheric environment of an urban area. *Environmental Pollution, 183*, 166-174.

Chen, B., & Kan, H. (2008). Air pollution and population health: a global challenge. *Environment Health and Preventive Medicine, 13*(2), 94-101.

Chow, J. C., Watson, J. G., Fujita, E. M., Lu, Z., & Lawson, D. R. (1994). Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California Air Quality Study. *Atmospheric Environment, 28*(12), 2061-2080.

Chow, J. C., Watson, J. G., Lowenthal, D. H., Solomon, P. A., Magliano, K. L., Ziman, S. D., & Richards, L. W. (1992). PM_{10} source apportionment in California's San Joaquin Valley, *Atmospheric Environment, 264*, 3354-3354.

Dominick, D., Juahir, H., Latif, M. T., Zain, S. M., & Aris, A. Z. (2013). Spatial assessment of air quality patterns in Malaysia using multivariate analysis. *Atmospheric Environment, 60*, 172-181.

Dong, T. T. T., & Lee, B. K. (2009). Characteristics, toxicity, and source apportionment of polycylic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea. *Chemosphere, 74*, 1245-1253.

Department of Statistics Malaysia. (2015). Population and Housing Census. 26 April 2016. Retrieved from : https://www.statistics.gov.my/index.php?r=column/cone&menu_id=bDA2VkxRSU40STcxdkZ4OGJ0c1ZVdz09

Fadzil, M. F., Tahir, N. M., & Zin, W. M. K. W. M. (2008). Concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) in the town of Kota Bharu, Kelantan Darul Naim. *The Malaysian Journal of Analytical Sciences, 12*(3), 609-618.

Franco, S. S., Nardocci, A. C., & Gunther, W. M. R. (2008). PAH biomarkers for human health risk assessment: a review of the state-of-the-art. *Scientific Electronic Library Online*, 569-580.

Gocht, T., Klemm, O., & Grathwohl, P. (2007). Long term atmospheric bulk deposition of polycyclic aromatic hydrocarbons (PAHs) in rural areas of Southern Germany. *Atmospheric Environment, 41*, 1315-1327.

Golomb, D., Barry, E., Fisher, G., Varanusupakul, P., Koleda, M., & Rooney, T. (2001). Atmospheric deposition of polycyclic aromatic hydrocarbons near New England coastal waters. *Atmospheric Environment, 35*, 6245-6258.

Google Earth. (2016). Accessed on 17 May 2016.

Hassan, S. K., El-Abssawy, A. A., AbdEl-Maksoud, A. S., Abdou, M. H., & Khoder, M. I. (2013). *Aerosol and Air Quality Research, 13*, 1552-1562.

He, C., Ge, Y., Tan, J., You, K., Han, X., & Wang, J. (2010). Characteristics of polycyclic aromatic hydrocarbons emissions of diesel engine fuelled with biodiesel and diesel. *Fuel, 89*, 2040-2046.

Hui, T. J., Seng, H. T., Abas, M. R., & Tahir, N. M. (2008). Distribution and health risks of polycyclic aromatic hydrocarbons (PAHs) in smoke aerosols from burning of selected garden wastes. *The Malaysian Journal of Analytical Sciences, 12*(2), 357-366.

Ismail, W. I. F. W. (1996). Urban growth determinants for the state of Kelantan: opinions of the state's policy makers. *Buletin Ukur, 7*(3), 176-189.

Jamhari, A. A., Sahani, M., Latif, M. T., Chan, K. M., Tan, H. S., Khan, M. F., & Tahir, N. M. (2014). Concentration and source identification of polycyclic aromatic hydrocarbons (PAHs) in PM_{10} of urban, industrial and semi-urban areas in Malaysia. *Atmospheric Environment, 86*, 16-27.

Jandacka, D. (2015). Sources of PM_{10} air pollution in rural area in the vicinity of a highway in Zilina selfgoverning region, Slovakia. *Civil and Environmental Engineering, 11*(1), 58-68.

Jang, E., Alam, M. S., & Harrison, R. M. (2013). Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. *Atmospheric Environment, 79*, 271-285.

Jedrychowski, W., Whyatt, R. M., Camann, D. E., Bawle, U. V., Peki, K., Spengler, J. D., Dumyahn, T. S., Penar, A & Perera, F. F. (2003). Effect of prenatal PAH exposure on birth outcomes and neurocognitive development in a cohort of newborns in Poland. Study design and preliminary ambient data. *International Journal of Occupational Medicine and Environmental Health, 16*(1), 21-29.

Jeli Land and Administration Office. (2014). *Keluasan dan komposisi penduduk* Retrieved 26 April 2016 : http://www.ptjj.kelantan.gov.my/v4/index.php?option=com_content&view=article&id=45&Itemid=281&lang=ms

Jia, C., & Batterman, S. (2010). A critical review of naphthalene sources and exposures relevant to indoor and outdoor air. *International Journal of Environmental Research and Public Health, 7*, 2903-2939.

Juneng, L., Latif, M. T., & Tangang, F. (2011). Factors influencing the variations of PM_{10} aerosol dust in Klang Valley, Malaysia during the summer. *Atmospheric Environment, 45*, 4370-4378.

Jung, K. H., Perzanowski, M., Rundle, A., Moors, K., Yan, B., Chillrud, S. N., Whyatt, R., Camann, D., Pereira, F. P & Miller, R. L. (2014). Polycyclic aromatic hydrocarbon exposure, obesity and childhood asthma in an urban cohort. *Environmental Research* (128), 35-41.

Jyethi, D. S., Khillare, P. S., & Sarkar, S. (2014). Risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in school children. *Environmental Science Pollution Research, 21*(1), 366-378.

Karar, K., Gupta, A. K., Kumar, A., Biswas, A. K., & Devotta, S. (2006). Statistical interpretation of weekday/weekend differences of ambient particulate matter, vehicular traffic and meteorological parameters in an urban region of Kolkata, India. *Indoor and Built Environment, 15*(3), 235-245.

Karimi, P., Peters, K. O., Bidad, K., & Strickland, P. L. (2015). Polycyclic aromatic hydrocarbons and childhood asthma. *European Journal of Epidemiology, 30*(2), 91-101.

Kaur, S., Senthilkumar, K., Verma, V. K., Kumar, B., Kumar, S., Katnoria, J. K., & Sharma, C. S. (2013). Preliminary analysis of polycyclic aromatic hydrocarbons in particles (PM_{10}) in Amritsar, India: sources, apportionment, and possible risk implications to humans. *Archives of Environmental Contamination and Toxicology, 65*(3), 382-395.

Kavitha, M., Juliana, J., & Abdah, M. A. (2011). Relationship between exposure to particulate matter and biomarkers among bus drivers in Klang Valley, Malaysia. *Health and Environment Journal, 2*(2), 1 - 5.

Kelly, F. J., & Fussel, J. C. (2012). Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmospheric Environment, 60*, 504-526.

Kim, K.-H., Jahan, S. A., Kabir, E., & Brown, R. J. C. (2013). A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International, 60*, 71-80.

Kim, Y. (2010). *Impacts of transportation, land uses and meteorology on urban air quality*. Unpublished Doctorate thesis, The Ohio State University

Lai, C.-H., Chen, K.-S., & Wang, H.-K. (2009). Influence of rice straw burning on the levels of polycyclic aromatic hydrocarbons in agricultural county of Taiwan. *Journal of Environmental Sciences, 21*, 1200-1207.

Lamichhane, S., Bal Krishna, K. C., & Sarukkalige, R. (2016). Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: a review. *Chemosphere, 18*, 336-353.

Lammel, G. (2015). Polycyclic aromatic compounds in the atmosphere: a review identifying research needs. *Polycyclic Aromatic Compounds*, 1-14.

Lee, B. K., & Vu, V. T. (2010). Sources, Distribution and Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) in Particulate Matter. *Air Pollution* (pp. 370).

Lee, Y. J., Shin, H. J., Bae, S. Y., Kim, Y. P., & Kang, C.-H. (2008). Seasonal variation of particle size distributions of PAHs at Seoul, Korea. *Air Quality, Atmosphere & Health, 1*, 57-68.

Li, X., Kong, S., Yin, Y., Li, L., Yuan, L., Li, Q., Xiao, H & Chen, K. (2016). Polycyclic aromatic hydrocarbons (PAHs) in atmospheric $PM_{2.5}$ Around 2013 Asian youth games period in Nanjing. *Atmospheric Research*.

Lenschow, P., Abraham, H. J., Kutzner, K., Lutz, M., Preub, J. D., & Reichenbacher. (2001). Some ideas about the sources of PM_{10}. *Atmospheric Environment, 35*, S23-S33.

Liu, G., Tong, Y., Luong, J. H. T., Zhang, H., & Sun, H. (2010). Asource study of atmospheric polycyclic aromatic hydrocarbons in Shenzhen, South China *Environmental Monitoring Assessment, 163*, 599-606.

Lv., Y., Li, X., Xu, T. T., Cheng, T. T., Yang, X., Chen, J. M., Iinuma, Y & Herrmann, H. (2016). Size distributions of polycyclic aromatic hydrocarbons in urban atmosphere: sorption mechanism and source contributions to respiratory deposition. *Atmospheric Chemistry and Physics, 16*, 2971-2983.

Ma, J., & Zhou, Y. (2011). Soil pollution by polycyclic aromatic hydrocarbons: a comparison of two Chinese cities *Journal of Environmental Sciences, 23*(9), 1518-1523.

Mahmoodi, M., Safahieh, A., Nikpour, Y., & Ghanemi, K. (2012). Distribution and sources of polycyclic aromatic hydrocarbons in the sediment of Bushehr coastal zone-Iran. *Iranica Journal of Energy & Environment, 3*(2), 173-179.

Majra, J. P. (2011). Air quality in rural areas. Chapter 23: Chemistry, Emission Control, Radioactive Pollution and Indoor Air Quality, 307-316.

Maliszewska-Kordybach, B. (1999). Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. *Polish Journal of Environmental Studies, 8*(3), 131-136.

Manzetti, S. (2013). Polycyclic aromatic hydrocarbons in the environment : environment fate and transformation. *Polycyclic Aromatic Hydrocarbons, 33*, 311-330.

Ministry of Water, Land and Air Protection. (2003). Particulate Matter in British Columbia: A report on PM_{10} and $PM_{2.5}$ mass concentrations up to 2000.

Mohanraj, R., Dhanakumar, S., & Solaraj, G. (2012). Polycyclic Aromatic Hydrocarbons bound to $PM_{2.5}$ in urban Coimbatore, India with emphasis on source apportionment. *The Scientific World Journal*.

Mohanraj, R., Solaraj, G., & Dhanakumar, S. (2011). Fine particulate phase PAHs in ambient atmosphere of Chennai metropolitan city, India. *Environmental Science Pollution Research, 18*, 764-771.

Motallebi, N., Tran, H., Croes, B. E., & Larsen, L. C. (2003). Day of the week patterns of particulate matter and its chemical components at selected sites in California. *Journal of the Air & Waste Management Association, 53*, 876 - 888.

Mu, L., Peng, L., Cao, J., He, Q., Li, F., Zhang, J., Liu, X & Bai, H. (2013). Emissions of polycyclic aromatic hydrocarbons from coking industries in China. *Particuology, 11*, 86-93.

Naser, T. M., Yoshimura, Y., Sekiguchi, K., Wang, Q., & Sakamoto, K. (2008). Chemical composition of $PM_{2.5}$ and PM_{10} and associated polycyclic aromatic hydrocarbons at a roadside and an urban background area in Saitama, Japan *Asian Journal of Atmospheric Environment, 2*(2), 90-91.

Okuda, T., Kumata, H., Zakaria, M. P., Naraoka, H., Ishiwatari, R., & Hideshige, T. (2002). Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atmospheric Environment, 36*, 611-618.

Ollivon, D., Blanchoud, H., Motelay-Massei, A., & Garban, B. (2002). Atmospheric deposition of PAHs to an urban site, Paris, France. *Atmospheric Environment, 36*, 2891-2900.

Omar, N. Y. M. J., Abas, M. R., Ketuly, K. A., & Tahir, N. M. (2002). Concentrations of PAHs in atmospheric particles (PM_{10}) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmospheric Environment, 36*, 247-254.

Polish Iron Lungs. (2015). Retrieved from:www.krakowskialarmsmogowy.pl/infoair/download/id/668

Rahman, S. R. A., Ismail, S. N. S., Ramli, M. F., Latif, M. T., Abidin, E. Z., & Praveena, S. M. (2015). The assessment of ambient air pollution trend in Klang Valley, Malaysia. *World Environment, 5*(1), 1 - 11.

Rai, R., Rajput, M., Agrawal, M., & Agrawal, S. B. (2011). Gaseous air pollutants: a review on current and future trends of emissions and impact on agriculture. *Journal of Scientific Research, 55*, 78-102.

Ravindra, K., Mittal, A. K., & Van Grieken, R. (2001). Health risk assessment of urban suspended particulate matter with special reference to polycyclic aromatic hydrocarbons: a review. *Review on Environmental Health, 16*, 169-189.

Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulations. *Atmospheric Environment*.

Rengarajan, T., Rajendran, P., Nandakumar, N., Lokeshkumar, B., Rajendran, P., & Nishigaki, I. (2015). Exposure to polycyclic aromatic hydrocarbons with special focus on cancer. *Asian Pacific Journal of Tropical Biomedicine, 5*(3), 182-189.

Ruchirawat, M., Settachan, D., Navasumrit, P., Tuntawiroon, J., & Autrup, H. (2007). Assessment of potential cancer risk in children exposed to urban air pollution in Bangkok, Thailand. *Toxicology Letters, 168*, 200-209.

Salam, M. A., Shirasuna, Y., Hirano, K., & Masunaga, S. (2011). Particle associated polycyclic aromatic hydrocarbons in the atmospheric environment of urban and suburban residential area. *International Journal of Science and Technology, 8*(2), 255-266.

Saffarini, G., & Odat, S. (2008). Time series analysis of air pollution in Al-Hashimeya town Zarqa, Jordan. *Jordan Journal of Earth and Environmental Sciences, 1*(2), 63-72.

Shaadan, N., Jemain, A. A., Latif, M. T., & Deni, S. M. (2015). Anomaly detection and assessment of PM_{10} functional data at several locations in the Klang Valley. *Atmospheric Pollution Research, 6*, 365-375.

Shaheen, N. , Shah, M. N., & Jaffar, M. (2005). A study of airborne selected metal and particle size distribution in relation to climatic variables and their source identification. *Water and Soil Pollution*, 164, 275-294.

Sienra, M. D. R., Rosazza, N. G., Prendez, M. (2005). Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in urban atmospheric respirable particulate matter. *Atmospheric Research, 75*, 267-281.

Silva Junior, R, S., Oliveira, M. G. L., & Andrade, M. F. (2009). Weekend/weekday differences in concentrations of ozone, NO_X and non-methane hydrocarbon in the metropolitan area of Sao Paulo. *Revista Brasileira de Meteorologia, 24*(1), 100-110.

Sharma, H., Jain, V. K., & Khan, Z. H. (2007). Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in the urban environment of Delhi. *Chemosphere, 66*, 302-310.

Srogi, K. (2007). Monitoring of environmental exposure to polycyclic aromatic hydrocarbons :a review. *Environment Chemistry Letters, 5*, 169-195.

Suman, S., Sinha, A., & Tarafdar, A. (2016). Polycyclic aromatic hydrocarbons (PAHs) concentration levels, pattern, source identification and soil toxicity assessment in urban traffci soil of Dhanbad, India. *Science of the Total Environment, 545-546*, 353-360.

Suvarapu, L. N., Seo, Y.-K., Cha, Y.-C., & Baek, S.-O. (2012). A review on the atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) in Asia since 2000-part ii: data from developing countries *Asian Journal of Atmospheric Environment, 6*(3), 169-191.

Tuntawiroon, J., Mahidol, C., Navasumrit, P., Autrup, H., & Ruchirawat, M. (2007). Increased health risk in Bangkok children exposed to polycyclic aromatic hydrocarbons from traffic-related sources. *Carcinogenesis, 28*(4), 816-822.

Turk, Y. A., & Kavraz, M. (2011). Air Pollutants and Its Effects on Human Healthy: The Case of the City of Trabzon In P. A. Moldoveanu, *Advanced Topics in Environmental Health and Air Pollution Case Studies*: InTech.

The British Geographer. (2016). Urban climates Retrieved from: http://thebritishgeographer.weebly.com/urban-climates.html

Valavanidis, A., Fiotakis, K., & Thomais, V. (2008). Airborne particulate matter and human health : toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. *Journal of Environmental Science and Health, 26*(4), 339-362.

Wahid, N. B. A., Latif, M. T., Suan, L. S., Dominick, D., Sahani, M., Jaafar, L. S., & Tahir, N. M. (2014). Source identification of particulate matter in a semi-urban area of Malaysia using multivariate techniques. *Bulletin of Environmental Contamination and Toxicology, 92*(2), 317-322.

WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. (2005).

Yadav, R., Sahu, L. K., Jaaffrey, S. N. A., & Beig, G. (2014). Temporal variation of particulate matter (PM) and potential sources at an urban site of Udaipur in Western India. Ae*rosol and Air Quality Research, 14*, 1613-1629.

Yatkin, S., & Bayram, A. (2007). Elemental composition and sources of particulate matter in the ambient air of a metropolitan city. *Atmospheric Research, 85*, 126-139.

Yu, B., Xie, X., Ma, L. Q., Kan, H., & Zhou, Q. (2014). Source, distribution and health risk assessment of polycyclic aromatic hydrocarbons in urban street dust from Tianjin, China. *Envronmental Science Pollution Research, 21*, 2817-2825.

Zhang, Y., Tao, S., Shen, H., & Ma, J. (2009). *Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population*. Proceedings of the National Academy of Sciences, *106*(50), 21063-21067.

APPENDIX A

Table A1: PM_{10} sampling data at Kota Bharu SMK Kubang Kerian 1 (Urban)

No	Date	Concentration of PM_{10} ($\mu g/m^3$)
1	22 April 16	71.563
2	23 April 16	51.0069
3	24 April 16	99.550
4	28 April 16	66.389
5	29 April 16	86.528
6	06 May 16	55.590
7	07 May 16	56.076
8	13 May 16	45.410
9	14 May 16	37.535
10	20 May 16	52.741
11	03 June 16	35.915
12	04 June 16	24.861
13	23 June 16	37.941
14	24 June 16	32.326
15	25 June 16	35.104

Table A2: PM_{10} sampling data at Batu Melintang SK Batu Melintang (Rural)

No	Date	Concentration of PM_{10} ($\mu g/m^3$)
1	25 April 16	37.639
2	26 April 16	38.389
3	27 April 16	32.778
4	02 May 16	35.139
5	03 May 16	29.722
6	09 May 16	76.632
7	10 May 16	57.986
8	17 May 16	33.213
9	18 May 16	38.576
10	22 May 16	18.008
11	01 June 16	23.056
12	05 June 16	34.028
13	06 June 16	86.051
14	07 June 16	19.417
15	13 June 16	27.500

Table A3: Group statistics between two locations for April

Sampling Location		N	Mean	Std. Deviation	Std. Error Mean
PM_{10}	Jeli	3	36.2687	3.04618	1.75871
	Kota Bharu	5	75.0072	18.68960	8.35824

Table A4: Result of Independent Sample t-Test between both locations for April

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	Df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
PM_{10}	Equal variances assumed	4.585	.076	-3.453	6	.014	-38.73851	11.21809	-66.18820	-11.28883
	Equal variances not assumed			-4.535	4.345	.009	-38.73851	8.54127	-61.72841	-15.74861

Table A5: Group statistics between two locations for May

Sampling location		N	Mean	Std. Deviation	Std. Error Mean
PM_{10}	Jeli	7	41.3251	19.63888	7.42280
	Kota Bharu	5	49.4704	7.91708	3.54063

Table A6: Result of Independent Sample t-Test between both locations for May

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
PM_{10}	Equal variances assumed	2.549	.141	-.869	10	.405	-8.14526	9.37748	-29.03959	12.74908
	Equal variances not assumed			-.990	8.389	.350	-8.14526	8.22399	-26.95766	10.66715

Table A7: Group statistics between two locations for June

Sampling site		N	Mean	Std. Deviation	Std. Error Mean
PM_{10}	Jeli	5	38.0104	27.40244	12.25475
	Kota Bharu	5	33.2294	5.09343	2.27785

Table A8: Result of Independent Sample t-Test between both locations for June

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
PM_{10}	Equal variances assumed	4.034	.079	.384	8	.711	4.78100	12.46465	-23.96252	33.52452
	Equal variances not assumed			.384	4.276	.720	4.78100	12.46465	-28.96281	38.52481

Table A9: Group statistics for total sample for Jeli and Kota Bharu

Sampling location		N	Mean	Std. Deviation	Std. Error Mean
PM_{10}	Jeli	15	39.2089	19.64091	5.07126
	Kota Bharu	15	52.5690	21.02238	5.42795

Table A10: Independent Sample T-test between Jeli and Kota Bharu

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
PM_{10}	Equal variances assumed	.232	.634	-1.79	28	.083	-13.36006	7.42835	-28.5763	1.85622
	Equal variances not assumed			-1.79	27.87	.083	-13.36006	7.42835	-28.5795	1.85938

APPENDIX B

Figure B1: Glassware washed and baked before used

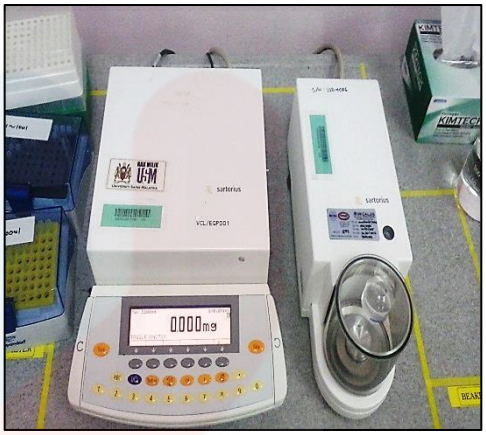


Figure B2: Microbalance

Figure B3: Ultrasonic bath

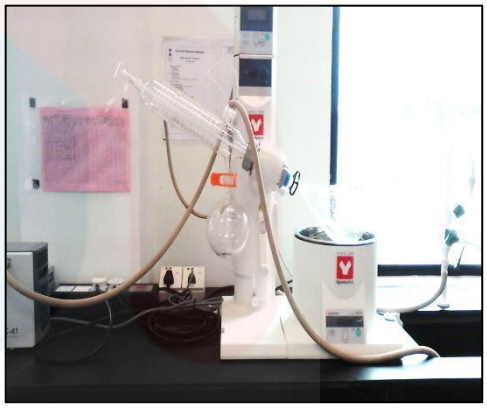


Figure B4: Rotary evaporator

Figure B5: Centrifuge

Figure B6: Nitrogen evaporator

Figure B7: Gas Chromatography

Mass Spectrometry

Figure B8: Samples prior to extraction

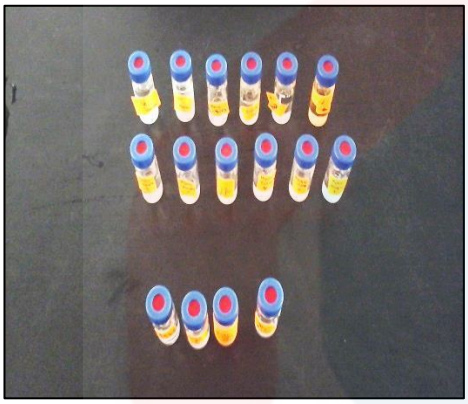


Figure B9: Samples in GC vials

APPENDIX C

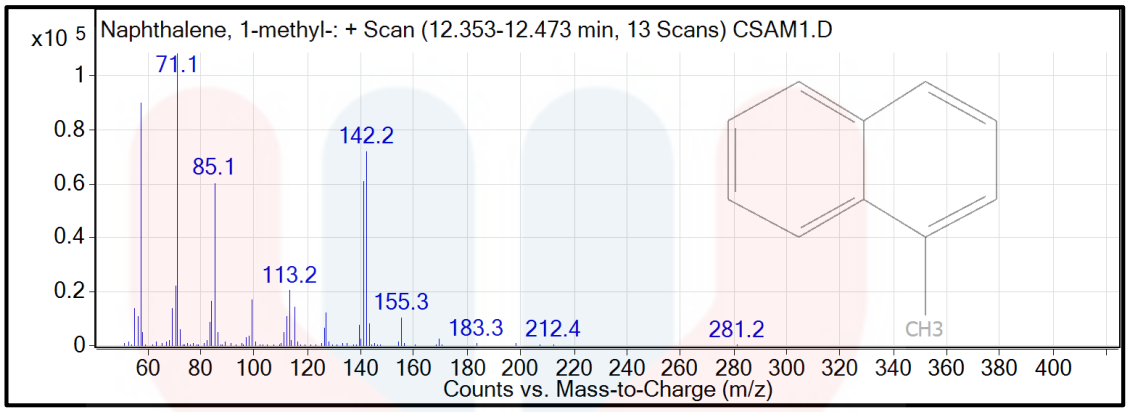


Figure C1: Qualitative analysis result from urban sample for April

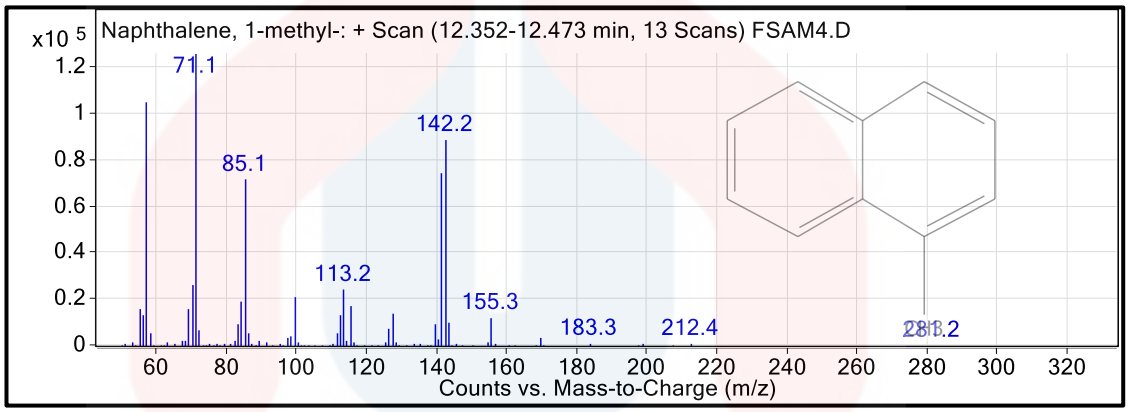


Figure C2: Qualitative analysis result from urban sample for May

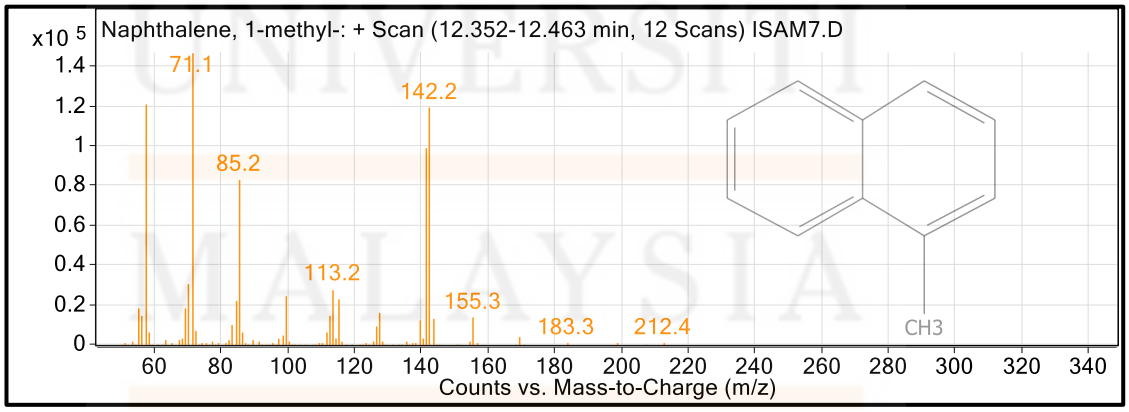


Figure C3: Qualitative analysis result from rural sample for April