

**CHARACTERIZATION AND RISK ASSESSMENT OF
ATMOSPHERIC POLLUTANTS IN KLANG VALLEY, MALAYSIA**

MUHAMMAD IKRAM BIN A WAHAB

2014

ABSTRACT

This study aimed to evaluate the characteristics of trace elements and polycyclic aromatic hydrocarbon (PAHs) in atmospheric particulate matter (PM) and whole blood samples; and the source apportionment and risk assessment associated with these pollutants. The ambient atmospheric PM is collected in Bangi and Petaling Jaya; both located in Klang Valley vicinity, while the blood samples are obtained among pregnant women at the Department of Obstetrics & Gynecology University Malaya Medical Center, Kuala Lumpur. Analysis of trace elements in atmospheric PM was done using a high volume air sampler (HVAS) with a six-stage Cascade Impactor (Staplex) in the size range of $>7.2\mu\text{m}$, $3.0\text{--}7.2\mu\text{m}$, $1.5\text{--}3.0\mu\text{m}$, $0.95\text{--}1.5\mu\text{m}$, $0.49\text{--}0.95\mu\text{m}$ and $<0.49\mu\text{m}$. Meanwhile for PAHs, aerosol samples were collected using $\text{PM}_{2.5}$ HVAS (Thermo Fisher). Additionally, the whole blood/plasma samples were analyzed by means Total Reflection X-Ray Fluorescence (TXRF) after simple dilution and also the OxiSelect BPDE Protein Adduct ELISA kit.

The results indicate that the 24-h TSP levels in Petaling Jaya were higher compared to Bangi. Chromium (Cr) in Bangi and Strontium (Sr) in Petaling Jaya recorded relatively higher concentrations than other trace elements in their groups. Result sources of characterization study shows that the trace elements are believed to be originated from vehicles emission/oil combustion, re-suspended dust/brake emission and industry emission. Regarding non-cancer effects, all trace elements exhibit Hazard Index that is lower than safe level (1). For cancer risk, only carcinogenic risk for inhalation exposure model was considered. Cr has the highest Incremental Lifetime Cancer Risk (ILTCR) values among all the carcinogens.

The average ΣPAHs concentrations for June and July were recorded at $1.63\text{ng}/\text{m}^3$ and $0.99\text{ng}/\text{m}^3$; respectively. Diagnostic ratio study, concluded that the mixed of petrogenic origin, vehicles emission and biomass burning act as the main sources of PAHs in Bangi ambient atmospheric PM. Using a Inhalation Cancer Unit Risk Factor of Benzo(a)Pyrene (UR_{BaP}) value of 1.1×10^{-6} per ng/m^3 , the estimated cancer risk for a lifetime of 70 years is 0.32 and 0.26 cancer cases per million people in June and July; accordingly. Alternatively, by using a UR_{BaP} value of 8.7×10^{-5} per ng/m^3 , the inhalation cancer is 25 and 20 cancer cases per million people in June and July; accordingly. Thus, when using the value from epidemiology study, the value of inhalation cancer risk greatly increased but below health guideline of 10^{-5} . Dermal contact exposure route is one of the major contributor lifetime cancer risks in Bangi as indicated by the high ILTCR values found in this study.

Result from TXRF analysis of blood found no unusual toxic elements that could be due to exposure from various environmental pollutants. Only important trace elements that are categorized as micronutrients required in the body for its normal function such as zinc, copper, calcium and other elements were found in the present study. Based on the result, it can be concluded that exposure of pregnant women in Kuala Lumpur from environmental pollutants still in the safe limit. Additionally, the concentrations of benzo(a)pyrene-diol-epoxides with human serum albumin (BPDE-HSA) adducts found in this study are relatively small compared to the reported value from other studies.

ACKNOWLEDGEMENT

I wish to express my warm and sincere thanks to all of those people that have made my thesis possible and my international experience at Kyoto University that I will remember forever. Without their continuous help, support and guidance, I would never have been able to complete this research.

I owe my most sincere gratitude to my advisor, Professor Minoru Yoneda for his persistent support, understanding, patience, guidance and encouragement that have provided a good basic for the present thesis. His wide knowledge, technical and editorial advice was a great value for me to the completion of this thesis. I am also thankful to Dr Yasuto Matsui for his invaluable support, advice and guidance throughout the completion of this research. I also gratefully acknowledge and recognize the support and sincere encouragement of Dr Yoko Shimada for supporting me.

I am deeply grateful to my reviewer committee, Professor Yoshihisa Shimizu and Professor Takano for their positive and constructive comments and important guidance, which was essential during this research study. Their knowledge and experience with insight have taught me innumerable lessons and developed my understanding of this research.

I would also like to give a special token of appreciation to Professor Talib Latif and Dr Nobumitsu Sakai, who are continuously directed me in the interesting explorations of this research. Their kindness and excellent advice are gratefully acknowledged.

I warmly thank to all administrative staff and member of the laboratory of Environmental Risk Analysis; for their friendly help that making my research run smoothly. My acknowledgement is further extended to Ms Hanae Hoshihara for her assistance and support during my stays in Kyoto, Japan.

I am very grateful to Ministry of Education, Culture, Sports, Science & Technology Japan (MEXT) and Universiti Kebangsaan Malaysia for providing all necessary funding and scholarship throughout my graduate study in Kyoto University.

My loving thanks to my parents, parents in-law and also to all of my family members for their endless encouragement and support during my difficult moments. My special gratitude is due to my wife, Nurulhuda Noh for her love, companionship, morale support and motivation throughout this doctoral research.

Lastly, I would like to thank all to my past and present Malaysian friends in Japan for their friendship, exchanges of knowledge, skills and vent of frustration during my graduate program, which help enrich experiences.

Thank you.

TITLE

CHARACTERIZATION AND RISK ASSESSMENT OF SOME ATMOSPHERIC POLLUTANTS IN KLANG VALLEY, MALAYSIA

SUMMARY

Background

In Malaysia, air pollution has been recognized as one of the major concerns that have high potential for deleterious effects on health. Increased urbanization, human activities and changing urban setting in the country as a result of development have resulted in elevated air pollution and the occurrence of urban heat islands. Klang Valley is the most prone region to serious air pollution compared to other parts of the country. With mountains in the east and the Straits of Malacca to the west, and being highly developed and densely populated, the Klang Valley provides a conducive environment for pollutants to accumulate particularly when atmospheric conditions are stable.

The term atmospheric particulate matter (PM) or atmospheric aerosols is a mixture of solid particles and/or liquid droplet that may vary in concentration, composition and also size distribution. The inorganic components constitute a small portion by mass of the particulates; however, it contains some trace elements such as As, Cd, Co, Cr, Ni, Pb and Se which are human or animal carcinogens even in trace amounts. PAHs have attracted a substantial amount of attention due to their persistent, bio-accumulative, carcinogenic and mutagenic properties. The highest concentrations of atmospheric PAHs are generally found in the urban environment due to increasing vehicular traffic and the dispersion of the atmospheric pollutants. Due to high density of population in cities, the risk associated with the human exposure to atmospheric PAHs is the highest.

Purpose

This study aimed to evaluate the characteristics of trace elements and polycyclic aromatic hydrocarbon (PAHs) in atmospheric particulate matter (PM) and whole blood/plasma samples; and the source apportionment and risk assessment associated with these pollutants.

Methodology

Analysis of trace elements in airborne particles was done using a high volume air sampler (HVAS) with a six-stage Cascade Impactor (Staplex). Stage 1 until 5, slotted with glass fiber filter papers (Westech Instrument) were used to collect particles infive size fragment ($>7.2\mu\text{m}$, $3.0\text{-}7.2\mu\text{m}$, $1.5\text{-}3.0\mu\text{m}$, $0.95\text{-}1.5\mu\text{m}$ and $0.49\text{-}0.95\mu\text{m}$). For the backup stage, a backup filter paper (Whatman EPM 2000) was used to collect fine mode aerosol samples (diameter size $<0.49\mu\text{m}$). Meanwhile for PAHs, aerosol samples were collected using PM_{2.5} HVAS (Thermo Fisher). On the other hand, the whole blood sample was obtained from among pregnant women at the Department of Obstetrics & Gynecology University Malaya Medical Center, Kuala Lumpur.

HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) was used for backward trajectories for both locations during sampling period. The backward trajectories can be used to identify the potential sources regions and transport pathways of pollutants.

Exposure assessment for both inhalation and dermal exposure of trace elements were calculated using the framework that was developed by USEPA. After the exposure assessment was calculated, Hazard Quotient and Hazard Index that were based on non-cancer risk were then calculated. The assessment of cancer risk for inhalation exposure is determined by multiplying the lifetime average daily dose (LADD) with corresponding slope factor.

For PAHs, exposure assessment is expressed in terms of lifetime average daily dose and calculated for inhalation and dermal contact according to USEPA model. Most of PAHs have been recognized as mutagenic and carcinogenic compounds. This study estimated and compared the PAHs concentration with respect to their carcinogenicity and mutagenicity. Carcinogenicity was calculated based on the set of toxicity equivalent factors (TEF) while the mutagenicity was calculated based on mutagenic equivalent factors (MEF). In both TEF and MEF systems, B(a)P was recognized as reference chemical and was assigned a value of 1. In addition, the carcinogenic risk was calculated based on the inhalation cancer unit risk factor value that was developed by both WHO and OEHA. Meanwhile, the cancer slope factor for dermal in combination with LADD was used for the calculation of incremental lifetime cancer risk dermal exposure route.

Concentration and Size Distributions of Atmospheric Particulate Matter

In this study, the analysis of the size and concentration distribution of the airborne particles and associated metals were determined from samples collected from urban and semi urban areas in Malaysia. The results indicate that, Petaling Jaya documented the higher mean concentrations for all particles size group compared to Bangi. Similarly, the 24-h TSP levels in Petaling Jaya were higher compared to Bangi with the concentrations of $79.48\mu\text{g}/\text{m}^3$ and $22.66\mu\text{g}/\text{m}^3$; respectively. In addition, particles size of $<0.49\mu\text{m}$ contribute more than 50% of total PM concentrations in both locations; which is 68% in Bangi and 55% in Petaling Jaya. The result clearly showed that fine particles mode dominated the overall of percentage PM concentrations in both locations.

Among the trace metals that were studied, Cr in Bangi and Sr in Petaling Jaya have recorded an outstanding higher concentrations than other trace elements in their groups, in all particle sizes; except for Sr in Petaling Jaya for particle size $<0.49\mu\text{m}$. Cr in Bangi and Sr in Petaling Jaya recorded the highest concentrations for particle sizes of $<0.49\mu\text{m}$ and $0.49\text{--}0.95\mu\text{m}$; respectively. Meanwhile, apart from Cr and Sr; Cu, Li, Mn, Ni and Pb show almost similar trends of moderate concentrations in all particles size groups; except for Cu in particle size $<0.49\mu\text{m}$, which shows relatively higher concentrations for both locations. Other trace elements such as Ag, Co and Cd recorded relatively lower concentrations in all particle sizes compared to other trace elements. The size distributions of elements in atmospheric aerosols may have resulted from a combination of processes including local anthropogenic and natural sources, long-range transport and re-suspension.

In both locations, the average concentrations of fine particles are higher than the coarse particles. In addition, the average concentrations of PM for size (coarse and fine) in Petaling Jaya are higher compared to Bangi. In the coarse mode aerosols, high concentrations of Cr (21.88ng/m^3) and Sr(10.96ng/m^3) were found in Bangi. On top of that, the chemical composition of PM coarse is found to have higher concentration of Sr(18.74ng/m^3), Mn(8.58ng/m^3), Cu (7.94ng/m^3) and Cr (6.34ng/m^3) than other elements in Petaling Jaya. In the case of PM fine, the Cr, Sr and Cu showed higher concentration in Bangi with the reading of 32.49ng/m^3 , 8.46ng/m^3 and 7.75ng/m^3 ; respectively. Meanwhile in Petaling Jaya, the results indicate the abundance of Sr, Cu, and Cr with the recorded concentration 18.05ng/m^3 , 12.27ng/m^3 and 8.31ng/m^3 ; accordingly.

Principle Component Analysis (PCA) and Risk Assessment of Trace Elements in Atmospheric Particulate Matter

At Bangi sampling site, the observed result show two possible factor representing different contributing sources for airborne elements. Factor 1 explain 89.4% of total varians of the data and has high loading for Ag (0.994), Cd (0.967), Co (0.978), Cr (0.986), Cu (0.995), Li (0.993), Mn (0.988), Ni (0.997) and Pb (0.986); which can be identified as vehicles emission/oil combustion, re-suspended dust/brake emission and industry emission. The factor 2 with 9.01% of total varians is solely related to Sr (0.903); indicated their origin from soil as it is contain typical elements from crustal origin. At Petaling Jaya sampling site, 88.38% varians of the data was observed in factor 1. High loading of Ag (0.989), Cd (0.951), Co (0.891), Cr (0.993), Cu (0.994), Li (0.987), Mn (0.789), Ni (0.988), Pb (0.836) and Sr (-0.955) indicates that the contributing sources in factor 1 of Petaling Jaya are similar to the factor 1 of the Bangi site. Factor 2 with total varians 10.96% and considerable contributions from Co, Mn and Pb may be due to industrial/re-suspension.

Backward trajectories of Bangi showed that the trajectories mostly start over from the Pacific Ocean and directly move westward through the South China Sea, passing the Sulu Sea before arriving to the south of Klang Valley (Bangi). Based on its pathway and origin, this air mass is expected to bring in relatively clean air from the Pacific Ocean to the Klang Valley. Meanwhile, backward trajectories of Petaling Jaya showed that most of the wind came from the Malacca Straits during southwest monsoon. Peninsular Malaysia has been affected by severe smoke haze due to forest fires in the region periodically. With its pathways above the populated areas, and short passages over the sea, these air masses have a potential to bring in the long-range transport air pollution to the Malaysia.

The non-carcinogenic risk assessment in terms of Hazard Quotient (HQ) and Hazard Index (HI) were calculated according to exposure to particulate bound metals. Based on the result, it was found that inhalation is an important pathway of for exposure to trace elements in the circumstance of particulate matter in Bangi and Petaling Jaya. HQ for non-cancer risk due to dermal contact of particulate matter is in lower magnitude and it is unlikely that this exposure route would pose a higher risk than inhalation.

For both sampling location Bangi and Petaling Jaya, the same trend of results was observed. Inhalation of particles appeared to have much higher risk for Cr, Co and Mn, which were one to three orders of magnitude higher than the corresponding risks of the dermal exposure route. Regarding non-cancer effects, all trace elements exhibit Hazard Index lower than safe level (1). In comparison to the children and adult cases, the inhalation and dermal exposure route has higher values for children than that for adult and hence the overall values of risk are higher than adult.

In this study, the incremental lifetime cancer risk (ILTCR) for Cr, Pb, Cd, Ni, and Co was calculated to see the probability of getting cancer from the exposure of ambient atmospheric particulate matter. Cr has the highest ILTCR values among all the carcinogens. In Bangi, the estimated Cr risk values for adults were 3.50×10^{-5} (coarse mode) and 5.19×10^{-5} (fine mode); while for children the values were 1.26×10^{-5} (coarse mode) and 1.87×10^{-5} (fine mode). Similarly, the Cr ILTCR values in Petaling Jaya for adults were 1.01×10^{-5} (coarse mode) and 1.33×10^{-5} (fine mode); as for the children were 3.65×10^{-6} (coarse mode) and 4.78×10^{-6} (fine mode). Therefore, it can be confirmed that exposure to Cr is quite a serious problem in respect for both adult and children population in Bangi and Petaling Jaya.

The risk assessment suggested that there was an acceptable potential adverse health effects for adults and children in both localities (Bangi and Petaling Jaya) caused by particulate metals except for Cr. Although generally the probability of developing cancer risk is low, it was thus clear that the exposure of residents living nearby the study area to the coarse and fine particles with toxic contents should be of special concern for certain trace elements.

Determination of Trace Elements in Whole Blood

Several whole bloods were analyzed by means of TXRF after simple dilution. It can be concluded that analysis of the nutrition-relevant elements by simple dilution with ultrapure water is sufficient. From the TXRF analysis, no unusual toxic elements have been found in this study that could be due to exposure from various environmental pollutants. Only important trace elements that are micronutrients required in the body for its normal function, especially through various enzymes, hormones, vitamins etc., were found in the pregnant women in the present study.

Generally, all the trace elements detected in this study are lower in concentration compared to the concentration from the literature value. The result is consistent with other research that indicates the nutritional level of elements Zn, Cu, Fe, Ca and K are in lower concentration compared to non-pregnant women. The result showed that trace elements such as zinc, copper, calcium and other elements have significant influences on the health of pregnant women and growing fetus. Deficiency of each one gives rise to specific clinical features. Based on the result, it can be said that exposure of pregnant women in Kuala Lumpur from environmental pollutants is still in the safe limit.

PAHs Composition in Atmospheric Particulate Matter

The average Σ PAH concentrations for June and July were recorded at $1.63 \pm 0.16 \text{ ng/m}^3$ and $0.99 \pm 0.11 \text{ ng/m}^3$; respectively. It can be seen that the Σ PAH concentrations in June was higher than July, with a total difference of 0.64 ng/m^3 between the two months. This finding could be caused by an impact of first haze episode in June, which was the peak of haze in Malaysia; together with the influences of localized emission from motor vehicles. These concentrations are on the lower side compared to the data obtained from other places. B(ghi)P contribute the highest percentage of total PAHs concentrations with readings of 0.51 ng/m^3 (19.3%) in June and 0.31 ng/m^3 (12.0%) in July. This indicated that Benzo(g,h,i)perylene could be contributed from diesel or gasoline powered vehicles.

According to present study, indicated that six ringed PAHs were predominant observed followed by five and four ringed forms respectively. In June, 52 % of PAHs are six ringed, followed by 34% five ringed and 14% of four ringed. Similar trend was observed in July where 56% are six ringed, followed by 40% five ringed and 4% of four ringed. This suggests that PAH residues found in this study may have all originated from the combustion of gasoline and diesel fuel.

The result also indicated that 61% of the total PAHs found in this study area for June and July are carcinogenic PAHs whereas 39% are non-carcinogenic PAHs. For carcinogenic compound of PAHs, Indeno[1,2,3-cd]pyrene indicated the highest concentrations for both June and July with $0.35 \pm 0.19 \text{ ng/m}^3$ and $0.24 \pm 0.17 \text{ ng/m}^3$ respectively. Meanwhile, for non-carcinogenic, Benzo(g,h,i)perylene showed the highest concentration for both June and July with the concentrations $0.51 \text{ ng/m}^3 \pm 0.39$ and $0.31 \pm 0.24 \text{ ng/m}^3$, respectively. The abundance of Benzo(g,h,i)perylene indicates the high contributions from gasoline powered vehicles.

At present, there are no ambient air quality standards for PAHs in Malaysia. Therefore, the concentration of PAHs mainly Benzo(a)pyrene was compared the Dutch National Institute of Public Health and the Environment (DNIPHE) guideline. It was found that, the Benzo(a)pyrene concentrations in Bangi (0.13 ng/m^3) was lower than the DNIPHE maximum permissible concentration.

Diagnostic Ratio and Risk Assessment of PAHs in Atmospheric Particulate Matter

Diagnostic ratio of individual PAHs is applied to determine the sources of PAHs in ambient particulate matter. From the result, it can be concluded that the concentrations of deposited PAHs and contamination in the study indicate the mixed of petrogenic origin, vehicles emission and biomass burning as the main sources of PAHs in Bangi ambient atmospheric particulate matter. The backward trajectories showed that, during the haze event, the origins of air mass are normally located at low latitudes in the Indian Ocean. It follows the southwest monsoon direction through Sumatera, Java Sea and other areas impacted by forest and peat fires before arriving at Malaysia.

Values of ΣBaPE and ΣBaPMEQ were significantly higher in June compared to July with the reading $2.98\text{E-}01\text{ng/m}^3$ and $4.39\text{E-}01\text{ng/m}^3$; respectively. The largest contribution PAHs to ΣBaPE in Jun and July were made by B(a)P ($1.26\text{E-}01\text{ng/m}^3$ and $1.15\text{E-}01\text{ng/m}^3$; accordingly) . On the other hand, in June, both InPy and B(a)P showed the highest contribution of individual PAH to ΣBaPMEQ ($1.08\text{E-}01\text{ng/m}^3$ and $1.26\text{E-}01\text{ng/m}^3$). The results emphasize and confirm the importance of B(a)P as a surrogate compound for PAH mixture for ambient atmospheric particulate matter in Bangi.

When using a URBaP value of 1.1×10^{-6} per ng/m^3 , the estimated cancer risk for a lifetime of 70 years is 0.32 cancer cases per million people in June and 0.26 cancer cases per million people in July will be attributable to inhalation of PM_{2.5} bound PAHs. Of the individual PAHs, DiB(a,h)An and B(a)P contributed the most to the estimated inhalation cancer risk in June with the reading $1.04\text{E-}07$ and $1.39\text{E-}07$; respectively. Meanwhile, in July, B(a)P ($1.26\text{E-}07$) contributed the most of the estimated inhalation cancer risk.

Alternatively, if URBaP value of 8.7×10^{-5} per ng/m^3 , the inhalation cancer is 25 cancer cases per million people in June and 20 cancer cases per million people in July for an average lifetime of 70 years. For all sample studied in June and July, the largest contribution of individual PAHs to the estimated inhalation cancer risk was made by B(a)P. Thus, when using the value from epidemiology study, the value of inhalation cancer risk greatly increased but still below the health guideline value 10^{-5} .

The ILTCR value for dermal contact associated with $\Sigma\text{PAH}_{10}\text{-BaPe}$ in June for adult is 2.1 cancer cases per million people, compared with 3.1 cancer cases per million people exposure for children. The dermal cancer risks due to $\Sigma\text{PAH}_{10}\text{-BaPe}$ exposure during July were 1.6 cancer cases per million people for adult and 2.4 cancer cases per million people for children respectively. B(a)P contributed the most to the estimated cancer risk due to dermal contact in both adult and children during in the month of June and July. All the calculated values for ILTCR due to dermal contact were within the USEPA acceptable level.

Determination of Benzo(A)PyreneDiol Epoxide Adducts in Human Plasma Exposed to PAHs

In summary, the concentrations of BPDE-HSA adducts found are relatively small compared to the reported value from other studies. Thus, the exposure of airborne B(a)P during haze among is still low among pregnant women in Klang Valley. Although, the BPDE adducts level is lower, no threshold for dose response relationship appears to be exit for PAHs. Therefore, no absolutely safe levels could be established for these compounds.

In addition to that, human populations are commonly exposed to low levels of PAHs carcinogens. Some study, proved that even at low concentrations with long exposure time resulted in mutations cell. Thus, it is to highlight that even at low concentrations of carcinogens/mutagens are more relevant to human exposure.

TABLE OF CONTENTS

	Page
Abstract	i
Acknowledgement	ii
Summary	iii
Table of Contents	ix
List of Tables	xii
List of Figures	xiv
 CHAPTER 1 INTRODUCTION	
1.1 Background Information of Air Quality in Malaysia	1
1.1.1 Sources of Air Pollution in Malaysia	1
1.1.2 Air Quality in Klang Valley	1
1.2 Rationale of the Study	2
1.3 Aim	3
1.4 Objectives	4
1.5 Study Area	4
1.6 Chapter Analysis	5
 CHAPTER 2 LITERATURE REVIEW	
2.1 Atmospheric Aerosols	7
2.1.1 Size Distribution	7
2.1.2 Atmospheric Lifetime of Particles	10
2.1.3 Chemistry of Ambient Particulate Matter	11
2.1.4 Anthropogenic Particles	12
2.1.5 Natural Particles	13
2.1.6 Health Effects of Aerosols	14
2.1.7 Environmental Effect of Atmospheric Aerosols	16
2.2 Trace Elements	18
2.2.1 Sources of Pollution	19
2.2.2 Heavy Metals Uses	19
2.2.3 Movement of Trace Elements in the Environment	20
2.2.4 Metal Deposition	21
2.2.5 Metal Toxicity	23
2.2.6 Trace Elements in Whole Blood	25
2.3 Polycyclic Aromatic Hydrocarbon (PAHs)	25
2.3.1 Physical and Chemical Characteristic of PAHs	26
2.3.2 Toxicity and Carcinogenicity of PAHs	30
2.3.3 Sources of PAHs	31
2.3.4 Chemical Transformation and Deposition of PAHs	31
2.3.5 PAHs in Whole Blood	33

CHAPTER 3	CONCENTRATION AND SIZE DISTRIBUTION OF ATMOSPHERIC PARTICULATE MATTER	
3.1	Introduction	34
3.2	Methodology	35
3.2.1	Sampling Sites	35
3.2.2	Samples Acquisition	36
3.2.3	Samples Preparation	37
3.2.4	Samples Analysis	37
3.2.5	Quality Control	39
3.3	Results and Discussion	40
3.3.1	Concentration and Size Distribution of Particulate Matter	40
3.3.2	Concentration and Size Distribution of Trace Elements in Atmospheric Particulate Matter	44
3.4	Conclusion	59
CHAPTER 4	PRINCIPAL COMPONENT ANALYSIS (PCA) AND RISK ASSESSMENT OF TRACE ELEMENTS IN ATMOSPHERIC PARTICULATE MATTER	
4.1	Introduction	60
4.2	Methodology	60
4.2.1	Principal Component Analysis	61
4.2.2	Backward Trajectory Analysis	63
4.2.3	Health Risk Assessment Methods	64
4.3	Result and Discussion	69
4.3.1	Sources Apportionment of Atmospheric Aerosol	69
4.3.2	Backward Trajectory Modeling	72
4.3.3	Health Risk Assessment	75
4.4	Conclusion	86
CHAPTER 5	DETERMINATION OF TRACE ELEMENTS IN WHOLE BLOOD	
5.1	Introduction	88
5.2	Principle of Total Reflection X-Ray Fluorescence (TXRF) Spectroscopy	88
5.3	Methodology	90
5.3.1	Samples Collection	90
5.3.2	Instrumentation	91
5.3.3	Direct Sample Preparation	91
5.4	Results and Discussion	92
5.4.1	X-ray Spectrum	92
5.4.2	Trace Elements in Whole Blood	92
5.5	Conclusion	95

CHAPTER 6	PAHs COMPOSITION IN ATMOSPHERIC PARTICULATE MATTER	
6.1	Introduction	96
6.2	Method of Extraction	96
	6.2.1 Solid Phase Extraction (SPE)	96
	6.2.2 SPE Procedure	97
6.3	Methodology	98
	6.3.1 Sampling Site	98
	6.3.2 Sample Acquisition	98
	6.3.3 Sample Extraction and Fractionation	99
	6.3.4 Sample Analysis	100
6.4	Results and Discussion	101
	6.4.1 PAHs in Atmospheric Particles	101
	6.4.2 Comparison of PAHs Concentrations with Other Studies	106
	6.4.3 Comparison of PAHs Distribution in Atmospheric Particles	107
	6.4.4 Comparison with Ambient Standards	111
6.5	Conclusion	112
CHAPTER 7	DIAGNOSTIC RATIO AND RISK ASSESSMENT OF PAHs IN ATMOSPHERIC PARTICULATE MATTER	
7.1	Introduction	114
7.2	Methodology	115
	7.2.1 PAHs Diagnostic Ratio	115
	7.2.2 Health Risk Assessment	116
7.3	Results and Discussion	120
	7.3.1 Diagnostic Ratio	120
	7.3.2 Backward Trajectory Analysis	121
	7.3.3 Health Risk Assessment	126
7.4	Conclusion	133
CHAPTER 8	DETERMINATION OF BENZO(A)PYRENE DIOL EPOXIDE ADDUCTS IN HUMAN PLASMA EXPOSED TO PAHs	
8.1	Introduction	134
8.2	Metabolism of Benzo(a)pyrene	135
8.3	Methodology	136
	8.3.1 Samples Collection	136
	8.3.2 BPDE Protein Adduct Procedure	136
8.4	Result and Discussion	137
8.5	Conclusion	140
CHAPTER 9	CONCLUSION AND RECOMMENDATIONS	
9.1	Conclusion	141
9.2	Recommendations	146
REFERENCES		147

LIST OF TABLES

Table	Description	Page
2.1	Comparison of ambient fine and coarse particles	11
2.2	Most recent studies of air pollution health effects in Malaysia	16
2.3	Percentage release of heavy metals from natural sources	19
2.4	Uses of some metals	20
2.5	Trace elements and the medical conditions arising from their deficiency and toxicity	24
2.6	Chemical structure and physical properties of selected of PAHs	26
3.1	Microwave oven parameters	37
3.2	Elemental recoveries (%) by using laboratory reference standard	38
3.3	Summary of PM measurement in Bangi and Petaling Jaya	40
3.4	Average concentrations of trace elements in APM (Bangi)	44
3.5	Average concentrations of trace elements in APM (Petaling Jaya)	45
3.6	Comparison of TSP ($\mu\text{g}/\text{m}^3$) and trace element levels (ng/m^3) in atmospheric particulate matter around the world	57
4.1	Typical markers elements and ions associated with PM sources	62
4.2	Mathematical models in the exposure assessment of trace elements	65
4.3	Mathematical models in the carcinogenic assessment of trace elements	66
4.4	Exposure parameter values used in the risk assessment calculations	67
4.5	Mathematical models in non-cancer risk for trace elements	68
4.6	Mathematical models in the cancer risk for trace elements	68
4.7	Relative toxicity values used in this study	69
4.8	Varimax rotated factor loading for Bangi	69
4.9	Varimax rotated factor loading for Petaling Jaya	70
4.10	Calculated daily dose ($\text{mg}/\text{kg}/\text{d}$) for inhalation exposure route	76
4.11	Calculated daily dose ($\text{mg}/\text{kg}/\text{d}$) for dermal exposure route	77
4.12	Hazard quotient and hazard index for non-cancer risk in Bangi	79
4.13	Hazard quotient and hazard index for non-cancer risk in Petaling Jaya	80
4.14	Calculated LADD ($\text{mg}/\text{kg}/\text{d}$) for inhalation exposure route	82
4.15	Calculated LADD ($\text{mg}/\text{kg}/\text{d}$) for dermal exposure route	83
4.16	Incremental lifetime cancer risks for inhalation exposure route	84
5.1	TXRF result in whole blood in comparison with concentrations given by literature value	93
6.1	Operating conditioned of GC-MS for PAHs analysis	100
6.2	Quantitation ion and retention time for PAHs	101
6.3	LOD and LOQ for calculated PAHs	102
6.4	Recovery rate for PAHs during the study	102
6.5	Mean ($\pm$ SD) PAH concentrations and percentage of total PAH	104

6.6	PAHs concentration found in other studies around the world	106
6.7	Average concentrations of some PAHs in Bangi compared to the DNIPHE of MPCs, NCs and CritConc	112
7.1	Toxic Equivalency Factors for PAHs relative to B(a)P	116
7.2	Mutagenic Equivalency Factors for PAHs relative to B(a)P	117
7.3	Mathematical models in the risk assessment of PAHs study	118
7.4	Exposure parameter values used in the risk assessment calculations	119
7.5	Mathematical models in the cancer risk of PAHs study	119
7.6	Ratio of PAHs concentration in June and July	120
7.7	Diagnostic ratios of individual PAHs concentration for sources diagnosis	121
7.8	BaP-equivalent carcinogenicity and mutagenicity risk assessed in Bangi	127
7.9	Lifetime average daily dose (LADD) (mg/kg/day) for inhalation	128
7.10	Lifetime average daily dose (LADD) (mg/kg/day) for dermal	129
7.11	URBaP Values used in this study	129
7.12	Estimated inhalation cancer risks for PAHs using URBaP value from (OEHHA, 1993) and (WHO, 2000)	130
7.13	Incremental Lifetime cancer risk (ILCTR) due to dermal contact of PAHs	132
8.1	Environmental parameters of atmospheric PM in Klang Valley	137
8.2	Concentrations of BPDE-HSA adduct levels in pregnant women	138
8.3	BDPE-HSA level from other study	139

LIST OF FIGURES

Figure	Description	Page
2.1	Types of aerosol particles and their size ranges	8
2.2	Scheme diagrams of distributions of particles surface area in atmospheric aerosol	9
2.3	Global-average radiation forcing estimates and ranges in 2005 for anthropogenic and natural radioactive forcing (RF) agents, the typical geographic extent of these forcing and the level of scientific understanding (LOSU)	18
2.4	Movement of trace metal elements within the environment	21
2.5	Schematic diagram transport and effects of air pollution in urban area	23
2.6	Molecular structures of PAHs	27
2.7	Atmospheric depositions of HOCs	32
3.1	Sampling locations in Petaling Jaya and Bangi	36
3.2	Diagrams of samples collection and analysis	39
3.3	Distribution of PM concentrations of different particle size groups	41
3.4	Contributions of PM distributions in Bangi	42
3.5	Contributions of PM Distribution in Petaling Jaya	42
3.6	Box plots of trace element concentrations in Bangi	46
3.7	Box plots of trace element concentrations in Petaling Jaya	47
3.8	Mass concentration of trace elements in particle size $>7.2\mu\text{m}$	48
3.9	Mass concentration of trace elements in particle size $3.0\text{-}7.2\mu\text{m}$	49
3.10	Mass concentration of trace elements in particle size $1.5\text{-}3.0\mu\text{m}$	50
3.11	Mass concentration of trace elements in particle size $0.95\text{-}1.5\mu\text{m}$	50
3.12	Mass concentration of trace elements in particle size $0.49\text{-}0.95\mu\text{m}$	51
3.13	Mass concentration of trace elements in particle size $<0.49\mu\text{m}$	52
3.14	Comparison of PM coarse and PM fine in Bangi and Petaling Jaya	54
3.15	Average concentrations of trace elements in PM coarse	55
3.16	Average concentrations of trace elements in PM fine	55
4.1	Methodology of analysis	61
4.2	Size distributions of several TSP sources emissions	63
4.3	Trajectory computation method of HYSPLIT trajectory model	64
4.4	Backward trajectories of Bangi	73
4.5	Backward trajectories of Petaling Jaya	74
5.1	Scheme of the TXRF principle	89
5.2	Steps for the TXRF analysis of liquids	90
5.3	Method of analysis	91
5.4	X-ray spectrum	92
5.5	Box plots of whole blood concentrations using TXRF	93
6.1	Schematic view SPE procedure	97

6.2	Activation of C-18 chains with organic solvent	98
6.3	Diagram of PAHs extraction	99
6.4	Box plots of PAHs concentrations in June	103
6.5	Box plots of PAHs concentrations in July	103
6.6	Average concentration of PAHs compounds	105
6.7	Distributions of PAHs based on number of aromatic rings	107
6.8	Concentrations of PAHs based on number of aromatic rings	108
6.9	Percentage distributions of carcinogenic and non-carcinogenic PAHs	109
6.10	Average concentrations of carcinogenic PAHs compounds	110
6.11	Average concentrations of non-carcinogenic PAHs compounds	111
7.1	Methodology of Analysis	115
7.2	Relative humidity over Southern Asean	122
7.3	Fires in Sumatera	123
7.4	Backward trajectory of air masses for sampling site in Bangi on Jun	124
7.5	Backward trajectory of air masses for sampling site in Bangi on July	125
8.1	Carcinogenic activation and detoxification of benzo(a)pyrene	135
8.2	Assay protocol	137
8.3	Concentrations of BPDE-HSA adduct levels in pregnant women	138

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND INFORMATION OF AIR QUALITY IN MALAYSIA

1.1.1 Sources of Air Pollution in Malaysia

In Malaysia, air pollution has been recognized as one of the major concerns that have high potential for deleterious effects on health (Jamal et al., 1998; Jamal et al., 1994; Juliana, 1998; Zailina, 1996; Zailina et al., 1997). Increased urbanization, human activities and changing urban setting in the country as a result of development have resulted in elevated air pollution and the occurrence of urban heat islands.

The sources of air pollutants are both localized and transboundary. Localized sources are both mobile and stationary. Mobile sources are from private and public motor vehicles. These sources are especially significant in the Klang Valley. Stationary sources include power plants, industrial waste incinerators, cement plants, iron and steel mills from the industrial and suburban areas, the clearing and burning of old oil palm trees in plantations, emissions of dusts from urban constructions and quarries, and open burning at some solid waste dumpsites.

The four main local sources of air pollution in Malaysia in 2001 were vehicular emissions (89%) in the downtown areas with very high traffic volumes; power plants (9.2%) which are commonly located in the suburban areas; industrial processes (1.5%) such as cement plants, iron & steel mills from industrial zones; and open burning at solid waste dumpsites (0.3%). The large increase in the number of motor vehicles in Peninsular Malaysia from 7 million in 1994 to 11.3 million in 2001 is the main contributor of high particulate matter in congested industrial and urban areas (DOE, 2002).

Transboundary pollutants from neighboring countries such as Indonesia are fine particulate matter from forest fires during the dry seasons, especially between the months of August and November each year. This transported air pollution from forest fires has resulted in what is now commonly referred to as haze, not only in Malaysia but also in other countries in the region, including Singapore, Brunei Darussalam and Thailand. The worst of these recurring haze episodes was the one that prevailed over much of Southeast Asia in 1997. Widespread forest fires in Kalimantan and Sumatra were triggered by extremely dry weather brought about by the El Nino phenomenon. The Klang Valley and Kuching in Sarawak were among the worst hit areas in Malaysia (Brauer and Jamal, 1998).

1.1.2 Air Quality in Klang Valley

The Department of Environment monitors the status of air quality throughout the country to detect any significant change which may cause harm to human health and the environment. This involves the continuous or real-time measurement of pollutants in the ambient air at 50 National Air Quality Monitoring Stations throughout the country. These stations are located strategically to meet the specific objectives. Most of them are located in residential areas to monitor population exposure to

environmental pollution hazards, while others are located within industrial or commercial areas to monitor pollution trend in those localities (DOE, 2002; DOE, 2003).

The overall air quality for Malaysia throughout 2001 was good to moderate for most of the year, with the exception of few unhealthy days (when the level of one or more of the 5 criteria air pollutants were above their MAAQG) experienced during the dry season particularly in the month of July 2001. Particulate matters (PM₁₀) and ozone were the prevalent pollutants throughout the country in 2001 (DOE, 2002). The overall air quality for Malaysia in 2002 dropped slightly compared to 2001. Generally, the air quality was between good to moderate for most of the year, except for a number of unhealthy days at various locations in the States of Selangor, Negeri Sembilan and Sarawak. The overall air quality was affected by peat swamp burning and forest fires during the dry periods between February and March and from mid-July to September 2002 (DOE, 2003).

According to the DOE (2003), the Klang Valley is the most prone region to serious air pollution compared to other parts of the country. With mountains in the east and the Straits of Malacca to the west, and being highly developed and densely populated, the Klang Valley provides a conducive environment for pollutants to accumulate particularly when atmospheric conditions are stable. The unhealthy air quality in the Klang Valley from February to March 2002 was due to peat swamp and forest fires in several areas of Selangor and Kuala Lumpur as a result of hot and dry weather with reduced rainfall. The number of days with unhealthy air quality ranged from 17 for Kajang to 67 days for Shah Alam. This represents an increase from 2001 with the number of days with unhealthy air quality ranging from 4 to 37 days. The cleanest among 7 different locations in the Klang Valley was Petaling Jaya with no day with unhealthy air quality (DOE, 2003).

About 70% of the days with unhealthy air quality in the Klang Valley in 2002 were due to high levels of respirable particulate matter (PM₁₀) while the remaining 30% were due to high ozone levels.

1.2 RATIONALE OF THE STUDY

Air pollution is the presence of undesirable material in air, in quantities large enough to produce harmful effects. The undesirable materials may damage human health, vegetation, human property, or the global environment, as well as create aesthetic insults in the form of brown or hazy air or unpleasant smells.

The air quality standards must protect human health. However, the current standards of air quality in Malaysia are for the Total Suspended Particulates (TSP) and PM₁₀, which do not provide a total picture of human exposure to pollution and the effects of exposure on health and welfare since fine particles PM_{2.5} have closer relationship with health effect when compared with coarse particles.

Particulate matter air pollution less than 2.5µm has received great international attention due to its diverse contribution to the global burden of disease. Study done by Brauer et al, (2012) mentioned that majority of the planet still resides in areas where the World Health Organization Air Quality Guidelines of 10µg/m³ (annual) and 25µg/m³(24hrs) is exceeded.

Ground level measurement of PM_{2.5} or lower are still limited in most of the places in the world. Therefore studies are needed to evaluate and provide insight in high risk as to the exposure and risk as many of the form of air pollution are beyond the control of individual and require policy at national and international levels.

Studies conducted during the last two decades have evaluated the association between the size distribution of PM and metal concentrations in urban areas. In the past, many researchers in Europe have conducted experiments to study the size distributions of PM-based metals (Voutsas and Samara, 2002; Allen *et al.*, 2001; Fernandez Espinosa *et al.*, 2001). In Malaysia, research is still evolving with a limited number of published studies on PM based metal and elemental size distribution and concentration.

The inorganic components constitute a small portion by mass of the particulates; however, it contains some trace elements such as As, Cd, Co, Cr, Ni, Pb and Se which are human or animal carcinogens even in trace amounts (ATSDR, 2003; Wang *et al.*, 2006). The high level of Pb can induce severe neurological and hematological effects on the exposed population especially children, whereas Cd and Ni are known for inducing carcinogenic effects in humans through inhalation. Occupational exposure of Cd is a risk factor for chronic lung diseases (Benoff *et al.*, 2000). Cr (VI) is known to have toxic and carcinogenic effects on the bronchial tree (Hu *et al.*, 2002; Manalis *et al.*, 2005). Mn exposure leads to increased neurotoxic impairments (Santos-Burgoa *et al.*, 2001). The increased level of Cu can lead to respiratory irritation (ATSDR, 2002; Manalis *et al.*, 2005).

PAHs have attracted a substantial amount of attention due to their persistent, bio-accumulative, carcinogenic and mutagenic properties related to health problem such as cataracts, kidney and liver damage, and jaundice (Dong & Lee, 2009). The highest concentrations of atmospheric PAHs are generally found in the urban environment due to increasing vehicular traffic and the dispersion of the atmospheric pollutants. Due to high density of population in cities, the risk associated with the human exposure to atmospheric PAHs is the highest (Sharma *et al.*, 2008).

There have been a few studies done in Malaysia to evaluate the concentrations of PAHs associated with atmospheric particles (Radzi Bin Abas *et al.*, 2004; Omar *et al.*, 2006; Omar *et al.*, 2002). However, limited study was conducted to assess the lifetime cancer risk assessment from the exposure to atmospheric PAHs via inhalation and dermal contact.

1.3 AIM

The purpose of this study is to evaluate the characteristic of trace elements and PAHs in atmospheric particulate matter (APM) and whole blood/plasma samples; and the source apportionment and risk assessment associated with these pollutants.

1.4 OBJECTIVES

The objectives to be achieved are:

- i. To obtain the concentrations of atmospheric PM in different particle size groups in Klang Valley
- ii. To identify types of trace elements in different particle size groups of atmospheric PM in Klang Valley
- iii. To estimate the concentrations of trace elements of atmospheric PM in different particle size groups in Klang Valley
- iv. To determine the concentrations and profiles of PAHs components in atmospheric PM_{2.5} in Klang Valley
- v. To identify types of trace elements in whole blood samples of pregnant women in Kuala Lumpur
- vi. To attain benzo(a)pyrene-diol-epoxides (BPDEs) adducts in plasma samples of pregnant women in Kuala Lumpur
- vii. To derive source apportionment of trace elements in APM in Klang Valley
- viii. To examine the backward trajectory analysis for trace elements and PAHs of APM in Klang Valley
- ix. To analyse Diagnostic Ratio of PAHs components in Klang Valley
- x. To evaluate risk assessment associated with the health effects of trace elements and PAHs to human being
- xi. To discuss the results in relation to the aim of the study and to make comparisons with other studies
- xii. To suggest recommendations for improvement in environmental policy making regarding the atmospheric pollutants in Klang Valley

1.5 STUDY AREA

The Klang Valley region is an area in Malaysia with rapid development and population growth. An alternative reference to Klang Valley would be Kuala Lumpur metropolitan area or Greater Kuala Lumpur. The Klang Valley area comprise the capital city Kuala Lumpur (latitude 3°8'N; longitude 101°44'E) and its suburbs, along with the adjoining cities in the state of Selangor.

Klang Valley is geographically delineated by Titiwangsa Mountains to the north and east and the Strait of Malacca to the west. There is no official designation of Klang Valley boundaries; but it is often assumed to comprise Federal Territory of Kuala Lumpur, Federal Territory of Putrajaya and Selangor District of Petaling, Klang, Gombak and Hulu Langat. The current estimated population is more than 5 million.

The weather in Klang Valley is relatively hot and humid with uniform temperatures throughout the year between 25°C to 35°C. The winds over the region are light and variable, however there are uniform periodic changes in the wind flow patterns namely; the southwest monsoon, northeast monsoon and the inter monsoon seasons. The southwest monsoon season is usually established in the latter half of May or early June and ends in September while the northeast monsoon season usually commences in early November and ends in March. The seasonal wind flow patterns coupled with the local topographic features determine the rainfall distribution patterns over the country. Generally, the primary maximum rainfall occurs in October and November

while February is the month with minimum rainfall. The secondary maximum generally occurs in March to May while in June–July; very little rainfall occurs but it may be overcast.

Economic growth with uncontrolled development of industrial premises, non-regulated motor vehicles and human activities related to the high population density in Klang Valley are responsible for the emissions of various pollutants in the area. During the haze episodes in 1997, 1998, 2003, 2004, and 2006 arising from forest fires in a neighboring country, the area of Klang Valley was the most affected. The pollutants emitted from forest fires as well as from vehicles and industrial activities have given rise to severe air pollution in the area.

1.6 CHAPTER ANALYSIS

This thesis writing comprises of nine chapters, not including the abstract, summary and references. The outline for each chapter is summarized as follows.

Chapter 1 – Introduction provides information on background information of air quality in Malaysia and specifically addressing the condition in Klang Valley. In addition, the aim, objectives and rationale of the study will also be determined.

Chapter 2 – Literature review covers three main sub-chapters which include the atmospheric aerosols, trace elements and PAHs. The atmospheric aerosols will give brief information and explanation on size distribution, atmospheric lifetime of particles, chemistry of ambient PM, anthropogenic and natural particles, the health effects of aerosols and also the environmental effect of atmospheric aerosols. The second sub-chapters will cover the details related to trace elements; including the source and movement of trace elements in the environment, the use of metals in various activities and also metal deposition and toxicity. Consequently, the next sub-chapter will provide information related to PAHs; including the physical and chemical characteristic, toxicity, carcinogenicity, sources, chemical transformation and deposition of PAHs.

Chapter 3 – This chapter highlights the concentrations and size distributions of trace elements in atmospheric PM. In addition, methodology on sampling procedures and samples analysis will be explained. Besides, interpretation and further discussion of the result obtained from the study will also being justified.

Chapter 4 – Analysis and evaluation of source apportionment and backward trajectory analysis for trace elements in atmospheric PM are summarized in this chapter. Besides, investigation and estimation of health risk assessment associated with trace elements in atmospheric PM are also being discussed.

Chapter 5 – This chapter will determine the types of trace elements found in the analysis of whole blood samples using the Total Reflection X-Ray Fluorescence (TXRF). In addition, steps involved in sampling procedures and samples preparation prior to analysis will be explained. Consequently, interpretation and further discussion of the result, in relation to accumulation of trace elements in the whole blood samples of pregnant women will also be explained.

Chapter 6 – This chapter will present the composition and profiles of PAHs components in atmospheric PM. Also, methodology on sampling procedures and samples extraction and fractionation will be explained. Further discussion and interpretation of the result, in relation to distribution of PAHs in atmospheric PM will be covered at the end of the chapter.

Chapter 7 – Determination of Diagnostic Ratio for PAHs is highlighted in this chapter. Next, investigation and estimation of risk assessment associated with PAHs in atmospheric PM are also being discussed.

Chapter 8 – This chapter comprises of topic related to determination of benzo(a)pyrene diol epoxide (BPDE) adducts in human plasma exposed to PAHs. Sub-topic including the methodology of samples collection and BPDE protein adduct procedure will be explained in this chapter. Additionally, results and discussion related to the findings will also be covered.

Chapter 9 – The conclusion briefly summarizes the main findings of the study and what can be concluded from them. In addition, recommendations for improvements and references to future research will also be given.

CHAPTER 2

LITERATURE REVIEW

2.1 ATMOSPHERIC AEROSOLS

The term particulate matter (PM) or atmospheric aerosols is a mixture of solid particles and/or liquid droplet that may vary in concentration, composition and also size distribution. According to Wilson & Spengler (1996), aerosols can be defined as suspensions of solid or liquid in a gas. Therefore, aerosols include both the particle and the gas in which they are suspended. Although aerosol and particle are different, they are often used interchangeably throughout the literature to refer to the particle only.

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, microorganisms, pollen, etc.). On the other hand, secondary particles are formed by gas-to-particle conversion in the atmosphere. Primary gaseous species might undergo chemical reaction to produce low-volatility products. Then, these products partitions to the particulate phase, i.e. new particles are formed by nucleation and condensation of gaseous precursors (Aiken et al., 2008).

2.1.1 Size Distribution

Atmospheric particles emitted from air pollution sources and formed by natural processes have a multitude of different shapes and densities. That is why in air pollution control, it is necessary to use a particle size definition that directly relates to how the particle behaves in a fluid such as air. For this purpose, the aerodynamic diameter is defined as the diameter of a spherical particle having a density of 1g/cm^3 that has the same inertial properties (i.e. terminal settling velocity) in air as the particle of interest.

Different types of aerosol particles and their sizes ranges are displayed in Figure 2.1. Small aerosol particles predominantly contribute to number concentrations; however they only play a smaller role for the volume distribution. On the other hand, larger particles play a role for the volume distribution but do not contribute substantially to the number concentration (Heintzenberg et al., 2003). Particles are conventionally divided into different size of fractions; based on the physical and chemical processes involved in the particle formation and growth. The different size of fractions is generally called “modes”. As illustrated in Figure 2.1, there are four types of denomination, which refers to how particles are formed; nucleation, Aitken, accumulation and coarse modes (CAFÉ, 2004).

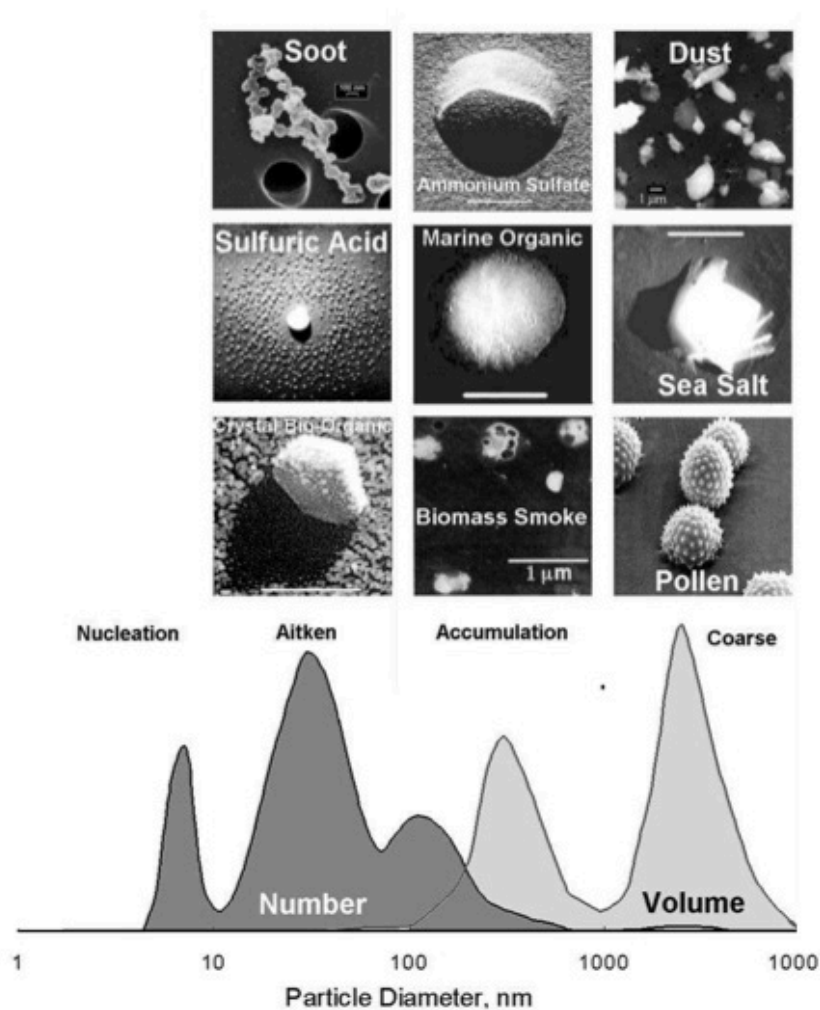


Figure 2.1 Types of aerosol particles and their size ranges

The nucleation (or ultrafine) mode resides in the range below $0.02\mu\text{m}$ of particle diameter and usually presents its maximum number-density around 5-15nm of particle diameter. H_2SO_4 , NH_3 and H_2O are examples of precursor gases to form new particles by homogenous nucleation in the ambient atmosphere. However, due to the condensation by other condensing gases, organic and inorganic components, the newly formed particles rapidly grow bigger. These particles have hours lifetime in the atmosphere as they rapidly coagulate with larger particles or grow into larger sizes due to condensation. Classical nucleation theory shows that the nucleation highly depends on the concentrations of the gaseous precursors, relative humidity and temperature. In particular, the nucleation is favoured by decreases in the temperature and/or increases in the relative humidity (Easter & Peter, 1994).

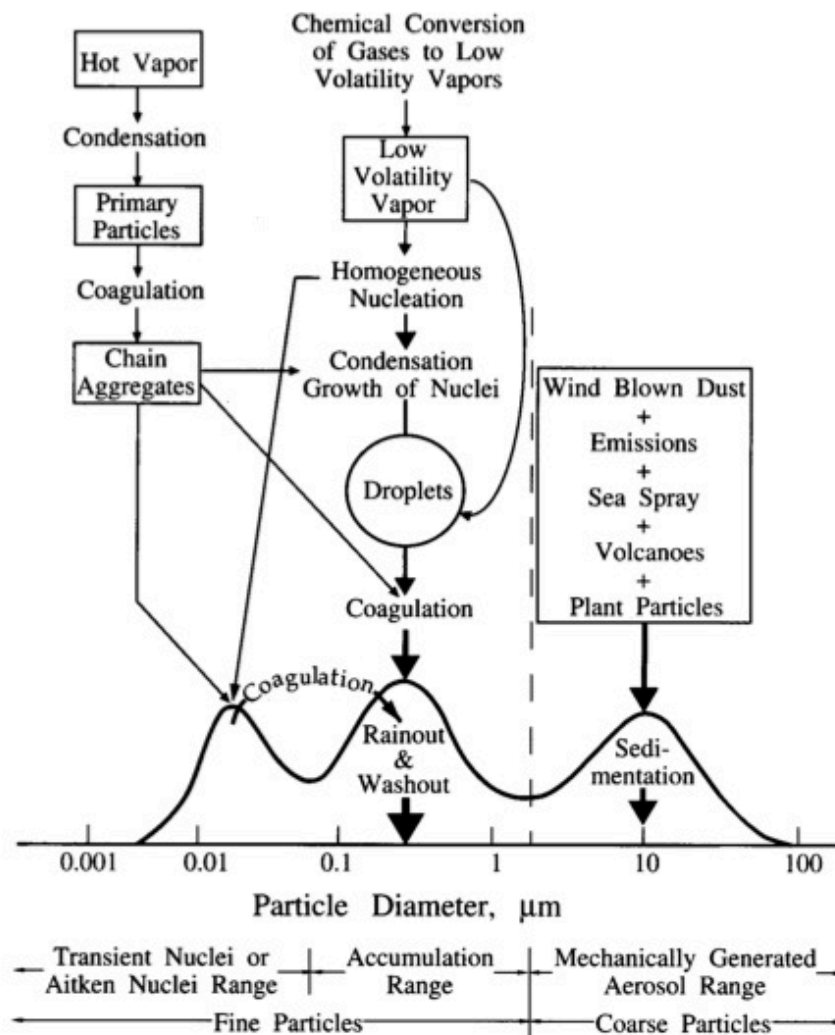


Figure 2.2 Scheme diagrams of distributions of particles surface area in atmospheric aerosol

Figure 2.2 illustrates the idealized scheme for distribution of the particles surface area of an atmospheric aerosol. Principle modes, sources and particles formation and removal mechanisms are indicated (Seinfeld & Pandis, 1998).

Aitken mode particles range from 0.02 to 0.1 μm and originate from either primary particles, natural and anthropogenic, or by growth of nucleation mode particles. Secondary Aitken mode particles are likely to be formed by coagulation of ultrafine particles, by condensation and by liquid phase reactions. Combustion process is a primary source that has very large emissions of Aitken mode particles. Aitken mode particles are present at relatively stable concentration in the atmosphere; indicating a long residence time of Aitken particles at ambient atmosphere. The accumulation mode covers the range between 0.1 and up to 1 μm . Aitken mode particles have a tendency to grow to accumulation mode particles due to coagulation and liquid phase reactions occurring in cloud droplets. Hoppel et al. (1986) stated that the mass transfer by condensation and/or nucleation/coagulation is not enough to cause any significant change in particles size compared with the observed growth.

The coarse mode includes particles $>1\mu\text{m}$. Most particles in the coarse mode range are formed by mechanical processes, such as the erosion of the earth's crust (mineral dust) or other materials, or the bursting bubbles on the ocean surface (sea spray). Coagulation processes do not affect the particle number concentration of coarse particles. The processes of formation and growing of particles in the range $<1\mu\text{m}$ do not tend to produce particles $>1\mu\text{m}$. On the other hand, mechanical processes forming primary particles cannot easily reduce the size of particles to diameters $<1\mu\text{m}$ owing to energetic limitations. Thus, the transfer of particles from different modes of the size spectrum presents a barrier around $1\mu\text{m}$. The coarse mode particles are characterized by a low number concentration and a relatively high mass concentration. Although in the coarse mode the primary particles predominate, "secondary particles" may also be found.

Nucleation mode particles are usually observed in heavy traffic situation. It is still not clear at the present as whether these particles are primarily part of the engine exhaust or formed by nucleation processes when the exhaust gases are mixed with cold ambient air. Nucleation mode particles occur with a very high variability in remote to urban background conditions. It can reach comparably high concentrations only in few hours under certain specific conditions.

2.1.2 Atmospheric Lifetime of Particles

Once the particles have been emitted into or formed in the atmosphere, they are subject to removal from the atmosphere by different processes, which together determine the atmospheric lifetime of the particles. Coarse particles are removed from the atmosphere by sedimentation and precipitation (the residence time for particles $>20\mu\text{m}$ is several hours while it is 2-4 days for $2\text{-}3\mu\text{m}$ particles). Particles in the range $0.1\text{-}1\mu\text{m}$ (accumulation mode and larger Aitken mode particles) exhibit the longest lifetime in the atmosphere, ranging from days to a few weeks. Primary particles from combustion and secondary aerosols are usually found in this size range. Consequently, these particles have a long residence time and as a result can be transported over long distances ($\sim$ several 1,000 km).

The lifetime of a particle in the air determines to what extent it changes its properties, and its properties determine its lifetime. For example, a very small particle emitted from an automobile exhaust pipe will grow in size as it travels from the pipe toward the kerbside and further on. Since the exhaust particles are quite small and hydrophobic it will mainly be subject to dry deposition by diffusion, which is small. As the particles grow and accumulate inorganic components that usually are quite hygroscopic, they become subject to deposition by precipitation, which is the dominant deposition path for fine particles. The extent of such growth does not only depend on the distance travelled by the particle, but also on the atmospheric conditions. In addition, a particle's chemical composition changes with growing distance from the source depending on the nature of other pollutants present in the air. Natural particles, such as inorganic secondary species from volcanic emissions or African dust, may be transported at super-long-range scale ($>5000\text{ km}$) due to: a) the large emission volumes, b) the release of PM into higher zones of the atmosphere where transport is favoured, and c) to the fine particle size caused by the photochemical origin (sulphate from volcanic SO_2 emissions) or by the size segregation caused by long-range transport (desert dust).

Particles in the range 0.1-1 μ m often are efficient cloud condensation nuclei, i.e. easily forming cloud droplets, due to a sufficient water-soluble fraction. Thus, the time of residence of particles in the range 0.1-1 μ m is considered similar to the time of residence of the water (around 10 days; Posfai & Molnar, 2000). However, carbonaceous particles are usually difficult to wet and consequently, a period for surface oxidation is required before they can be wetted and removed from the atmosphere by wet deposition. This results in a longer lifetime of carbonaceous soot and organic particles (Gaffney et al., 2002) when compared to inorganic particles, e.g. sulphate.

On the other hand, the lifetime of several species depends also on their thermodynamic properties. Therefore, the distribution of mass between the gas and aerosol phases in some chemical species experiences wide variations induced by the variations in the temperature and relative humidity typical of ambient air. This is especially essential for species such as ammonium nitrate and some organic aerosols (Adams et al., 1999). Semi-volatile compounds tend to distribute their mass between the gas and aerosol phases to reach a thermodynamic equilibrium and this may be subject to important seasonal changes. Thus, in summertime a large proportion of particle-associated ammonium nitrate is not stable. Consequently, PM₁₀ and PM_{2.5} associated nitrate concentrations are usually characterized by low levels in summer and high levels in winter.

2.1.3 Chemistry of Ambient Particulate Matter

Particles of different size often have a different origin and also a different composition. A summary of the formation and sources of particles, as well as chemical information, residence time and transport distance for fine and coarse particles is presented in Table 2.1 as shown below.

Table 2.1 Comparison of ambient fine and coarse particles
(From Seinfeld & Pandis (1998), with modifications)

	Fine Particles	Coarse Particles
Formation pathway	• Chemical reactions • Nucleation • Condensation • Coagulation • Cloud/fog processes	• Mechanical disruption • Suspension of dust
Sources	• Combustion (coal, oil, petrol, diesel, wood) • Gas to particle conversion of NO_x, SO₂ and VOC • Smelters, mills, etc	• Resuspension of industrial dust and soil • Suspension of soil (farming, mining, unpaved roads) • Biological sources • Sea spray

	Fine Particles	Coarse Particles
Composition	• Sulphate • Nitrate • Ammonium • Elemental carbon (EC) • Organic compounds • Water • Metals (Pb, Cd, V, Ni, Cu, Zn, Fe, etc)	• Resuspended dust • Coal and oil fly dust • Crustal element (Si, Al, Ti, Fe, Mn, etc) oxides • CaCO₃, NaCl • Pollen, Mould, spores • Plant and animal debris • Tire wear debris
Solubility	• Largely soluble • Hygroscopic	• Largely insoluble • Non-hygroscopic
Atmospheric lifetime	• Days to weeks	• Minutes to days
Transport distance	• 100s to 1,000s km	• Up to 10s of km

2.1.4 Anthropogenic Particles

In urban environments, primary particles are emitted as a result of traffic-related combustion processes. The particles that are emitted constituted of elemental carbon and various inorganic and organic compounds. Moreover, primary particles result from erosion of the pavement by road traffic (road dust) and abrasion of brakes and tires. Particles mechanically generated by road traffic are coarse particles, while vehicles exhaust emitted primary fine particles.

Both diesel and spark ignition (gasoline) engines are emitted particles in the sub-micrometer. The particles generated by diesels are generally larger in number and size than those from spark ignition engines. Thus, higher emission of mass per vehicle km is produced. The difference in emissions between diesel and gasoline motor is greatest at low velocities. Particles collection technology for diesel engines has shown efficiencies of up to about 99%. This seems promising for achieving a lower mass emission of diesel engines (Matter et al., 1999).

Industrial activities such as building, mining, manufacturing of cement, ceramic and bricks, and smelters are typical sources of primary particles. Primary particles associated with smelter emissions are mostly fine particles, because most of these are formed by condensation of hot vapors. Ni, V, Mn and Cu are often emitted from various industries or smelter (Pacyna, 1998). Meanwhile, the other industrial sources mostly emit coarse primary mineral particles.

After emission of SO₂ by fossil fuel combustion and metal smelting, SO₂ undergo oxidation process lead to formation of sulphuric acid, which is to some extent neutralised by ammonia, and by reaction with calcium carbonate or sodium chloride to form the corresponding salts. Sulphuric acid and ammonium sulphate are found on fine particles (<1µm), whereas the fractions neutralised by calcium carbonate and sodium chloride are more present on particles in the coarse mode (> 1µm) (Evans et al., 2004). Calcium carbonate is a common component of mineral dust and a very reactive component of the aerosol present in the earth atmosphere (Krueger et al., 2003).

In urban environments nitrogen oxides are emitted by traffic and some industrial processes. The oxidation nitrogen oxides in the atmosphere produce nitric acid (Whitall et al., 2003). Nitric acid may be neutralized and thus transformed into NH_4^+ or Na^+ nitrate (particle). The size distribution of nitrate depends on the neutralising agent. Consequently, NH_4NO_3 is mostly present in the fine mode ($<1\mu\text{m}$), whereas Ca_2NO_3 (from reaction between HNO_3 and crustal CaCO_3) and NaNO_3 (from neutralisation by marine NaCl) exist in larger size (Pryor & Sorensen, 2000).

Combustion of biomass and fossil fuels in large agricultural areas are important precursors of anthropogenic secondary aerosol. These vapors are primarily emitted by gasoline evaporation (fugitive emission) and combustion processes (Watson et al., 2001). Particles in the range $<1\mu\text{m}$ to $10\mu\text{m}$ are formed following the oxidation of the gaseous precursor, mostly likely by condensation to the pre-existing aerosol. Large agricultural areas, combustion of biomass and fossil fuels are important sources of organic gaseous precursors of anthropogenic secondary aerosol. These vapors are mainly emitted by gasoline evaporation (fugitive emission) and combustion processes. Human activities may also generate anthropogenic bio-aerosols. Bacteria and fungi generated in solid waste recycling and composting plants (Pathak et al., 2012).

Brasseur et al., (1999) pointed out that the global scale that the anthropogenic $\text{PM}_{2.5}$ emissions contributed are about 30-100% of the natural PM emissions. The anthropogenic coarse particle emissions ($\text{PM}_{2.5} - \text{PM}_{1.0}$) are only slightly larger than the $\text{PM}_{1.0}$, hence the anthropogenic $\text{PM}_{1.0}$ emissions add mostly to the $\text{PM}_{1.0}$ budget. In addition, Abdul Rahman et al., (2011) studied the fine and coarse aerosol in Kuala Lumpur, Malaysia. Chemical analysis found that fine particles mainly originated from five anthropogenic sources: two strokes (35.7%), motor vehicles (31.9%), smoke/biomass burning (17.5%), soil dust (8.3%) and industry (16.7%). Meanwhile, the compositions of coarse particle included soil dust (8.5%), motor vehicles (42.4%), road dust (18.3%), industry (17.6%) and two strokes engine (13.1%).

2.1.5 Natural Particles

Volcanic emissions are a source of primary mineral particles, but perhaps mainly secondary sulphur compounds (from SO_2 emissions). Although the contribution of such events to bulk particle mass levels in ambient air is generally limited, the particles can be ejected into very high altitudes, even the stratosphere (e.g. during the last Pinatubo eruption), and then stay suspended for a year and more, which can bring about a considerable change of the radiation balance.

Sea salt aerosol is part of natural tropospheric aerosols. Sea salt aerosols readily absorb moisture from atmosphere as their various components included MgCl_2 , NaCl and MgSO_4 (Knipping & Dabdub, 2003). Sea salt aerosols form by two mechanisms namely the mechanical tearing of water droplets (spume) wave crest from wind speeds and the bubbles bursting at water surface (Norris et al., 2013). Sea salt is essential components of atmospheric as they may have profound impacts towards urban quality, ecosystems of estuaries and climate change (Max Zhang et al., 2005). Goodman et al., (2000) stated that sea salt (primarily NaCl) and mineral dust (CaCO_3) particles with aerodynamic diameters between 1 and $10\mu\text{m}$ play important roles in the formation of nitrate.

Biogenic aerosols are abundant in atmosphere and they have profound impacts on atmospheric chemistry and physics, biosphere, climate and public health (Despres et al., 2007). Primary biogenic aerosol (PBA) particles and components are emitted directly from the biosphere to the atmosphere. PBA particles range in size from millimeters down to tens of nanometers, and may thus be much smaller than originally thought (Jaenicke, 2005). Particles of biological origin, like pollen, bacteria, spores, viruses, plant and animal fragments (e.g., dandruffs, skin fragments), are all within this size range (Bauer et al., 2005; Ahern et al., 2007; Elster et al., 2007; Zhang et al., 2007). Particulate viruses and bacteria exhibit sizes in the range of $<2\mu\text{m}$, whereas plant debris and spores have sizes that extending into the coarse range of PM (Posfai and Molnar, 2000). However, the abundance, origin and components of biogenic aerosols are still poorly understood and quantified.

The natural secondary fraction of atmospheric particles is mostly consisting of sulphate, nitrate and organic aerosol. Natural sulphate particles are produced by the oxidation of sulphur containing gases, such as SO_2 emitted by volcanoes, or dimethylsulphide (DMS) of marine biogenic origin. They have been considered for many years to lead the mass of marine aerosols respectively in coarse and fine fraction (Vignati et al., 2009). Natural nitrate is the final product formed by oxidation of nitrogen oxides emitted by soil transpiration (Roelle et al., 2001) and lightning (Bryan & Loscalzo, 2011). Main sources of natural secondary organic aerosol precursors are found in the large forested areas (Harrison et al., 2001), from where important amounts of organic vapours, such as terpenes (Yu et al., 1999), are emitted.

2.1.6 Health Effects of Aerosol

The evidence of the association between airborne PM and public health outcomes is consistent in showing adverse health effects at exposures experienced by urban populations in cities throughout the world, in both developed and developing countries (WHO, 2005). The range of effects is broad, including effects on the respiratory and cardiovascular systems extending to children and adults within the general population (Pope & Dockery, 2006; Schlesinger et al., 2006; WHO, 2005), but also including lung cancer (Pope & Dockery, 2006; Schlesinger et al., 2006).

The risk for various outcomes has been shown to increase with exposure and there is little evidence for a threshold below which no adverse health effects would be anticipated (WHO, 2005). In one WHO report (WHO, 2004) it is stated that the public health significance of long-term health effects of exposure to PM outweighs that of short-term effects. Short-term exposure effects have been documented in numerous time series studies, and guidelines for both the short (24 hours) and the long term (annual average) are recommended (WHO, 2004). The recommendation is that both $\text{PM}_{2.5}$ and PM_{10} be assessed and controlled since fine and coarse particles have different sources and may have different effects. Regarding ultrafine particles, information is insufficient to permit a quantitative evaluation of the risks of health effects of exposures (WHO, 2006). The recently adopted guidelines for annual means of PM are $10\mu\text{g m}^{-3}$ and $20\mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ and PM_{10} , respectively, while for 24-hour means, they are $25\mu\text{g m}^{-3}$ and $50\mu\text{g m}^{-3}$ (WHO, 2006).

Particle size and surface area are important characteristics from a toxicological point of view. Pope & Dockery (2006); Schlesinger et al. (2006) recently review the current knowledge about PM and particle size, and health effects. Study done by Pope & Dockery (2006); Schlesinger et al. (2006) proved that there tends to be a stronger relation between fine particles, $PM_{2.5}$, and most health effects than between PM_{10} and effects on health. Ultrafine particles contribute little to the PM mass concentration; however, they do influence the surface area by their large number and are of interest in toxicological studies (Schlesinger et al., 2006). Study done by Nel et al. (2006) concluded that as the size of a particle decrease, its surface area increases, thus allowing a greater proportion of its atoms or molecules to be displayed on the surface. Furthermore, particle size is crucial for penetration and deposition efficiency into human lungs, since ultrafine particles ability to penetrate the membranes of the respiratory tract and enter the blood circulation.

Particulate organic matter in ambient air is a complex mixture of chemicals, i.e. polycyclic aromatic hydrocarbons (PAHs). The International Agency for Research on Cancer (IARC) classified some PAHs, i.e. benzo[a]pyrene, as human carcinogens (Bostrom et al., 2002). Another group that has gained interest in recent years is metals. Schlesinger et al. (2006) have summarized current knowledge regarding trace metals and their health impact. The assessment of the risk associated with exposure to PAHs is still a challenge. PAHs present in ambient air mainly as a complex mixture and the interactions among components may lead to additively, synergistic or antagonistic effects. In addition, a study conducted by Topinka et al. (2011) shows that organic matter extracted from $PM_{2.5}$ are likely to induce DNA adducts and oxidative DNA damage in in-vitro cell-free assay experiments.

The toxicological findings strongly suggest that transition metals such as V, Cr, Mn, Fe, Ni, Cu and Zn are components in PM with toxic capability based on their potential for oxidative activity and the production of reactive oxygen species (Schlesinger et al., 2006). Soil dust consists of crustal elements (e.g. Si, Ca, Al and Mg) and is present in ambient $PM_{2.5}$ but larger fractions are present in the coarse mode. Wind-blown soil dust, at least in rural areas, is not thought to be a significant health hazard but naturally occurring crustal material can be contaminated with road dust produced by moving vehicles. The contaminants can contain a variety of substances, including PAHs and various metals (e.g. Zn and Pb) that may modify the toxicology of the crustal particles.

Several studies indicated that particles produced from burning of biomass for domestic heating have increased and become one of the major sources of $PM_{2.5}$ in Europe and other parts of the world (Amann et al., 2005; Naeher et al., 2007). Incomplete combustion of biomass produces a multitude of different organic species as well as trace metals. In a review of some epidemiological studies conducted in areas where wood smoke is common, Boman et al. (2003) came to the conclusion that PM from wood smoke seems to be at least as harmful as PM derived from other sources.

Very large populations are exposed to high concentrations of air pollution in developing Asia. The WHO estimated that over 500,000 deaths in Asia in 2000 were due to outdoor air pollution exposure, accounting for approximately two thirds of the total global burden of deaths attributed to air pollution (WHO, 2002). Forest fire in Indonesia has continually affected the health of Malaysia resident particularly in Kuching, Sarawak; Kuala Lumpur and also Selangor during the 1997 haze episode. During the peak period of haze, respiratory disease outpatient visits to Kuala Lumpur General Hospital increased from 250 to 800 per day (WHO, 1998). In the 1997 haze episode the total health effects were estimated to include 285,227 asthma attacks, 118,804 cases of bronchitis in children, 3889 cases of chronic bronchitis in adults, 2003 respiratory hospital admission, 26,864 emergency room visits, and 5,000,760 restricted activity days (Nasir et al, 2001). Study indicated whole population in the country was at risk except in Perlis, Kelantan and Sabah. Table 2.2 summarizes the most recent studies of air pollution health effects in Malaysia.

Table 2.2 Most recent studies of air pollution health effects in Malaysia

Citation	Location	Summary
Hashim JH, Hashim Z, Omar A et al., 2000	Malaysia: Kuala Lumpur Kemaman Setiu	Respirable and blood lead concentrations were highest in schoolchildren in urban Kuala Lumpur, followed by semi-urban Kemaman and rural Setiu
Mott JA, Mannino DM, Alverson CJ et al., 2005	Malaysia: Kuching	Significant fire-related increases were observed in respiratory hospitalizations, especially for COPD and asthma
Sastry N., 2002	Malaysia: Multiple cities	Smoke haze had a deleterious effect on the health of the population

2.1.7 Environmental Effects of Atmospheric Aerosols

Another important effect of the aerosol particles is their impact on our climate. They scatter and absorb solar and terrestrial radiation, influence cloud formation and cloud microphysics in the atmosphere. This results in a considerable influence on the radioactive balance of the earth-atmosphere system and therefore aerosol particles play a central role in our climate (IPCC, 2007). Greenhouse gases such as carbon dioxide and methane have the most recognized influence on the earth's climate. They absorb part of the long-wave radiation emitted by the earth's surface and lower atmosphere and prevent its escaping into space.

The natural greenhouse effect is necessary to enable life on earth by keeping the mean temperature at around +15°C instead of about -18°C. If anthropogenic emissions are added, the radiation balance of incoming and outgoing energy can be disturbed. “Radioactive forcing” is defined as a measure of how the balance of incoming and outgoing energy of the earth-atmosphere system is influenced when factors that affect climate are altered. Positive forcing causes an increase of the surface temperature while a negative forcing does the opposite. Next to the gases responsible for the greenhouse effect other agents exhibit a radioactive forcing as well. Compared to those other effects the greenhouse effect is considered to be understood with a high degree of confidence.

Interest in atmospheric aerosols also extends to their influence on global climate change. The measure by which a climate factor alters the balance of earth’s atmosphere is given by the radioactive forcing (IPCC, 2007). A positive radioactive forcing represents a warming of the climate; conversely, a negative radioactive forcing represents a cooling. Figure 2.3 presents the radioactive forcing of aerosols and greenhouse gases and illustrates how aerosols can influence the climate. The large uncertainty bars on the negative radioactive forcing of aerosols in Figure 2.3 indicate that the absolute effects of aerosols have a high uncertainty, as reported by the IPCC. The warming effects of greenhouse gases like CO₂, CH₄, N₂O and halocarbons, on the other hand, are well-characterized and more precisely known.

The Intergovernmental Panel on Climate Change (IPCC) found a change in the average measured global temperature of +0.74°C during the 20th century, which is most likely due to anthropogenic activities. Predictions for a temperature rise within the next 100 years range from 2.4°C to 6.4°C, mostly depending on the emission scenario. Estimated average contributions to radioactive forcing with their error bars representing the confidence intervals are shown in Figure 2.3.

The influence of aerosol particles on the earth’s climate can be categorized into direct and indirect effects. The direct effect describes the fact that aerosol particles directly reflect incoming sunlight back to space and are thus cooling the planet. Furthermore, soot containing aerosol particles can also absorb the sunlight, leading to a local atmospheric heating that may change stability and convection patterns. The indirect effect is the modification of the microphysical properties of the clouds through changes in the atmospheric aerosol. To form a cloud, a cloud condensation nucleus (seed) and a super saturation, (excess) of water vapor have to be present. Depending on the aerosol size and the prevailing water vapor super saturation, additional anthropogenic aerosol particles can serve as additional cloud condensation nuclei (CCN) and can lead to a spread of the cloud’s liquid water content over more and smaller droplets (Haywood & Boucher, 2000). This results in a longer lifetime of the cloud, a higher cloud albedo and therefore increased cooling effects.

Reduction of atmospheric visibility is probably the most readily impact of air pollution. Visibility degradation is largely caused by the scattering of light particles with diameters that are close in size to the wavelength of visible light (particles in the accumulation mode) (Seinfeld & Pandis, 2006). Particles in the range 0.1 to 1µm in diameter are the most effective, per unit aerosol mass, in reducing the visibility. According Ramanathan et al., (2007), the brown haze characteristic of smoggy atmosphere is mostly due to aerosol scattering.

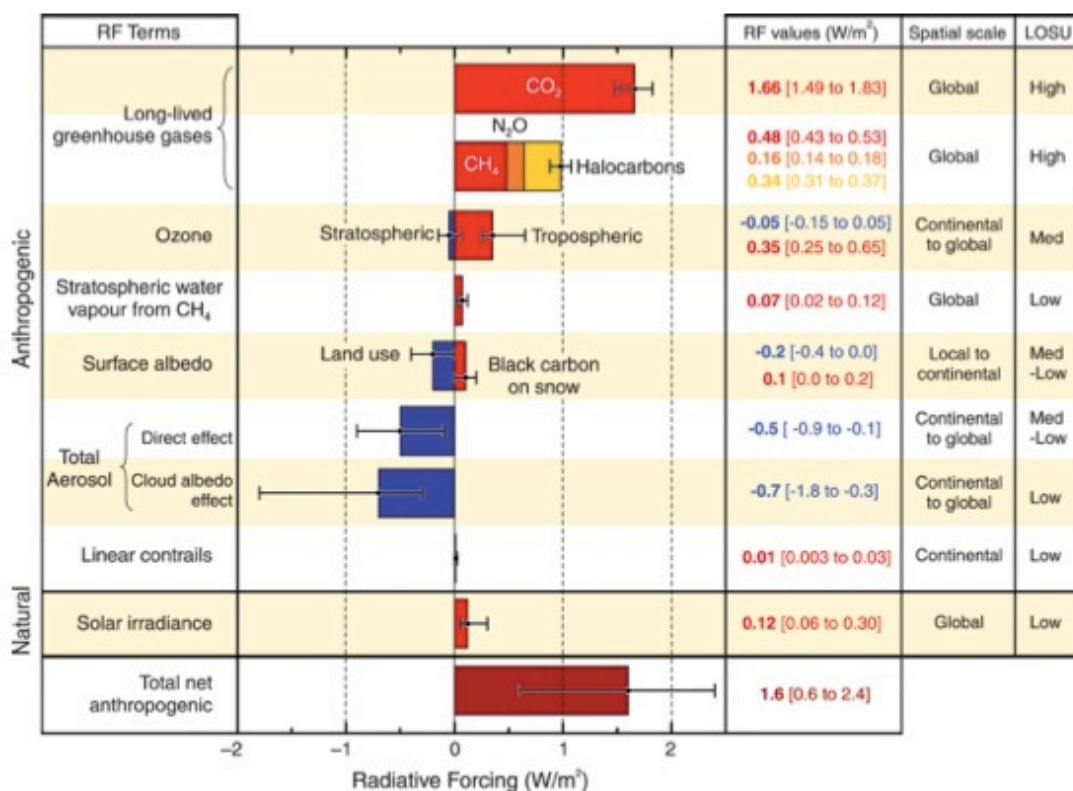


Figure 2.3 Global-average radiation forcing estimates and ranges in 2005 for anthropogenic and natural radioactive forcing (RF) agents, the typical geographic extent of these forcing and the level of scientific understanding (LOSU) (Source: IPCC, 2007)

Atmospheric particles can have impacts towards man-made structures and environmental media. In these instances, particles are deposited by wet or dry deposition, and the effects of the deposited particles are directly related to their chemical properties. Acidic aerosols can corrode metal structures and degrade building materials like concrete, limestone and marble, reducing structural integrity (Seinfeld & Pandis, 2006). Aerosols that contain toxic metals or organic compounds can be deposited on land and in water bodies, where they directly affect flora and fauna, and indirectly, through bioaccumulation and ingestion, affect human health. Soot particles formed through combustion processes can spoil surfaces and increase cleaning and maintenance costs.

2.2 TRACE ELEMENTS

Toxic heavy metals are one of the major hazardous that affects us today. Atmospheric deposition of toxic heavy metals has stimulated profound research all over the world due to effects on living organisms. Toxic metals like lead (Pb), cadmium (Cd), arsenic (As) and chromium (Cr) can essentially attack specific areas in the human body upon exposure (Shinggu et al., 2007). Their dispersion and transport in the atmospheric layers may be exacerbated by human activities and natural phenomenon. The resulting high concentrations of these metals in the air may lead to both ecotoxic effects on plants and animal species, and toxic effects to humans.

In the air, heavy metals exist in combination with dusts from sediments and suspended breathable particles (Adriaenssens, 2007). From the air, they may be released by precipitation events or direct dry deposition into various environmental compartments near or far from their sources. An intense study of the levels of heavy metals like Pb, Cd, Cr, and As in the atmosphere is therefore both necessary and vital to providing a safer environment and is imperative in securing man's general well being.

2.2.1 Sources of Pollution

Naturally heavy metals may exist in the form of vapors ions dissolved in water and as minerals or salts found in rock, soil and sand. According to Pacyna (2002), biogenic sources account for more than half the Hg and Mo released into the atmosphere, and for 30% to 50% of the As, Cd, Cu, Mn, Pb and Zn released (Table 2.3). Soils may account for a significant amount of heavy metals release into the atmosphere.

Table 2.3 Percentage release of heavy metals from natural sources

Natural sources	% released into the atmosphere
Biogenic	• 50% Hg, Mo • 30-50% As, Cd, Cu, Mn, Pb and Zn
Volcanic Gas	• 40% to 50% of Cd and Hg • 20% to 40% of the As, Cr, Cu, Ni, Pb, and Sb
Sea aerosols	• 10% various heavy metals

Heavy metals are not only introduced to the environment by way of natural sources but also through human activities that cause constant dispersion in various environmental compartments. Waste incineration sites, runoff from agricultural land, traffic emissions and effluent from urban areas release heavy metals into the environment (Qishlaqi & Moore, 2007). Industrial sources may cause a major hazard especially in heavily populated areas. In addition, the combustion of fuels from stationary sources by means of both external combustion and internal combustion may be significant to the dispersion of heavy metals in the atmosphere.

2.2.2 Heavy Metals Uses

Heavy metals have been used in various industrial ranges from electrical materials to stainless steel manufacturing. Other general use of heavy metals includes drilling muds, textiles, and copying machine toners (ATSDR,2010). Table 2.4 listed the uses of some heavy metals adopted from Hardy et al., 2008.

Table 2.4 Uses of some metals

Metals	Uses
Cadmium	Components in manufacture of solder, electrical supplies, barriers to control nuclear fission, phosphors in the production televisions, anticorrosive coatings for metals, bearing alloys, amalgam in dentistry and worm treatments for swine and poultry and cement production.
Arsenic	Component in manufacture of bronze materials, fireworks, shot, agricultural chemicals, laser materials, glass, semiconductor materials, wood preservatives, copper, and lead alloys and insecticides.
Nickel	Component of manufacture of stainless steel, other corrosion-resistant alloys, coins, nickel steel for armor plates, burglarproof vaults, vegetables oils, ceramics and greenish glass, Al-Ni-Co magnets and Ni-Cd batteries.
Lead	Component in manufacture of older paints, older plumbing hardware, ammunition, solder, metals, storage batteries, sound and vibration absorbers, lead gasoline, obsolete insecticides (lead arsenate), lead crystal and flint glass.
Chromium	Component of the manufacture of steel, stainless-steel, alloys, metal plating for prevention of corrosion, coloring agents for emerald green glass, chemical analysis, leather tanning, textile color pigments and mordants, and trace minerals essential to the nutrition of man and animals.
Copper	Component in metal alloys, electrical wiring, some water pipes, preservatives for wood, leather and fabrics and some agricultural fungicides.
Zinc	Widely used in industry to make dye, paint and rubber; wood preservatives and ointments.

2.2.3 Movement of Trace Elements in the Environment

Metals are constantly being transported between the spheres of the environment: the atmosphere, the hydrosphere and the lithospheres (the earth crust). Figure 2.4 shows a general schematic of the movement of trace elements in the environment (Abegaz, 2005). At each stage of the transportation, the concentration of the compounds or elements will be altered either by phase transfer, dilution or surprisingly, reconcentration (Reeve, 1994).

Once metals are released from anthropogenic origin derived from other various activities including road, construction, industrial input or automobiles, they may be introduced to terrestrial and aquatic environmental systems by precipitation (wet deposition) or direct release on land or water surface (dry deposition). Accumulation of metals in natural rocks and sediments may affect aquatic plants and animals whereas those released from the air may directly affect soils, terrestrial plants, animals and ultimately humans (Figure 2.4).

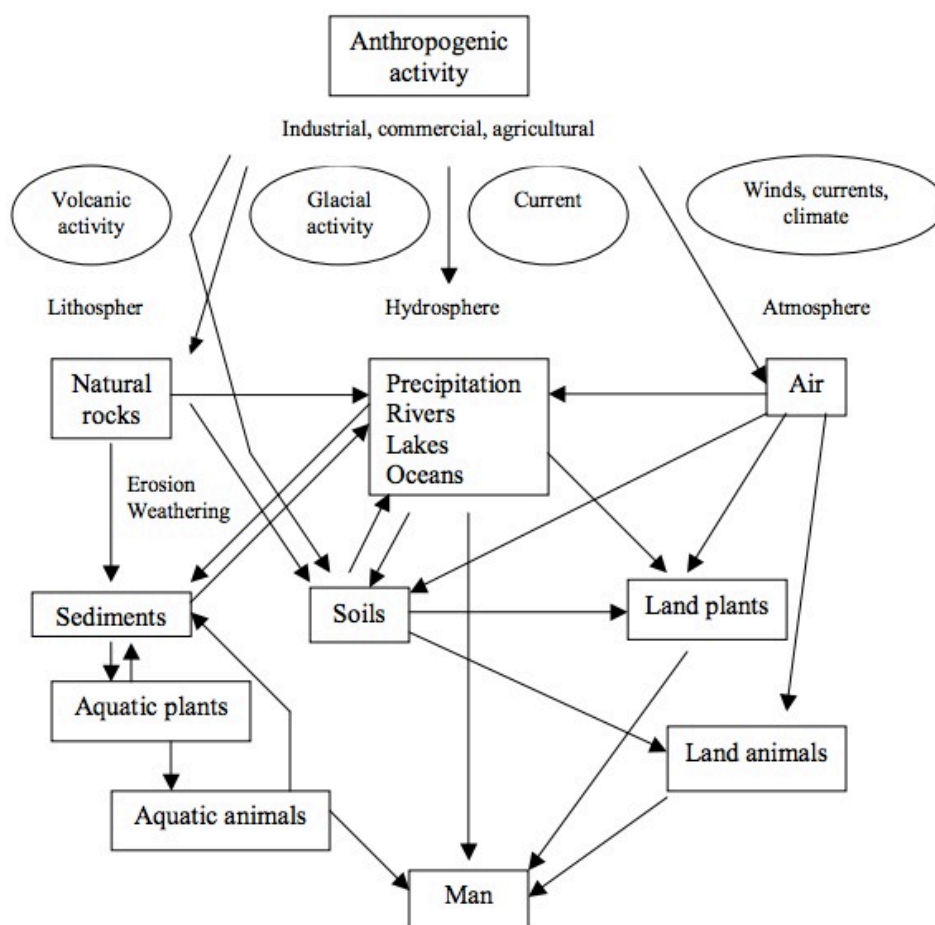


Figure 2.4 Movement of trace metal elements within the environment

The vertical extent of the atmosphere is thinner than the horizontal and as a result most of the motion that takes place in the atmosphere occurs horizontally rather than vertically (Jacob, 1999). The horizontal movement of particles in the air makes it easier for pollutants to reach surface water, soils and vegetation. Winds play a key role in this type of movement. Winds may carry atmospheric pollutants far distances away from their source. Pollutants are emitted from their source and they are dispersed with the help of wind speed and direction.

2.2.4 Metal Deposition

According to Jacob (1999), the concept of deposition means that all material in the atmosphere is deposited back on the surface of the earth. The process of atmospheric deposition is referred to as when atmospheric particles like aerosols and particulate matter are aggregated or washed out by precipitation (Azimi et al., 2003). This phenomenon of atmospheric deposition occurs in both wet and dry forms (Muezzinoglu & Cizmecioglu, 2006).

Dry deposition involves four distinct processes namely 1) gravitational settling, 2) impaction, 3) turbulent transfer and 4) transfer by Brownian motion. Research done by Azimi (2005) elucidates that in the process of atmospheric deposition, pollutants are partitioned between particulate liquid and vapor phases. This occurs due to the difference in physical and chemical properties, size and composition of the source particles. Meanwhile, Wesely & Hicks (2000) found that processes involved in dry deposition by the dry-air particle exchange significantly influence the emission of gases and other particles from the earth's surface.

Wet deposition involves two processes: nucleation and within and below cloud scavenging, whereby the wet aerosol particles are collected by falling raindrops. Scavenging of heavy metals by precipitation processes deposit heavy metals on land or water (Dumford et al., 2010). Some metals are deposited right at the point at which they are released into the atmosphere whereas others found in aerosols are much lighter and can travel longer distances further away from the source (Kanellopoulou, 2001).

Atmospheric concentrations of many compounds including nitrogen, mercury, copper, zinc, sulfur, and polyaromatic hydrocarbons have increased since the industrial revolution due to combustion of fossil fuels, industrial and manufacturing processes and agricultural operations. Deposition of atmospheric constituents to land and water surfaces occurs at a wide range of scales, from less than a kilometer to hundreds of kilometers from the emission sources. Thus, airsheds can encompass huge and often amorphous (depending on climate conditions) areas, usually 10 to 100 times greater than watershed area (Valigura, 2001). Atmospheric deposition represents a significant source of nutrients and other contaminants in many watersheds (Valigura, 2001). Deposition of these compounds onto land and water surfaces has a negative impact on plant and animal communities, ecosystem function and human health. In addition, accumulation of toxic contaminants in animal tissues can lead to reproductive failures. Accumulation of toxic compounds such as mercury and organic chemicals in food chains increases human health risk.

Asia has the highest mercury emissions, approximately 46% of worldwide emissions, with Europe and North America contributing between 15-16% (Pirrone et al., 1996). Mercury emissions to the atmosphere are primarily associated with coal burning power plants and waste incinerators (Pirrone et al., 2001; Pyle et al., 2003; Streets et al., 2003). Mercury in the atmosphere occurs in three different forms: elemental gaseous mercury (Hg^0), reactive gaseous mercury (RGM or Hg^{2+}) which is the oxidized form, and mercury associated with particles (HgP). Reactive gaseous mercury is usually deposited near the source of the emission (Dvonch et al., 1998; Lin & Pehkonen, 1999), while elemental gaseous mercury has a residence time in the atmosphere of 1-2 years, thus deposition may be worldwide (Lin & Pehkonen, 1999). Reactive gaseous mercury can be adsorbed directly onto plant and soil surfaces, as well as associated with soot, fog droplets or rain drops (Lin & Pehkonen, 1999).

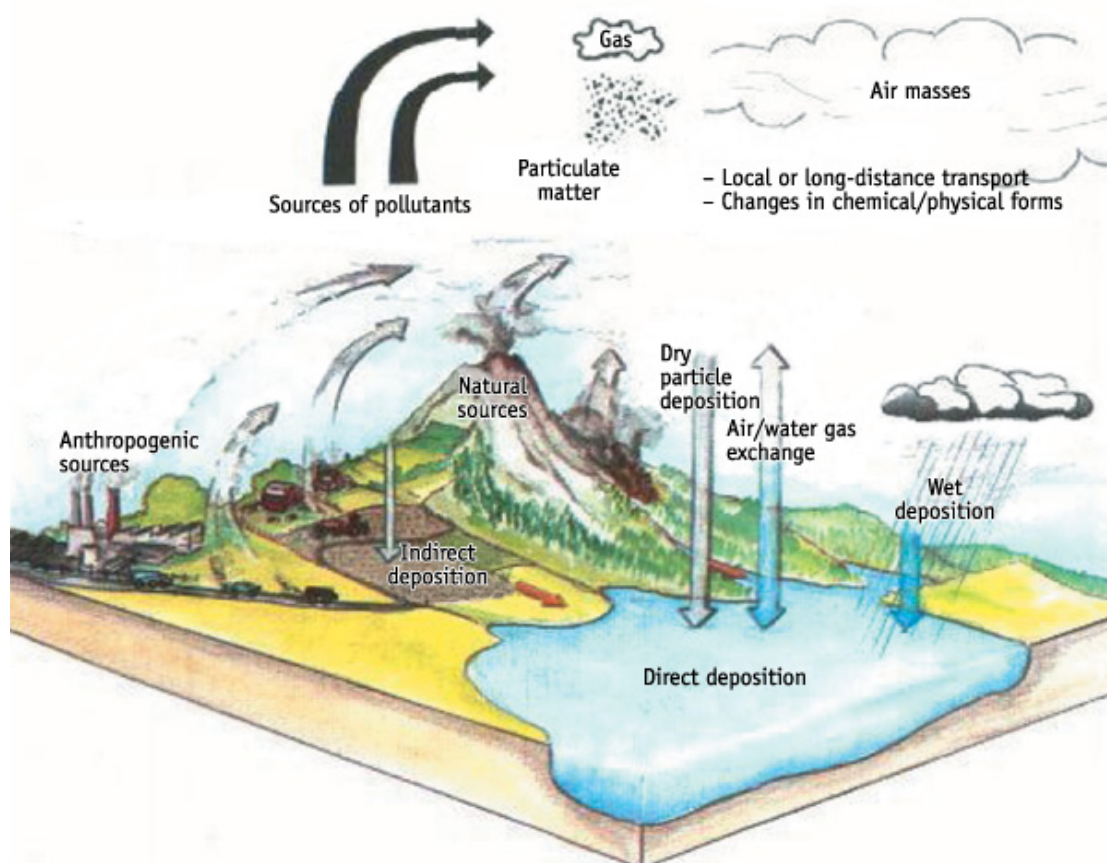


Figure 2.5 Schematic diagram transport and effects of air pollution in urban area

2.2.5 Metal Toxicity

A toxic material is a substance that has an adverse effect on health. Many chemicals could be classed as toxic, but some are more toxic than others. When metals bind to sulfhydryl groups in proteins, they may displace essential elements, disrupt functioning or inhibit sulfhydryl group activity leading to toxicity (Hall, 2002). Heavy metals such as arsenic, lead, mercury, cadmium, copper, gold, cobalt and zinc may be very toxic and relatively highly accessible to living organisms. Plants may show various signs of toxicity depending on the type of metal and the type of plant. Generally, in humans, heavy metal toxicity may range from reproductive defects to lung damage (Gidlow, 2004; ATSDR, 2008) while in plants, they may cause damage to root systems, disrupt the proper functioning of the stomata and inhibit growth (Onder *et al*, 2007). Some common trace elements and the medical conditions arising from deficiency and toxicity are listed in Table 2.5 (Selinus, 2004).

Table 2.5 Trace elements and the medical conditions arising from their deficiency and toxicity

Element	Deficiency	Toxicity
Fe	Anemia	Haemochromatosis
Cu	- Anemia “Sway back”	- Chronic copper poisoning - Wilson-Bedlington disease
Zn	- Dwarf growth - Retarded development of gonads - Akrodermatitis enteropathica	Metallic fever diarrhoea
Co	- Anemia “White liver disease”	- Heart failure - Polycythaemia
Mg	- Dysfunction of gonads - Convulsions - Malformations of the skeleton - Urolithiasis	Ataxia
Cr	Disturbance in the glucose metabolism	Kidney damage (Nephritis)
Se	- Liver necrosis - Muscular dystrophy (white muscle disease)	- Alkali disease - Blind staggers

During the past 50 years, there has been a rapid increase in the number of major trace element related to water pollution incidents. Examples include cadmium in the Jinshu River, Japan (traced to effluents from zinc mining) which produced Itai-Itai (Ouch-Ouch) or severe bone damage disease in the local human population and mercury in Minamata, Japan (methyl mercury from a chemical plant, where it was used as a catalyst in the production of vinyl chloride and acetaldehyde) (Fellenberg, 2000).

Although chromium is an essential trace element, chromate salts can produce severe effects in the skin, nasal septum and the lung (ATSDR, 2008). The homeostatic mechanisms usually operate to control gastrointestinal absorption so that entry into the body by other pathways circumvents this control. The other example is Zn, the inhalation of zinc oxide fumes can give rise to an allergic response resulting in metal fume fever (Cooper, 2008).

Many metals have no known biological importance in human biochemistry and physiology and the ingestion of even tiny quantities can be toxic. These metals include Cd, Pb and Hg (Duruibe et al., 2007). “Heavy metals” is a general collective term which includes any metal which is toxic or poisonous and which also has a relatively high density (Duruibe et al., 2007). General signs associated with poisoning by Cd, Pb, As, Hg, Zn, Cu and Al include gastrointestinal disorders, diarrhoea, stomatitis, hemoglobinuria, ataxia, paralysis, vomiting and convulsions, depression, and even pneumonia (Duruibe et al., 2007).

Metals interfere with the body biochemistry during normal metabolic processes. In the acid medium of the stomach, they convert to their stable oxidation states and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds, replacing hydrogen or essential metals in an enzyme and thus preventing the enzyme from functioning (Duruibe et al., 2007). Metal ions in the body's metallo-enzymes can be conveniently replaced by another metal ion of similar size. Sometimes enzymes for an entire sequence co-exist together as a single multi-enzyme complex, and the replacement of an essential metal by an interfering metal blocks the biological reaction of the enzymatic function. An example in point is the replacement of Zn by Cd and the resulting deleterious effects on body chemistry (Brzoska & Moniuszko-Jakoniuk, 2001). Thus, the metal remains embedded in the tissue and will result in a variety of bio-dysfunctions, not all equally serious (Duruibe et al., 2007). The most poisonous forms of the interfering metals are their most stable oxidation states, since these form very stable biotoxic compounds which are difficult to dissociate with detoxification therapies (Duruibe et al., 2007).

2.2.6 Trace Elements in Whole Blood

Heavy metals and trace elements can be measured in whole, serum, urine and other tissues. In blood, metals are distributed between the non-cellular (plasma/serum) and intra-cellular compartment (predominantly erythrocytes). For examples, lead (Pb) is known to have a strong affinity for erythrocyte (Bergdahl et al., 1997). Thus Pb is measured primarily in whole blood. Levels of metals in blood and serum have been extensively studied in different samples to identify the exposure of human population. Pregnant mother and their growing fetuses are especially vulnerable to exposure to pollutants. Air and water pollution, exposure to toxic elements, and exposure to persistent organic compounds have been associated with adverse pregnancy and developmental outcome (Landrigan et al., 2004; Bocskay et al., 2005).

In addition to that, trace elements are also required in the body for its normal function. Macrominerals are defined as minerals that are required by adults in amounts greater than 100 mg/day. Major (macro) minerals include sodium, potassium, chloride, calcium, magnesium and phosphorus. Trace elements (or trace minerals) are usually defined as minerals that are required in amounts between 1 to 100 mg/day by adults. Trace mineral group includes iron, copper, and zinc. Ultra-trace minerals are defined as minerals that are required in amounts less than 1 mg/day. They include chromium, manganese, fluoride, iodide, cobalt, selenium, silicon, arsenic, boron, vanadium, nickel, cadmium, lithium, lead and molybdenum (O'Dell & Sunde, 1997).

2.3 POLYCYCLIC AROMATIC HYDROCARBON (PAHs)

Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various functional groups which may contain several elements. An important group of polycyclic aromatic compounds are the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzenoid rings and no elements other than carbon and hydrogen (Henner et al., 1997). They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs (Marce & Borrull, 2000).

Organic compounds can be released from their sources in gas phase or can be associated with particles by nucleation and condensation, forming particulate matter. PAHs can be present in both particulate and gaseous phases, depending upon their volatility. Light molecular weight PAHs (LMW PAHs) that have two or three aromatic rings are emitted in the gaseous phase, while high molecular weight PAHs (HMW PAHs), with five or more rings, are emitted in the particulate phase. The particulate form of PAHs are initially in the gaseous phase at high combustion temperature, however when the temperature decreases, gaseous phase PAHs adsorb or deposit on fly ash particles. Smaller particle size offers greater surface area for the adsorption of PAHs. The ambient temperature is very important for the gas-particle distribution of PAHs.

PAH can be formed in any incomplete combustion or high temperature pyrolytic process involving fossil fuels, or more generally, materials containing C and H (Baek et al., 1991). The mechanism of formation of PAH involves the production of reactive free radicals by pyrolysis (at $\sim 500-800^{\circ}\text{C}$) of fuel hydrocarbons in the chemically reducing zone of a flame burning with an insufficient supply of oxygen. The C_2 fragments, as well as C_1 and higher radicals, combine rapidly in the reducing atmosphere to form partially condensed aromatic molecules. On cooling the reaction mixture, these PAH condense from the vapor phase onto co-existing particulate substrates, with a product distribution that generally reflects their thermodynamic stabilities in the oxygen-deficient flame.

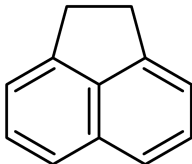
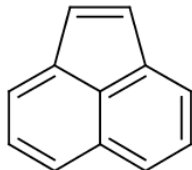
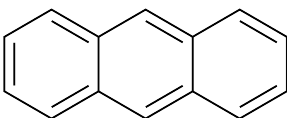
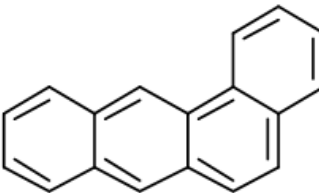
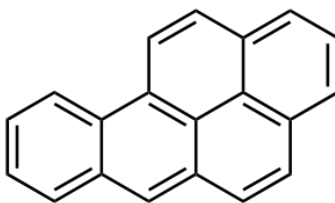
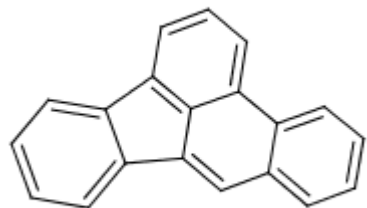
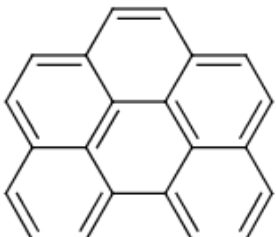
PAH formation and emission mechanisms can be classified in two processes, pyrolysis and pyrosynthesis in any fuel combustion system. Pyrolysis is the formation of the smaller and unstable fragments from an organic compound upon heating. Fragments are the highly reactive free radicals with a very short average life time. By recombination reactions, these free radicals lead to more stable PAHs and this process is called pyrosynthesis. For example B(a)P and other PAHs are formed through pyrolysis processes of methane, acetylene, butadiene and other compounds (Mastral & Callen, 2000).

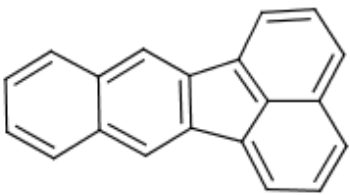
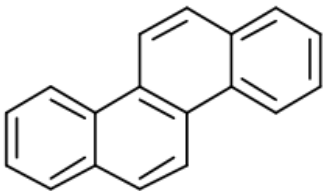
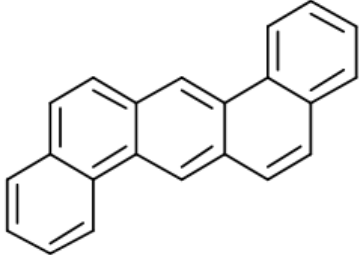
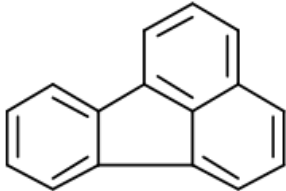
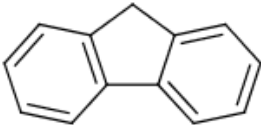
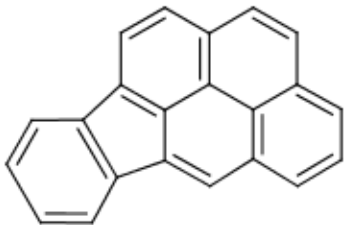
PAH formation in pyrolysis oils has been attributed by Diels-Alder reactions of alkenes to form cyclic alkenes. Upon dehydrogenation reactions of cyclic alkenes, stable rings of aromatic compounds form which further lead to formation of PAH compounds. However complex hydrocarbons do not have to necessarily break into small fragments before recombination processes. Compounds with several rings can suffer partial cracking. On the other hand, phenyl radicals also play an important role besides intermolecular and intramolecular hydrogen transfers at intermediary compounds in high temperature reactions that lead to PAH formation (Mastral & Callen, 2000).

2.3.1 Physical and Chemical Characteristics of PAHs

PAHs are classified by their melting and boiling point, vapor pressure, and water solubility; depending on their structure. Table 2.6 shows physical and chemical characteristics of 16 priority PAHs, listed by the USEPA. Most PAHs, especially as molecular weight increases, are soluble in non-polar organic solvents and are barely soluble in polar water. Their lipophilicity is high, as measured by water-octanol partition coefficients (K_{ow}). Due to their hydrophobic nature, the concentrations of dissolved PAHs in water are very low. PAHs show long half lives in geological

media. In an aerobic sediment, for example, half lives range from three weeks for naphthalene and up to 300 weeks for benzo(a)pyrene. PAHs are regarded as persistent organic pollutants (POPs) in the environment.

PAHs	CASRN	Abbreviation	Structure
Acenaphthene	83-32-9	ACE	
Acenaphthylene	208-96-8	ACY	
Anthracene	120-12-7	ANTH	
Benzo(a)anthracene	56-55-3	B(a)An	
Benzo[a]pyrene	50-32-8	B(a)P	
Benzo(b)fluoranthene	205-99-2	B(b)Fl	
Benzo(g,h,i)perylene	191-24-2	B(ghi)P	

PAHs	CASRN	Abbreviation	Structure
Benzo(k)fluoranthene	207-08-9	B(k)Fl	
Chrysene	218-01-9	CHR	
Dibenz(a,h)anthracene	53-70-3	DiB(a,h)An	
Fluoranthene	206-44-0	FLA	
Fluorene	86-73-7	FLU	
Indeno(1,2,3-cd)pyrene	193-39-5	InPy	

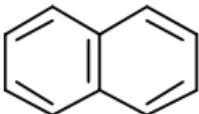
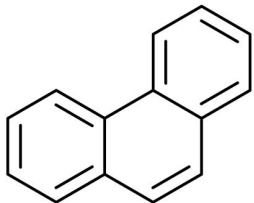
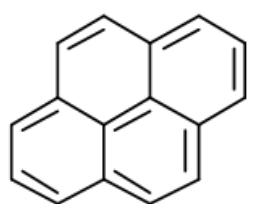
PAHs	CASRN	Abbreviation	Structure
Naphthalene	91-20-3	NAP	
Phenanthrene	85-01-8	PHE	
Pyrene	129-00-0	PYR	

Figure 2.6 Molecular structures of PAHs

Physical properties of the 16 PAHs defines as priority pollutants by the US Environmental Protection Agency (USEPA) are summarised in Table 2.6.

Table 2.6 Chemical structure and physical properties of selected of PAHs

Compound	Molecular Formula	Molecular weight	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (kPa)
Acenaphthene	C ₁₂ H ₁₀	154.20	90-96	278-279	2.1x10 ⁻³
Acenaphthylene	C ₁₂ H ₈	152.20	92-93	265-280	3.9x10 ⁻³
Anthracene	C ₁₄ H ₁₀	178.24	216-219	340	36x10 ⁻⁶
Benzo(a)anthracene	C ₁₈ H ₁₂	228.30	157-167	435	1.5x10 ⁻⁸
Benzo(a)pyrene	C ₂₀ H ₁₂	252.32	177-179	493-496	7.3x10 ⁻¹⁰
Benzo(b)fluoranthene	C ₂₀ H ₁₂	252.32	167-168	481	6.7x10 ⁻⁸
Benzo(g,h,i)perylene	C ₂₂ H ₁₂	276.34	275-278	525	1.3x10 ⁻¹¹
Benzo(k)fluoranthene	C ₂₀ H ₁₂	252.32	198-217	480-471	2.1x10 ⁻⁸
Chrysene	C ₁₈ H ₁₂	228.30	252-256	441-448	5.7x10 ⁻¹⁰
Dibenz(a,h)anthracene	C ₂₂ H ₁₄	278.35	266-270	524	1.3x10 ⁻¹¹

Compound	Molecular Formula	Molecular weight	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (kPa)
Fluoranthene	C ₁₆ H ₁₀	202.26	107-111	375-393	6.5x10 ⁻⁷
Fluorene	C ₁₃ H ₁₀	166.23	116-118	293-295	8.7x10 ⁻⁵
Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276.34	162-163	536	1.3x10 ⁻¹¹
Naphthalene	C ₁₀ H ₈	128.18	80.2	218	1.1x10 ⁻²
Phenanthrene	C ₁₄ H ₁₀	178.24	96-101	339-340	2.3x10 ⁻⁵
Pyrene	C ₁₆ H ₁₀	202.26	150-156	360-404	3.1x10 ⁻⁶

2.3.2 Toxicity and Carcinogenicity of PAHs

Air with high concentrations of PAHs causes many adverse effects on different types of organisms, including plants, birds, and mammals. Some studies reported that there is a significant positive correlation between mortality by lung cancer in humans and exposure to PAHs from exhaust from coke ovens, roofing-tar, and cigarette smoke. Concurrently, certain PAHs were shown to react with near ambient levels of NO₂+HNO₃ and with O₃ in synthetic atmospheres, to form directly mutagenic nitro-PAH and oxy-PAH.

Some of the PAHs and their metabolites can induce stable genetic alterations that have the potential to irreversibly alter the control of cell division. This may result in tumor growth and cancer in fish and mammals. Due to solubility of PAHs in fatty tissue, they may bioaccumulate and transferred in the food chain. Some of PAHs have been identified as possible or probable carcinogens in humans; notably benzo(a)anthracene, chrysene, benzo(b and k) fluoranthene, benzo(a)pyrene and others (Golomb et al., 1997). Epidemiological studies have proved that people exposed to mixtures containing PAH's (chimneys, coke oven emissions, cigarette smoke, roofing tar emissions) have increased rates of lung cancer (Fisher, 2001).

The lower molecular weight of PAHs, are known to be less toxic. They are predominantly found in the vapor phase in an urban air where they can react with other pollutants (O₃ and NO_x) to form more toxic derivatives. For example, PAHs react with NO₃ will form carcinogenic nitro-derivatives (Kameda, 2011).

Particulates less than 10µm in diameter are more likely to contain greater amounts (per unit mass) of PAHs due to their large surface area to volume ratio. This is a great concern since it is the smaller diameter particles that are retained by the lung. In human respiratory system, particles with diameters larger than 10µm do not reach the thorax, particles ranging from 2.1 to 10µm are preferentially retained by pharynx, trachea and bronchi and particles below 2.1µm can reach terminal bronchi and alveoli. Therefore, a physical detrimental action of inhalable particles (i.e., the development of pulmonary emphysema) is observed along with the chemical impact due to their toxicity (Cecinato et al., 1999).

Human exposure to PAHs can occur through inhalation of polluted air or cigarette smoke, ingestion of food containing PAHs, as well as dermal absorption from soil or material that contains PAHs. For the general population, ingestion and inhalation are the two major routes of exposure (ATSDR, 1995; Bostrom et al., 2002; Ramesh et al., 2004). For certain occupations, such as coal tar roofers and coke oven workers, dermal absorption can become the primary route of PAH exposure (ATSDR, 1995).

After entering the human body, PAHs undergo a series of biotransformation processes. In Phase I metabolism, PAHs are oxidized by the cytochrome P450 enzymes to form reactive epoxide intermediates, followed by reduction or hydrolysis to hydroxylated derivatives (OH-PAHs). In Phase II metabolism, the OH-PAHs are conjugated to glucuronic acid and/or sulfate to increase the water solubility of the metabolite and to facilitate elimination through urine, bile, or feces (Xue & Warshawsky, 2005 ; Grover, 1986). Urinary OH-PAHs have been used as biomarkers to assess human exposure to PAHs, with 1-hydroxypyrene (1-PYR) as the most commonly used indicator in biomonitoring studies (Jacob & Seidel, 2002).

2.3.3 Sources of PAHs

PAHs are mainly derived from anthropogenic activities related to pyrolysis and incomplete combustion of organic matter. Emission sources of PAHs affect their characterization and distribution, as well as their toxicity. It has been estimated that stationary sources contribute for approximately 90% of total PAH emission, but this is not true in urban and suburban areas, where the mobile sources are prevailing. The highest concentrations of atmospheric PAHs can be found in the urban environment, due to the increasing vehicular traffic and the scarce dispersion of the atmospheric pollutants. The risk associated with human exposure to atmospheric PAH is highest in the cities, considering the density of population (Caricchia et al., 1999).

The anthropogenic sources of PAH can be divided into stationary and mobile categories. Mobile sources are major causes of PAH emissions in urban areas. PAHs are mostly emitted from exhaust fumes of vehicles, including automobiles, railways, ships, aircrafts, and other motor vehicles. PAH emissions from mobile sources are related with use of diesel, coal, gasoline, oils, and lubricant oil. The stationary category includes a wide variety of combustion processes including residential heating, industrial activities (e.g. aluminum production and coke manufacture), incineration and power generation which result in high atmospheric PAH concentrations in the vicinity of the major sources. The amount and range of PAH produced from any pyrolytic process varies widely, being dependent upon the fuel type and combustion conditions. The contribution of any PAH source to the atmosphere will depend on a number of factors including the emission rate of the source, its geographical location and the local climatic conditions (Baek et al., 1991).

2.3.4 Chemical Transformation and Deposition of PAHs

The atmospheric chemical and photochemical reactions of the PAH are important mainly for two reasons:

- a) Particular PAHs can be removed from the atmosphere as a result of chemical reactions
- b) Decomposition product of the PAHs may be more hazardous to human health than the PAHs from which they were derived (Hansen & Eatough, 1991)

Baek et al., (1991) indicated that distribution of PAHs in the atmosphere between the gas and particulate phases is determined by several factors namely the vapor pressure of the PAHs (as a function of temperature); the amount of fine particles (in terms of available surface area for adsorption of PAHs); the ambient temperature; PAH concentration; and the affinity of individual PAH for the particles organic matrix.

Photochemical transformation have generally considered to be the most important mode of atmospheric decomposition of PAHs of both phases and extent of photochemical decay is strongly depend on the nature of the substrate on which they are adsorbed. Although photochemistry is the major mechanism for decomposition of PAHs, various PAHs may also degrade by non-photochemical pathways such as evaporative or oxidative reactions with gaseous pollutants (Baek et al.,1991).

As PAHs in the atmosphere are predominantly related with particulate matter, their atmospheric residence time is closely related to the behavior of the carrier particles. The physical removal or transport of airborne particles is a function of the particle size and meteorological conditions. Both coarse particles (larger than 3 to 5 μ m) and nuclei range particles (below 0.1 μ m) are similarly limited in their atmospheric residence times, and consequently in their effects, although their removal mechanisms are different. The former tend to be removed from the atmosphere by simple sedimentation, such as dry or wet deposition, while the latter are removed predominantly by coagulation with each other and larger particles. Particles in the size range between 0,1 and 3 μ m, with which airborne PAH are predominantly associated, are known to diffuse only slowly and have little inertia, and can be expected to remain airborne for a few days or longer. Particle of this size range are not removed efficiently by rain and may be transferred over long distances, dependent upon atmospheric conditions (Baek et al., 1991).

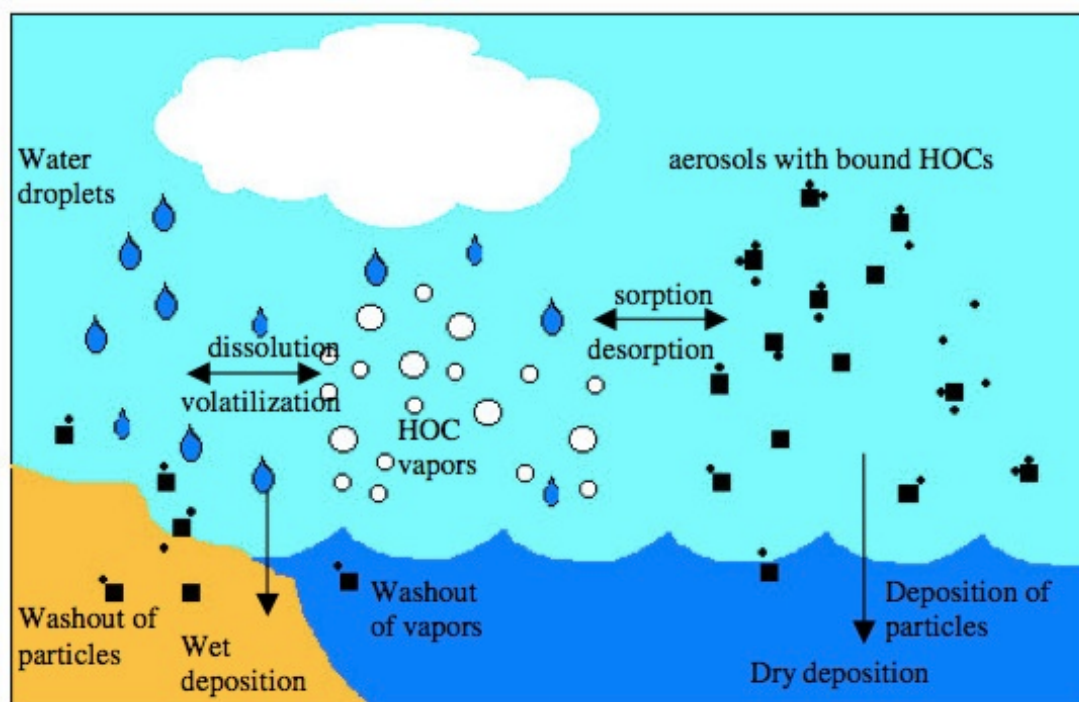


Figure.2.7 Atmospheric depositions of HOCs

Figure 2.7 shows schematically atmospheric deposition processes for Hydrophobic Organic Compounds (HOCs). Based on Figure 2.7, particles and vapors are removed from the atmosphere with both dry and wet deposition. Gas particle and gas liquid partitioning mechanisms are also important for the deposition of HOCs to earth surface (Leister and Baker, 1994).

2.3.5 PAHs in Whole Blood

Blood measurement for DNA adducts of PAHs have been employed as a markers for PAHs exposure in human populations. Environmental monitoring documents the presence of a environmental pollutant, but the biological consequences of exposure to the organism are found only intracellularly (Angerer & Ewers 2007; Gallo et al., 2008). Protein-adduct formation is considered a surrogate of DNA adducts formation, but only the latter results in critical mutagenic changes (Poirier et al., 2000).

Benzo(a)pyrene B(a)P is a 5 ring PAHs and a potent carcinogen that have been used a surrogate marker for PAHs in environmental sample. Human metabolism converts B(a)P to the reactive benzo(a)pyrene diol epoxide (BPDE), which forms adducts with DNA and proteins and further hydrolyzed to BPDE tetrols that are excreted from human body (Poirier & Weston, 1996). The concentrations of human serum albumin (HSA) is more than a thousandfold greater than that in DNA in human blood and unlike DNA adducts, HSA adducts are not repair. Therefore, BPDE-HSA should be relatively stable biomarker of B(a)P exposure, with human half life of 20 days that ensures integration B(a)P exposure over about a month (Kafferlein et al., 2010).

Over the years many studies have contributed to validation of PAH-DNA adduct measurements in human DNA using immunoassays, the most-sensitive of which is the chemiluminescence immunoassay (CIA) (Divi et al., 2002). A cohort study of US Army soldiers who were moved from an area with a clean ambient environment to one that was much more polluted revealed significant increases in blood cell PAH-DNA adduct levels for each individual (Jacobson-Kram et al., 1993; Poirier et al., 1998). Similarly, a significantly higher level of blood cell PAH-DNA adducts was found in young adults sampled in Mexico City in the dry season, when airborne PAH levels were higher, compared to the rainy season, when PAH levels were lower (Garcia et al., 2011).

CHAPTER 3

CONCENTRATION AND SIZE DISTRIBUTION OF ATMOSPHERIC PARTICULATE MATTER

3.1 INTRODUCTION

Airborne particulate matter (PM) includes a wide range of particles of different sources, sizes and compositions. The term PM is used for all solid and liquid particles that are suspended in the atmosphere as non-gaseous phases such as smoke, dust and droplets of liquids (i.e. acids, water). Particles vary in number, size, shape, surface area, chemical composition, solubility and origin in both space and time (Srimuruganandam & Shiva Nagendra, 2012). PM originates from a variety of natural or anthropogenic sources and possesses a range of morphological, physical, chemical and thermodynamic properties (USEPA, 2004). Particles can either be directly emitted into the atmosphere by anthropogenic activity or wind or can form during condensation of vapours and are then termed primary particles.

PM is broadly divided into two principal groups according to their size, which is often described as coarse particles (PM_{10}) and fine particles ($PM_{2.5}$). The size is characterized by the equivalent diameter, which is the diameter of a spherical particle with the same physical behavior as the particle in question. The coarse fraction of PM has an equivalent diameter larger than $2.5\mu m$ and smaller than $10\mu m$; while the fine fraction has an equivalent diameter of $2.5\mu m$ and smaller (Watson 2002).

Trace elements are the ubiquitous pollutants in the environment that predominantly originate from industrial activities, domestic emission, traffic emission and weathering of buildings and pavements (Chen et al., 2005; Kong et al., 2012). Among various emission sources; vehicle emission is the main contributors in urban area. Fine et al. (2004) found that vehicular emissions are one of the most prominent sources of ultrafine particles ($<2.5\mu m$) in urban atmosphere. Study done by Chow et al. (1996) proved that motor vehicular emissions contribute from 25% to 35% of $PM_{2.5}$ (particulate matter with diameter $<2.5\mu m$) to the atmosphere.

3.2 METHODOLOGY

3.2.1 Sampling Sites

A. Petaling Jaya (PJ)

The sampling was carried out at the Department of Chemistry, Malaysia headquarters which is located in moderately built up area of scattered government offices and residential houses in the town of Petaling Jaya. Samples were collected from 15th-24th July 2014 during southwest monsoon.

Petaling Jaya is situated in the Klang Valley region, which is a basin located in the southwestern part of the Malaysian Peninsular, surrounded by highland exceeding 1500m altitude in the east and the Straits of Malacca in the west (Abas et al., 1996). The dispersive capability in the Klang Valley is very restricted. For example, the pattern of the airflow is reversed; that is, the wind blows inland from the sea. Such a pattern causes much of the pollutants produced within the valley to remain very much where they are (Sani, 1987). The sampling sites were chosen so as to represent the busiest roads and road-intersections in the city. The average traffic volume for city roads is about 30,000 vehicles per day, whilst for the road-intersections it is about 100,000 vehicles per day.

B. Bangi

Another sampling was also carried out at the main campus of Universiti Kebangsaan Malaysia (UKM), which is located in Bandar BaruBangi. Ambient particulate matter was collected from 10th-16th December 2013 during northeast monsoon.

Bangi is a semi-urban area situated in the southern part of Kuala Lumpur, which is also included in the Klang Valley Region. This area is developing fast, particularly in Bandar BaruBangi (the new town of Bangi) and contains a large population and residential area with a high level of vehicles usage. Before Bangi was developed into a residential area spreading out from Kajang Town, it had a great number of plantations, predominantly for rubber and palm oil.

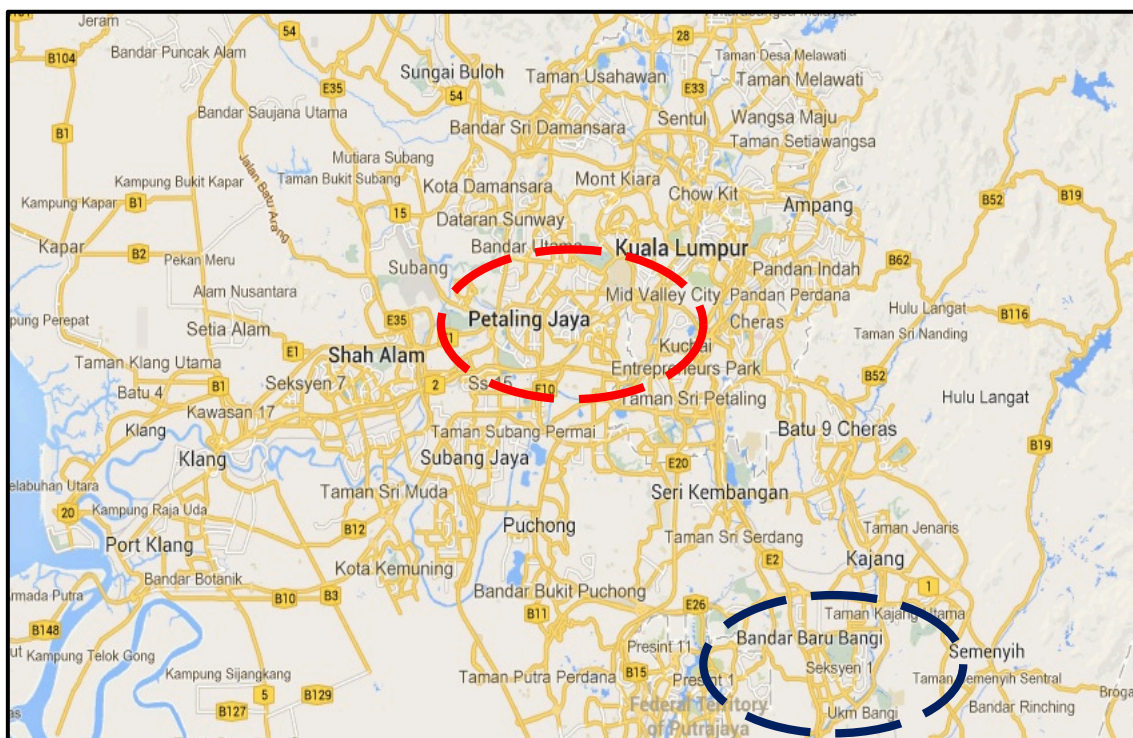


Figure 3.1 Sampling locations in Petaling Jaya and Bangi

3.2.2 Samples Acquisition

Airborne particles were acquired using a high volume air sampler (HVAS) with a six-stage Cascade Impactor (Staplex). Stage 1 until 5 were slotted with glass fiber filter papers (Westech Instrument) which are used to collect particles in five size fragment ($>7.2\mu\text{m}$, $3.0\text{--}7.2\mu\text{m}$, $1.5\text{--}3.0\mu\text{m}$, $0.95\text{--}1.5\mu\text{m}$ and $0.49\text{--}0.95\mu\text{m}$). For the backup stage, a backup filter paper (Whatman EPM 2000) was used to collect fine mode aerosol samples (diameter size $< 0.49\mu\text{m}$).

In order to remove organic matter, slotted filter papers and backup filter papers were packed in aluminium foil and pre-fired at 500°C in a muffle furnace for 4 hours prior to use. The filter papers were then conditioned in desiccators for 24 hours before being weighed with an electronic balance and stored in a refrigerator (4°C) until analysis. The high volume air sampler, with prepared filter papers, was placed in an open field to avoid any disturbance of material to the flow of aerosols entering the instrument.

The sampling was carried out for 24 hours with a flow rate of $1.13\text{ m}^3/\text{min}$. After the aerosol sampling, the filter papers were once again carefully packed in aluminium foil and conditioned in desiccators prior to weighing. The blank filter papers were treated in

the same manner as the filter paper used to collect aerosol samples. The filter paper was fitted to the high volume air sampler for 24 hours without the high volume sampler being switched on.

3.2.3 Samples Preparation

The filter papers with aerosol samples were cut into small pieces and put into digestion vessel. Exposed filter papers were subjected to acid digestion using a mixture of 6 mL nitric acid (HNO₃) and 4 mL perchloric acid (HClO₄). The microwave oven Model CEM MARS 6 was used to digest aerosol samples. The vessels were capped, fastened on the rack and placed in the microwave oven to undergo the digestion procedure. The samples were digested using the program summarized in Table 3.1.

Table 3.1 Microwave oven parameters

Power	1200 Watts
Ramp time	10 minutes
Final temperature	180 °C
Temperature hold time	10 minutes
Cool down time	10 minutes

Upon completion of the digestion, the carousel containing the vessels was removed from the microwave and placed in a fume hood in the clean room to cool. After cooling, the digestion vessel was rinse with ultrapure water and the sample solution was then filtered using 0.2µm 47 mm cellulos acetate filter papers (Whatman). The resulting solution were then diluted with ultrapure water and stored in refrigerator at 4°C until further analysis.

3.2.4 Samples Analysis

The elemental analysis of atmospheric particulate samples was carried-out by using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) (Model: Agilent 7500CE). Firstly, the instrument was tuned by testing a specially made solution prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions in 1% nitric acid to produce a concentration of 100 µg/L of each element as per Method 200.8 (USEPA, 1994). This solution is referred to as a tuning solution. Tuning solution was used to determine acceptable instrument performance prior to calibration and sample analysis.

After satisfactory tuning, sample sequences including calibration standards were prepared. Consequently, samples in the liquid matrix were introduced into the machine by pneumatic nebulization into radio frequency plasma where energy transfer processes cause atomization and ionization. The ions were extracted from the plasma through a differentially pumped vacuum interface and separated based on their mass to charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole were detected by an electron multiplier.

Calibration standards were prepared from AcuStandardInc, New Haven, and USA. All calibration standards are ensured to have residual mean square (R2) greater than or equal to 0.98. The first set prepared from the following elements: Silver (Ag), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Lithium (Li), Manganese (Mn), Nickel (Ni), Lead (Pb) and Strontium (Sr). Each set was prepared at the following concentrations of 0.2 ppb, 0.5 ppb, 1 ppb, 2 ppb, 5 ppb and 10 ppb.

The percentages of recovery for the elements were measured using laboratory controlled reference standards with known amount of concentration. These samples were extracted and analyzed with the same procedures as for the samples. As seen in Table 3.2, the percent recoveries for all the elements were satisfactory.

Table 3.2 Elemental recoveries (%) by using laboratory reference standard

Elements	MDL µg/L	Recoveries (%)
Ag	0.93	88
Cd	0.52	84
Co	0.24	90
Cr	0.45	80
Cu	0.13	91
Li	0.67	86
Mn	0.88	93
Ni	0.34	89
Pb	0.73	85
Sr	0.82	82

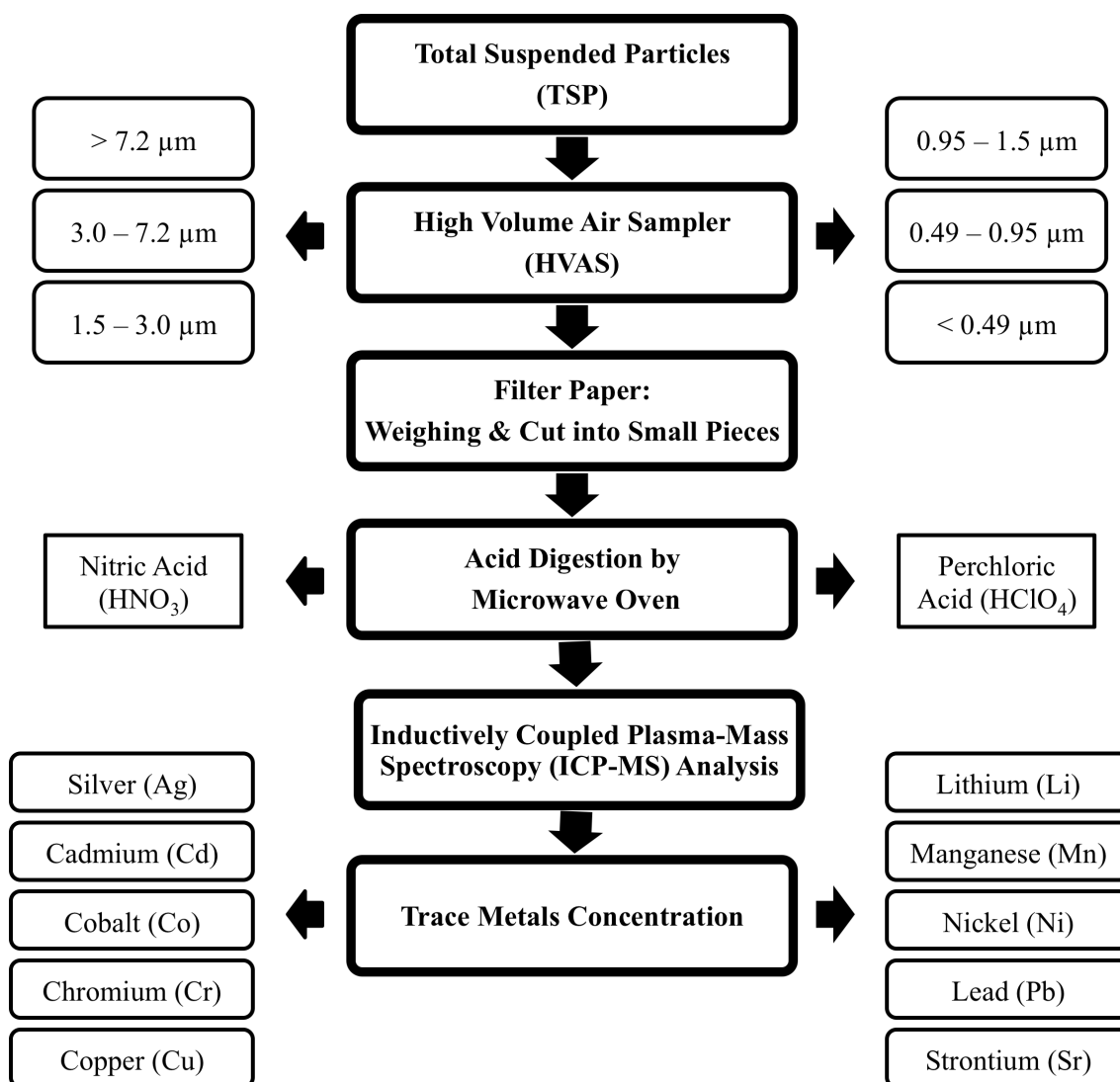


Figure 3.2 Diagrams of samples collection and analysis

3.2.5 Quality Control

All glassware and Teflon digestion vessels were cleaned in 10% nitric acid overnight; and then rinsed in ultra-pure water prior to extraction procedures. Procedure blanks were used for quality control.

3.3 RESULTS AND DISCUSSION

3.3.1 Concentration and Size Distribution of Particulate Matter

Table 3.3 presents the PM concentrations of all particle size groups measured in Bangi and Petaling Jaya during the study period. The mean concentrations in Bangi for group particle sizes of $>7.2\mu\text{m}$, $3.0\text{--}7.2\mu\text{m}$, $1.5\text{--}3.0\mu\text{m}$, $0.95\text{--}1.5\mu\text{m}$ and $0.49\text{--}0.95\mu\text{m}$ are range from $0.87\mu\text{g}/\text{m}^3$, $2.01\mu\text{g}/\text{m}^3$, $1.89\mu\text{g}/\text{m}^3$, $1.09\mu\text{g}/\text{m}^3$ and $1.32\mu\text{g}/\text{m}^3$; respectively. In contrast, Petaling Jaya recorded higher mean concentrations for all particle size groups; which are $5.21\mu\text{g}/\text{m}^3$ ($>7.2\mu\text{m}$), $8.43\mu\text{g}/\text{m}^3$ ($3.0\text{--}7.2\mu\text{m}$), $5.65\mu\text{g}/\text{m}^3$ ($1.5\text{--}3.0\mu\text{m}$), $6.79\mu\text{g}/\text{m}^3$ ($0.95\text{--}1.5\mu\text{m}$) and $9.51\mu\text{g}/\text{m}^3$ ($0.49\text{--}0.95\mu\text{m}$). A similar pattern can be seen in Bangi and Petaling Jaya for particle size of $<0.49\mu\text{m}$; as the mean concentrations showed an outstanding data of $15.48\mu\text{g}/\text{m}^3$ and $43.89\mu\text{g}/\text{m}^3$, respectively; compared to other groups of particle size.

Table 3.3 Summary of PM measurement in Bangi and Petaling Jaya

Location	Size (μm)	Concentrations ($\mu\text{g}/\text{m}^3$)		Coefficient of Variation (SD / Mean)
		(Min – Max)	Mean (Med) $\pm$ SD	
Bangi	>7.2	(0.16 – 2.03)	$0.87 (0.70) \pm 0.68$	0.78
	$3.0\text{--}7.2$	(0.45 – 3.85)	$2.01 (1.99) \pm 1.10$	0.55
	$1.5\text{--}3.0$	(0.43 – 3.01)	$1.89 (1.86) \pm 0.85$	0.45
	$0.95\text{--}1.5$	(0.45 – 1.52)	$1.09 (1.17) \pm 0.35$	0.32
	$0.49\text{--}0.95$	(0.47 – 1.80)	$1.32 (1.45) \pm 0.46$	0.35
	<0.49	(3.03 – 44.27)	$15.48 (10.16) \pm 14.73$	0.95
Petaling Jaya	>7.2	(1.91 – 8.05)	$5.21 (4.73) \pm 2.26$	0.43
	$3.0\text{--}7.2$	(2.83 – 12.48)	$8.43 (9.13) \pm 3.29$	0.39
	$1.5\text{--}3.0$	(4.12 – 7.87)	$5.65 (5.25) \pm 1.40$	0.25
	$0.95\text{--}1.5$	(2.95 – 12.66)	$6.79 (5.81) \pm 3.67$	0.54
	$0.49\text{--}0.95$	(5.84 – 14.81)	$9.51 (7.62) \pm 4.20$	0.44
	<0.49	(31.03 – 68.65)	$43.89 (36.66) \pm 15.86$	0.36

The 24-h TSP levels in Bangi and Petaling Jaya exhibited a mean concentration of $22.66\mu\text{g}/\text{m}^3$ and $79.48\mu\text{g}/\text{m}^3$. The 24-h TSP level in Bangi is below the guideline set by WHO ($80\mu\text{g}/\text{m}^3$) and USEPA ($60\mu\text{g}/\text{m}^3$) standard value, while the average 24-h TSP in Petaling Jaya was found to be significantly higher than USEPA standard value (ATSDR, 2002). The preset data on airborne TSP is compared with Malaysian guideline, international guideline as well as with other counterpart data from other sites around the world. The TSP values obtained for both sampling site in Bangi and Petaling Jaya were still well below the Recommended Malaysian Air Quality Guideline (RMAQG) for TSP (mean of 24-hour measurement = $260\mu\text{g}/\text{m}^3$, Department of Environment).

The average TSP level in Bangi and Petaling Jaya was substantially lower than those reported from Lahore (Harrison et al., 1997), Faisalabad (Qadir & Zaidi, 2006), Delhi (Shridhar et al., 2010), Beijing (Wang et al., 2001), Cartagena (Moreno-Grau et al., 2000), Bilbao (Aranguiz et al., 2002) and Rio-de Janeiro (Quiterio et al., 2004). Meanwhile, atmospheric TSP level in Petaling Jaya was slightly higher than TSP level observed from Yokohama (Khan et al., 2010), Delft (Wang et al., 2001), and Tito Scalo (Ragosta et al., 2002). However the TSP level from Ho Chi Minh City (Hien et al., 2001) was almost comparable with the levels measured in Petaling Jaya.

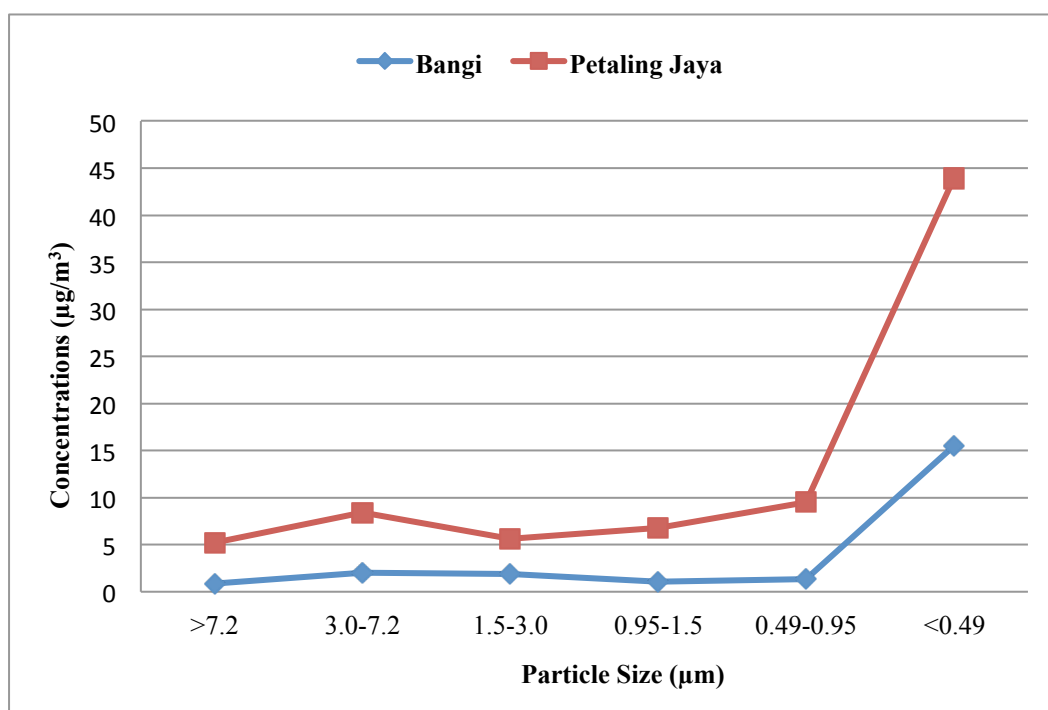


Figure 3.3 Distribution of PM concentrations of different particle size groups

Figure 3.3 outline the mean of PM concentrations of different particle size groups measured in Bangi and Petaling Jaya during the study period. A higher data of PM concentrations for all particle size groups are recorded in Petaling Jaya; as compared to PM concentrations in Bangi. The mean of PM concentrations for all particle size groups in Petaling Jaya are more than $5\mu\text{g}/\text{m}^3$ while PM concentrations in Bangi recorded an overall mean of less than $3\mu\text{g}/\text{m}^3$, except for the particle size of $<0.49\mu\text{m}$ ($15.48\mu\text{g}/\text{m}^3$).

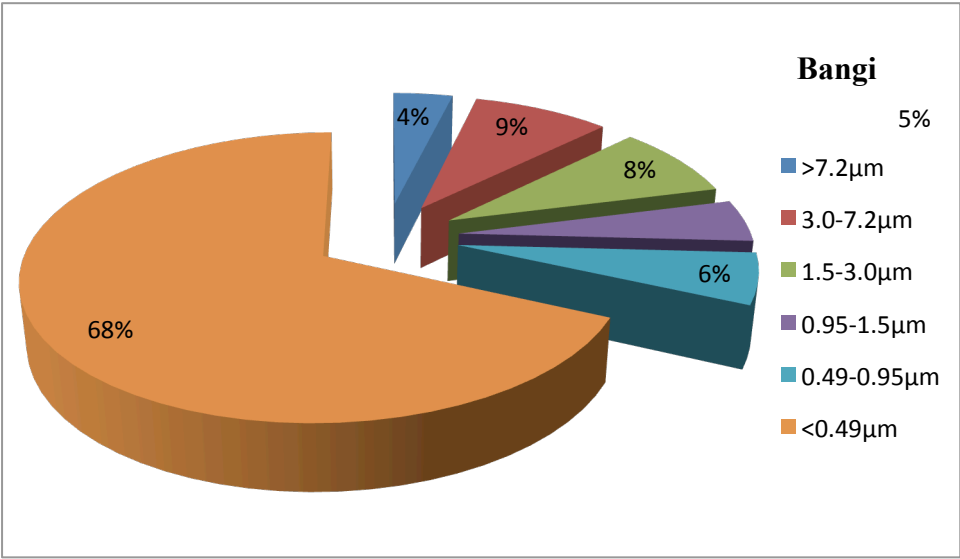


Figure 3.4 Contributions of PM distributions in Bangi

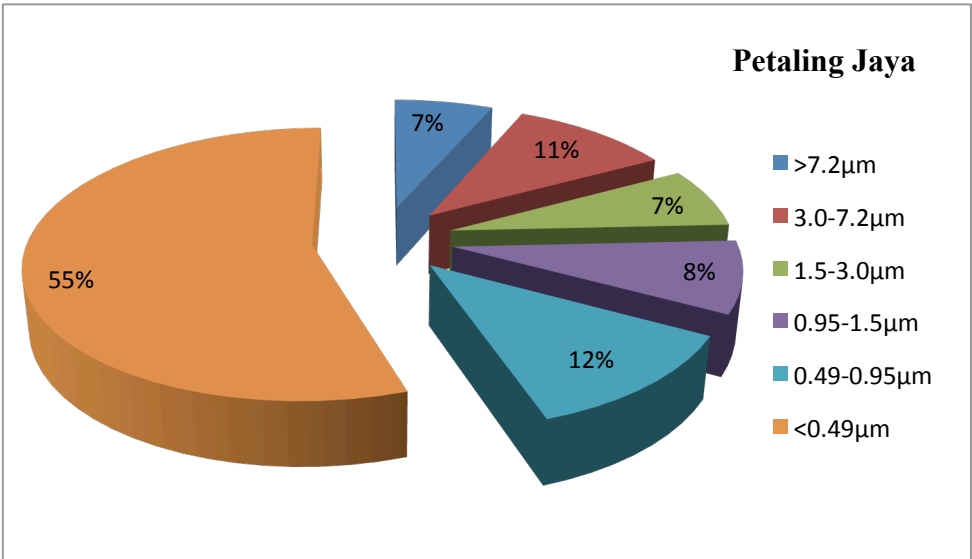


Figure 3.5 Contributions of PM distributions in Petaling Jaya

Percentage contributions of PM distributions of all particle size groups in Bangi and Petaling Jaya are shown in Figure 3.4 and 3.5; respectively. Particles size of $<0.49\mu\text{m}$ contribute more than 50% of total PM concentrations in both locations; which is 68% in Bangi and 55% in Petaling Jaya. The trending for other group of size particles in Bangi range from 4% to 9%, while a percentage between 7%-12% is recorded in Petaling Jaya. The result clearly showed that fine particles dominated the overall of percentage PM concentrations in both locations.

A strong peak of particulate concentration was observed in Petaling Jaya corresponding to a transboundary haze episode caused by forest fire in Sumatera and Kalimantan, Indonesia. During southwest monsoon (June to August), the prevailing wind flow was generally southwesterly from Sumatera. This usually contributes to the higher amount of biomass burning residue to Malaysian ambient atmosphere. Study done by Arimoto et al. (2006) stated that, biomass burning particularly in South East Asia produces substances, which contribute to the particulate matter present in the atmosphere.

The atmosphere is very stable and horizontal as well as vertical air movements are reduced. The subsiding air mass does not favour active cloud development, thus the weather is dry. Several factors such as prolonged dry weather, a stable atmosphere and an abundant supply of pollutants from urban or rural sources are the ideal ingredients for the formation of haze. Particulates emitted into the atmosphere are trapped within the stagnant air mass causing the particulate concentration to increase thus producing a hazy condition.

On top of that, Petaling Jaya is located in the urban area of Kuala Lumpur, where densely populated area with significant vehicles emissions around the study area influences the air quality. In addition, the location of Petaling Jaya in Klang Valley itself plays important role in pollutants concentration. Klang Valley was highly impacted by topography (generally wind came from the west and the southeast). Pollutants are trapped due to the valley topography and inadequate flushing along the valley which runs from the hilly terrains to the north and east, to the Straits of Malacca to the west.

Motor vehicles are expected to be main contributors to the high particulate matter concentration recorded in Petaling Jaya. Besides, particulate matter in Petaling Jaya might also be produced from other anthropogenic sources such as combustion and road dust. In addition, it is expected that the significant amount of particulate matter in fine mode aerosols is largely derived from combustion process, particularly from diesel vehicles (Chow et al., 2002; Latif et al., 2005; Poschl, 2005). According to Vassilakos et al. (2007), vehicles emission has been known to be one of the main contributors in urban areas.

3.3.2 Concentration and Size Distribution of Trace Elements in Atmospheric Particulate Matter

Analysis of atmospheric PM in Bangi and Petaling Jaya during the study period found 10 trace elements namely Ag, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb and Sr; with various concentrations. Table 3.4 and 3.5 shows average concentrations of trace elements in six particle size groups both in Bangi and Petaling Jaya, respectively. Even though majority of trace elements shows similar trends of concentrations; Cr in Bangi and Sr in Petaling Jaya have recorded relatively higher concentrations than other trace elements in their groups.

Table 3.4 Average concentrations of trace elements in APM (Bangi)

Size (μm)	Trace element concentrations (ng/m^3) in particle size group					
	>7.2	3.0-7.2	1.5-3.0	0.95-1.5	0.49-0.95	<0.49
Ag	0.02	0.03	0.02	0.01	0.03	0.21
Cd	0.02	0.02	0.02	0.02	0.06	0.14
Co	0.02	0.04	0.03	0.04	0.03	0.11
Cr	6.37	7.80	7.70	8.02	6.77	17.70
Cu	0.71	1.05	0.87	0.68	0.58	6.48
Li	1.40	1.29	1.58	1.16	1.31	3.39
Mn	0.72	1.13	0.93	0.91	1.20	2.99
Ni	0.53	0.74	0.56	0.54	0.80	2.52
Pb	0.47	1.07	1.27	1.25	1.11	3.77
Sr	2.97	3.87	4.12	1.38	3.80	3.27

Table 3.5 Average concentrations of trace elements in APM (Petaling Jaya)

Size (μm)	Trace element concentrations (ng/m^3) in particle size group					
	>7.2	3.0-7.2	1.5-3.0	0.95-1.5	0.49-0.95	<0.49
Ag	0.04	0.05	0.04	0.04	0.04	0.19
Cd	0.02	0.02	0.02	0.03	0.04	0.17
Co	0.04	0.06	0.05	0.03	0.02	0.08
Cr	2.22	2.20	1.92	1.82	1.75	4.74
Cu	1.84	3.30	2.80	1.90	1.67	8.70
Li	0.39	0.38	0.36	0.40	0.39	3.56
Mn	2.71	3.05	2.82	2.20	2.10	3.42
Ni	0.58	0.57	0.59	0.56	0.58	1.75
Pb	0.95	1.14	1.07	1.67	2.05	3.50
Sr	6.65	6.02	6.07	7.31	8.26	2.47

The distribution of concentrations data for trace elements in six particle size groups (>7.2 μm , 3.0-7.2 μm , 1.5-3.0 μm , 0.95-1.5 μm , 0.49-0.95 μm and <0.49 μm) in Bangi and Petaling Jaya are displayed in Figure 3.6 and Figure 3.7; respectively. The box plots are able to show the distributional characteristic of data in the group of trace elements. They include the display of median concentrations and also the range of upper and lower quartile.

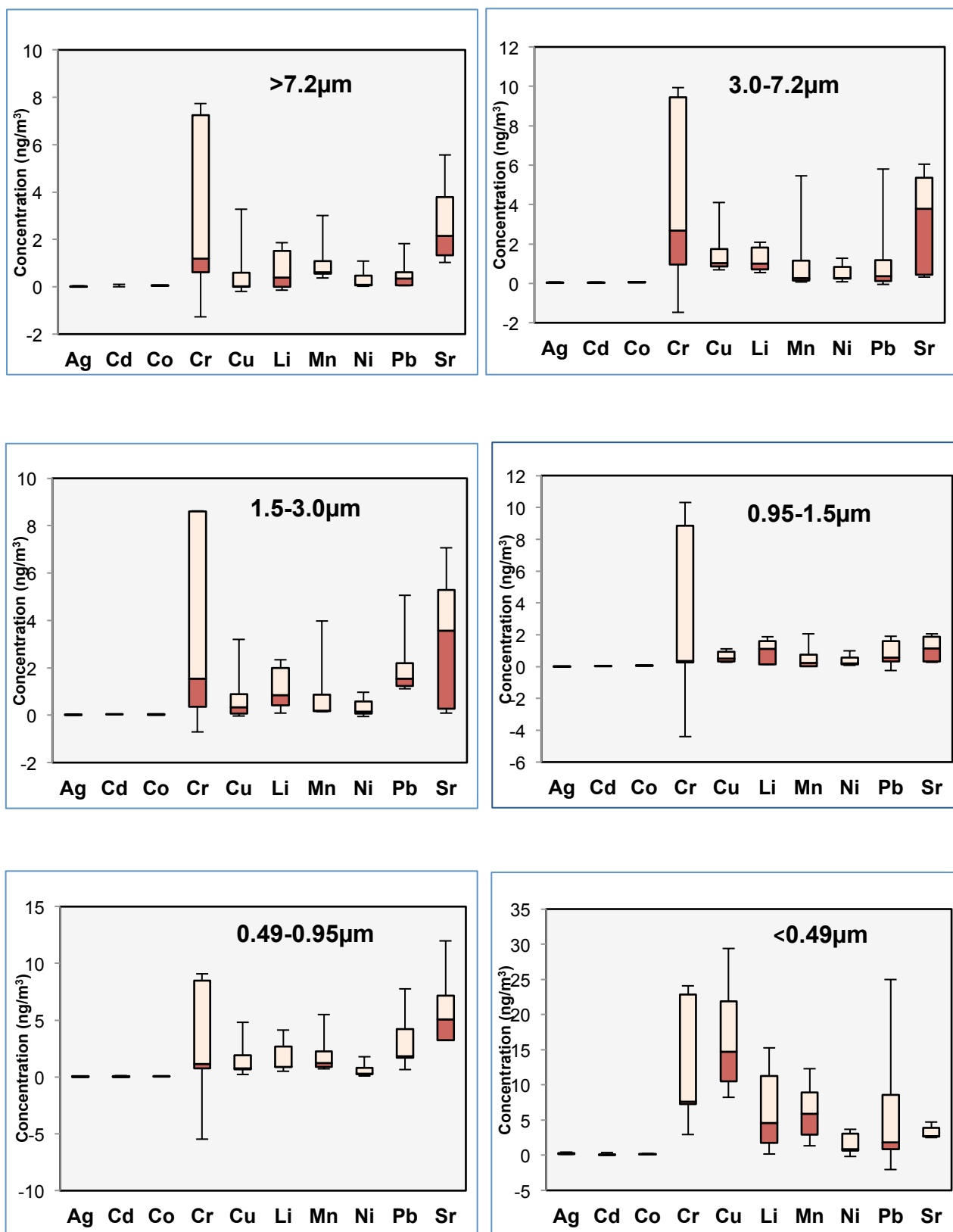


Figure 3.6 Box plots of trace element concentrations in Bangi

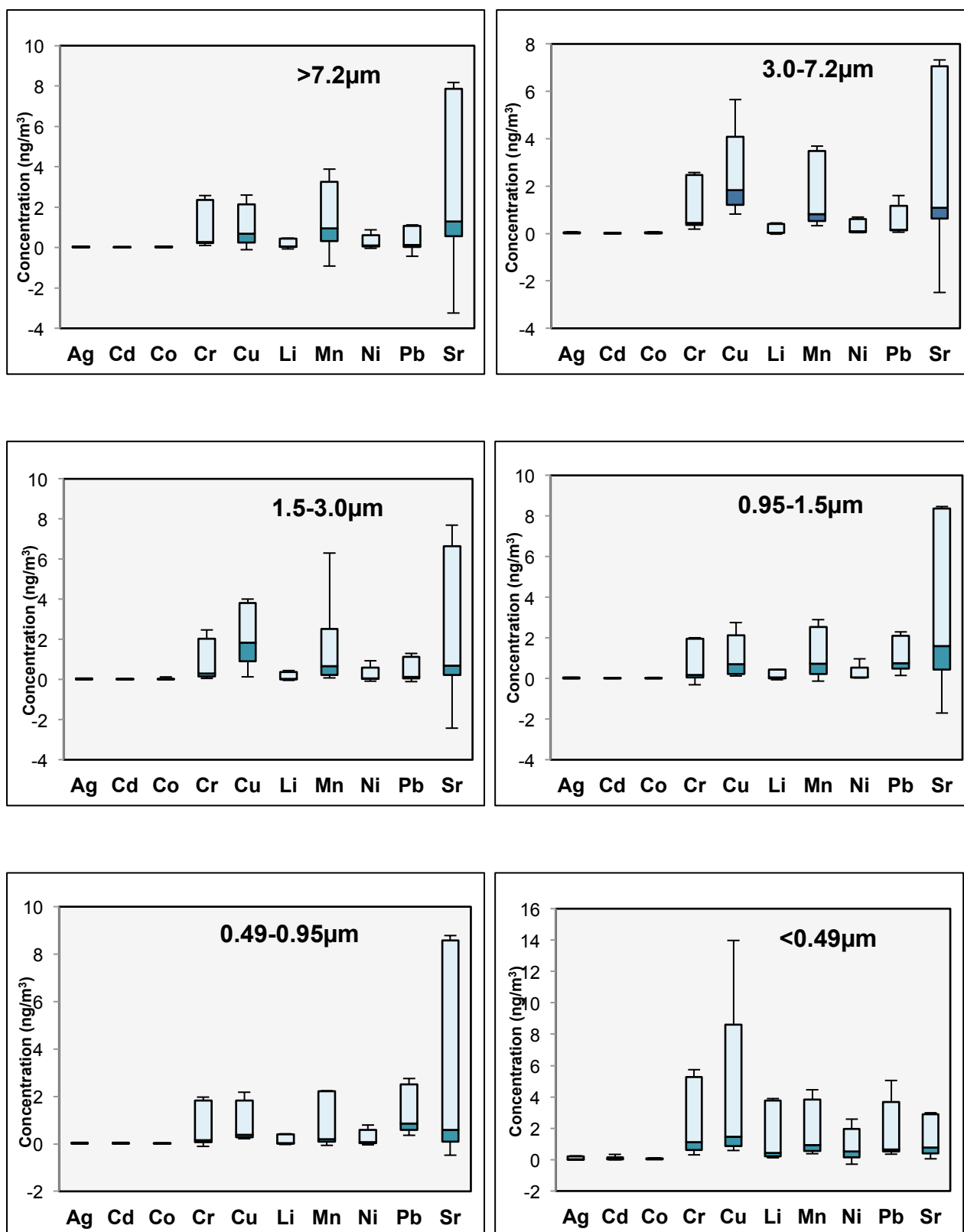


Figure 3.7 Box plots of trace element concentrations in Petaling Jaya

A. Average Concentrations of Trace Elements in Different Size of Particles

The mass concentrations of trace elements in particle size $>7.2\mu\text{m}$ for both locations are presented in Figure 3.8. The highest concentrations of trace elements in Bangi is Cr with 6.37ng/m^3 , followed by Sr (2.97ng/m^3) and Li (1.40ng/m^3). Other trace elements in Bangi recorded average concentrations below than 1.00ng/m^3 . In contrast, Sr accumulate the highest concentrations in Petaling Jaya with 6.65ng/m^3 , while Mn is in the second place with 2.71ng/m^3 . Other trace elements in Petaling Jaya that recorded average concentrations of more than 1.00ng/m^3 are Cr (2.21ng/m^3) and Cu (1.84ng/m^3). Both locations demonstrates the same pattern of a very low concentrations for Ag, Cd and Co in the range between $0.02\text{ng/m}^3 - 0.04\text{ng/m}^3$.

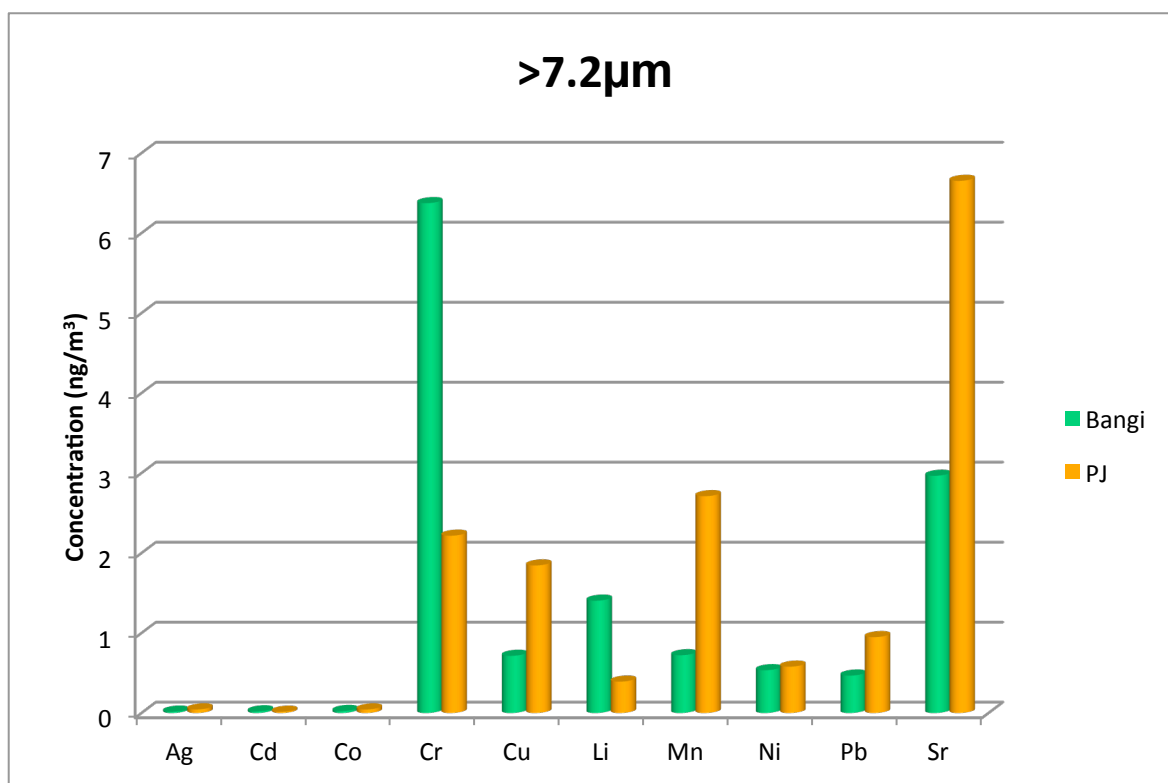


Figure 3.8 Mass concentration of trace elements in particle size $>7.2\mu\text{m}$

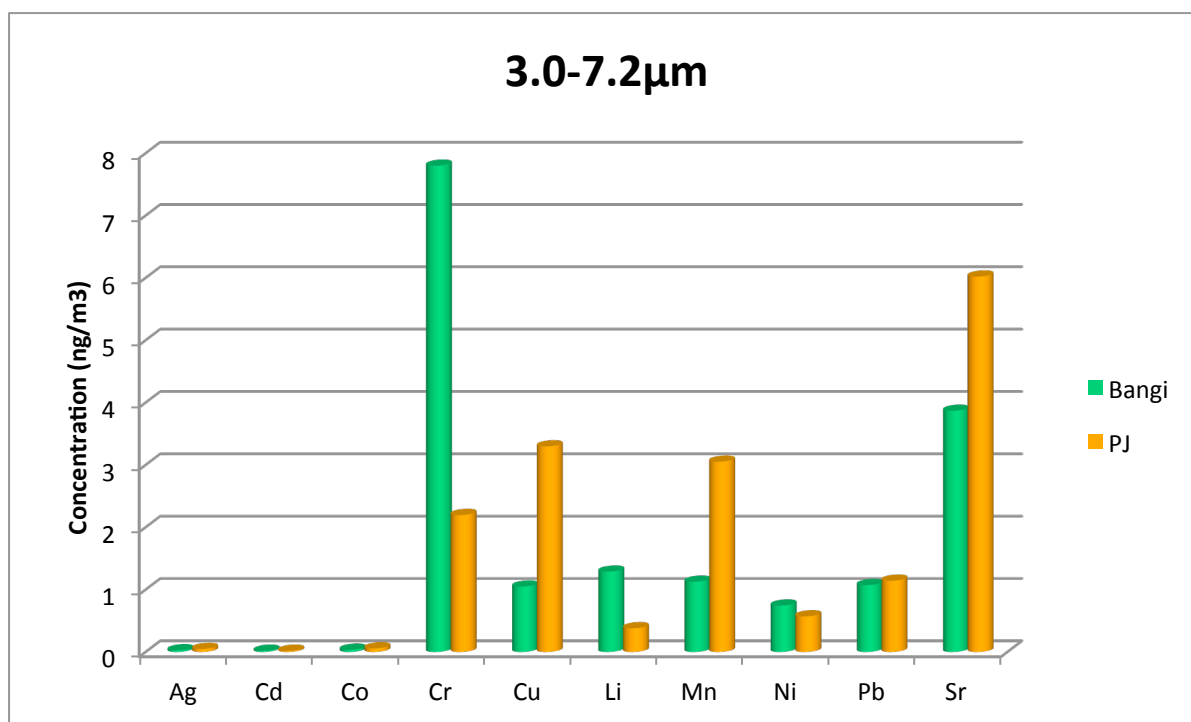


Figure 3.9 Mass concentration of trace elements in particle size 3.0-7.2 μ m

Figure 3.9 compares the average mass concentrations of trace elements in particle size 3.0-7.2 μ m between Bangi and Petaling Jaya. Concentrations of trace elements in Bangi and Petaling Jaya show almost a similar pattern with the trace elements concentrations of particle size >7.2 μ m at the same location. In Bangi, Cr is the highest with 7.80ng/m³, followed by Sr (3.87ng/m³). Other trace elements with concentrations of more than 1.00ng/m³ are Li (1.29ng/m³), Mn (1.13ng/m³), Pb (1.07ng/m³) and Cu (1.05ng/m³). Sr, Cu, Mn and Cr in Petaling Jaya demonstrate a relatively higher average concentrations than other trace elements in their group with reading of 6.02ng/m³, 3.30ng/m³, 3.05ng/m³ and 2.20ng/m³. Other trace elements in Petaling Jaya accumulate average concentrations below than 1.00ng/m³; except for Pb (1.14ng/m³).

The average mass concentrations of trace elements for particle size 1.5-3.0 μ m in Bangi and Petaling Jaya is shown in Figure 3.10. Cr accumulates the highest concentrations in Bangi with 7.70ng/m³; while in Petaling Jaya, the highest concentrations is 6.07ng/m³ for Sr. In Bangi, Li and Pb recorded average concentrations of 1.58ng/m³ and 1.27ng/m³; respectively. Other trace elements show average concentrations in the range of 0.02ng/m³ – 0.09ng/m³. In contrast; including Sr; Mn, Cu, Cr and Pb in Petaling Jaya also gathered average concentrations of more than 1.00ng/m³. Ag, Cd, Co, Li and Ni in Petaling Jaya recorded average concentrations of less than 1.00ng/m³.

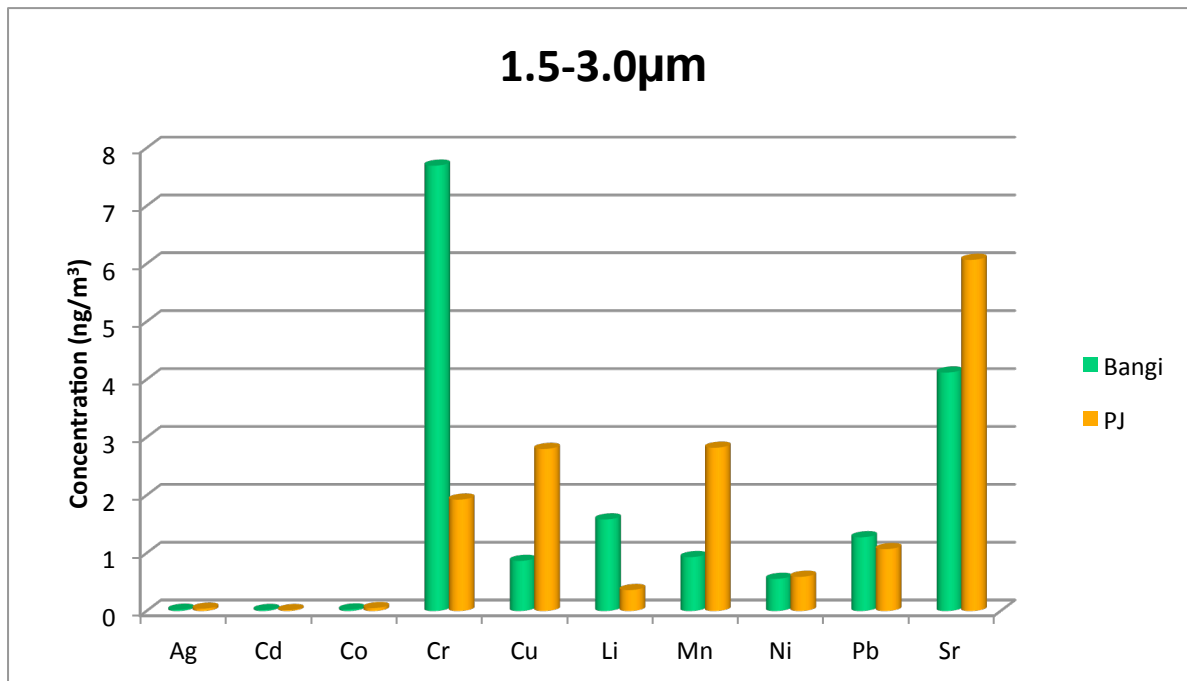


Figure 3.10 Mass concentration of trace elements in particle size 1.5-3.0 μ m

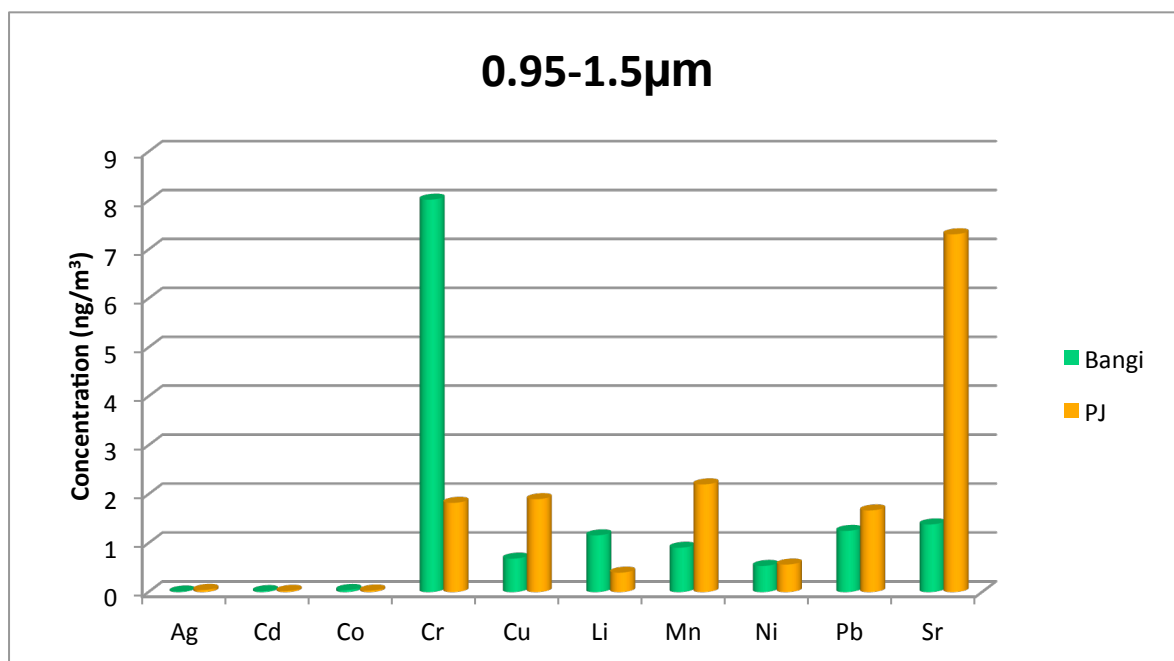


Figure 3.11 Mass concentration of trace elements in particle size 0.95-1.5 μ m

Figure 3.11 demonstrate the average mass concentrations of trace elements in Bangi and Petaling Jaya for particle size 0.95-1.5 μ m. Similar trends of concentrations are illustrated with other groups of particle size in both locations. Cr and Sr is the highest trace elements in Bangi and Petaling Jaya with reading of 8.02ng/m³ and 7.31ng/m³; respectively. Other trace elements in both locations recorded average concentrations in range of 0.01ng/m³ to 1.50ng/m³. Only Mn, Cu, Cr and Pb in Petaling Jaya show average concentrations of more than 1.50ng/m³; with 2.20ng/m³, 1.90ng/m³, 1.82ng/m³ and 1.67ng/m³, accordingly.

Similarly, the average mass concentrations of trace elements in particle size 0.49-0.95 μ m in Bangi and Petaling Jaya are displayed in Figure 3.12. Cr accumulates the highest concentrations with 6.77ng/m³; while in Petaling Jaya, the highest concentrations is 8.26ng/m³ for Sr. In Bangi, Li, Mn and Pb recorded average concentrations of 1.31ng/m³, 1.20ng/m³ and 1.11ng/m³; respectively. Other trace elements show average concentrations in the range of 0.03ng/m³ – 0.80ng/m³. On the other hand, the average concentration for Pb, Mn, Cr, and Cu in Petaling Jaya are locked at 2.05ng/m³, 2.10ng/m³, 1.75ng/m³ and 1.67ng/m³. Other elements are gathered at average concentrations between 0.04ng/m³ and 0.58ng/m³.

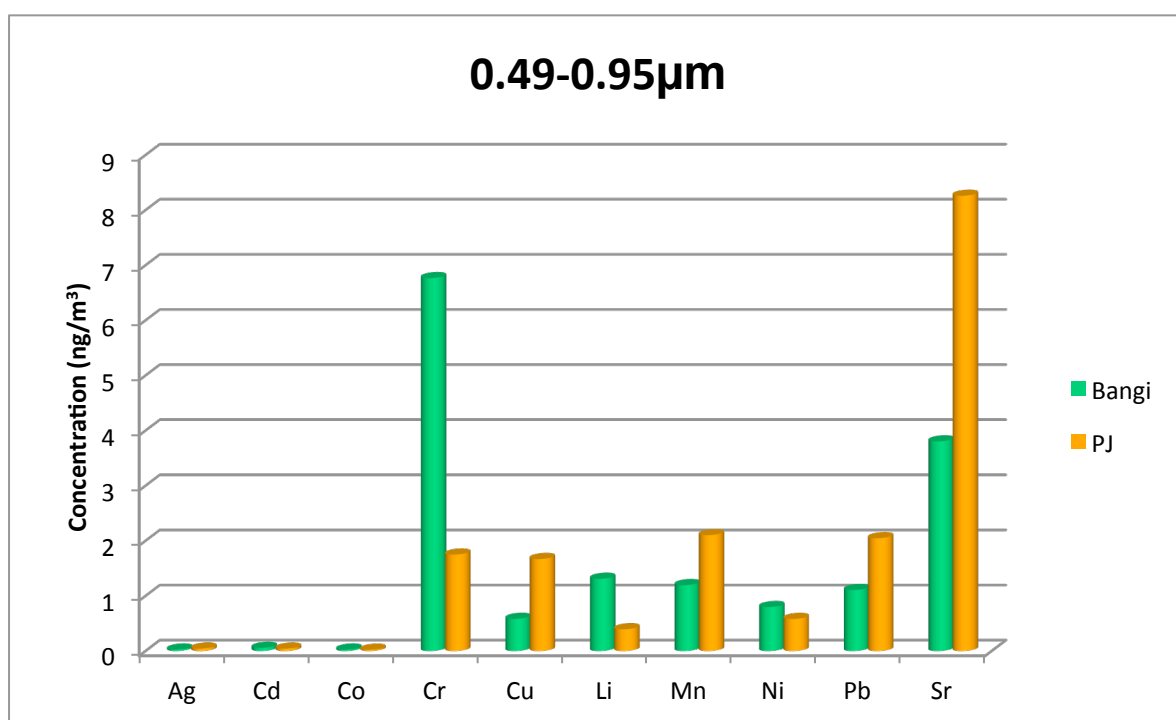


Figure 3.12 Mass concentration of trace elements in particle size 0.49-0.95 μ m

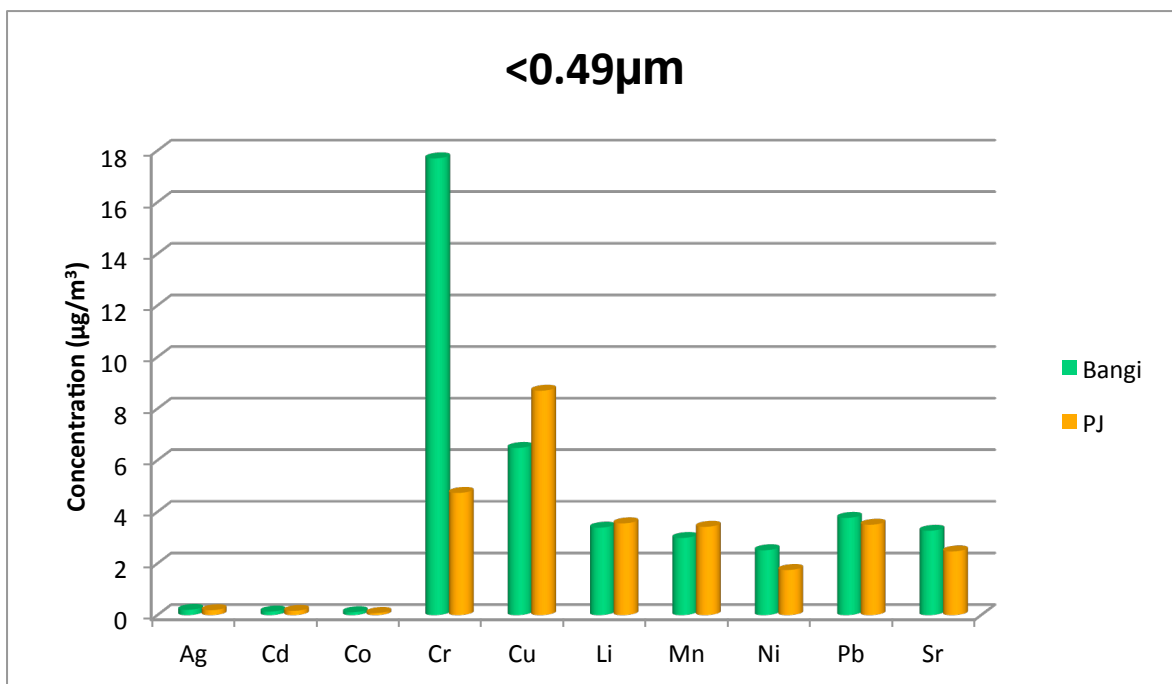


Figure 3.13 Mass concentration of trace elements in particle size $<0.49\mu\text{m}$

Figure 3.13 compares the average mass concentrations of trace elements in particle size $<0.49\mu\text{m}$ between Bangi and Petaling Jaya. Concentrations of trace elements in Bangi and Petaling Jaya show slightly different pattern from the other group of size fractions. In Bangi, Cr is the highest with 17.70ng/m^3 , followed by Cu (6.48ng/m^3). Other trace elements with concentrations of more than 3.00ng/m^3 are Pb (3.77ng/m^3), Li (3.39ng/m^3), and Sr (3.27ng/m^3). Meanwhile, Cu demonstrates higher average concentration in Petaling Jaya at 8.70ng/m^3 . Li, Pb, Mn, and Sr showed concentrations with reading of 3.56ng/m^3 , 3.50ng/m^3 , 3.42ng/m^3 and 2.47ng/m^3 . Other trace elements in Petaling Jaya accumulate average concentrations below than 2.00ng/m^3 .

Metals including Cu, Cr, Li, Ni, Mn and Pb observed much higher concentrations in fine particles ($<0.49\mu\text{m}$) as compared to other particles fraction. These trends of metal concentrations were almost matched with the size distribution characteristics of metals in urban aerosol studies by in the Karanasiou et al. (2007) and Espinosa et al. (2001). This group of metals suggests that anthropogenic sources were the dominant contributors to the formation of fine particles. The existence of some toxic metals in the fine particles, which can reach deeply into the alveolar region in the lungs, might increase respiratory symptoms or diseases via long term exposure.

On the other hand; Ag, Co and Cd were found at lower concentration in all particle size fractions with range concentrations between $0.02\mu\text{g}/\text{m}^3$ to $0.21\mu\text{g}/\text{m}^3$ in both locations.

Sr in this study showed increased concentrations with the increase of particle size. Similar study done by Allen et al. (2001) proved that Sr was mainly found within the coarse particle. Widory et al. (2010) conducted a trace study of Sr in China also demonstrated that Sr is significantly greater abundance in the coarse mode compared to fine mode particles. Sr represented a strong contribution to coarse particle and suggested the existence of combustion and / or industrial sources in addition to re-suspension and frictional processes (Allen et al., 2001).

The size distributions of elements in atmospheric aerosols may have resulted from a combination of processes including local anthropogenic and natural sources, long-range transport and re-suspension.

B. Comparison of Trace Elements Concentration between PM Coarse and PM Fine

PM coarse is defined by particles with size bigger than $1.5\mu\text{m}$; while PM fine is categorized by particles with size less than $1.5\mu\text{m}$. The definition of fine and coarse mode aerosols was made as suggested by Chow et al. (2002). Separation of fine and coarse mode aerosols using $1.5\mu\text{m}$ has also been undertaken by Zappoli et al. (1999). The two groups of PM are distinguished in separate groups as different sizes and compositions of particles cause different adverse health effects.

Atmospheric coarse particles can be trapped in the nose, throat and upper respiratory tract, while fine particles (e.g., $\text{PM}_{2.5}$) can penetrate deep into the respiratory system, after which they are retained and absorbed by the body. In addition, fine particles have the longer atmospheric residence time than coarse particles and the ability of long-range transport. In the recent past, researches have been carried out on the seasonal variations and the size distribution of atmospheric particulates and associated elements in various parts of world (Olmez et al., 2004; Song et al., 2006; Srivastava et al., 2008; Wang et al., 2010; Lee & Hieu, 2011; Gugamsetty et al., 2012; Hu et al., 2012a).

The mass concentrations of trace elements for PM coarse and PM fine in both locations are presented in Figure 3.14. In general, the average concentrations of fine particles are more than the coarse particles. Overall, the average concentrations of PM for coarse and finesize in Petaling Jaya are higher compared to Bangi. The average concentrations of fine particles in Petaling Jaya is $60.37\mu\text{g}/\text{m}^3$, while the concentration of fine particles in Bangi is $18.97\mu\text{g}/\text{m}^3$. Similarly, the average of coarse particles in Bangi is lower compared to Petaling Jaya with concentrations of $8.37\mu\text{g}/\text{m}^3$ and $19.36\mu\text{g}/\text{m}^3$.

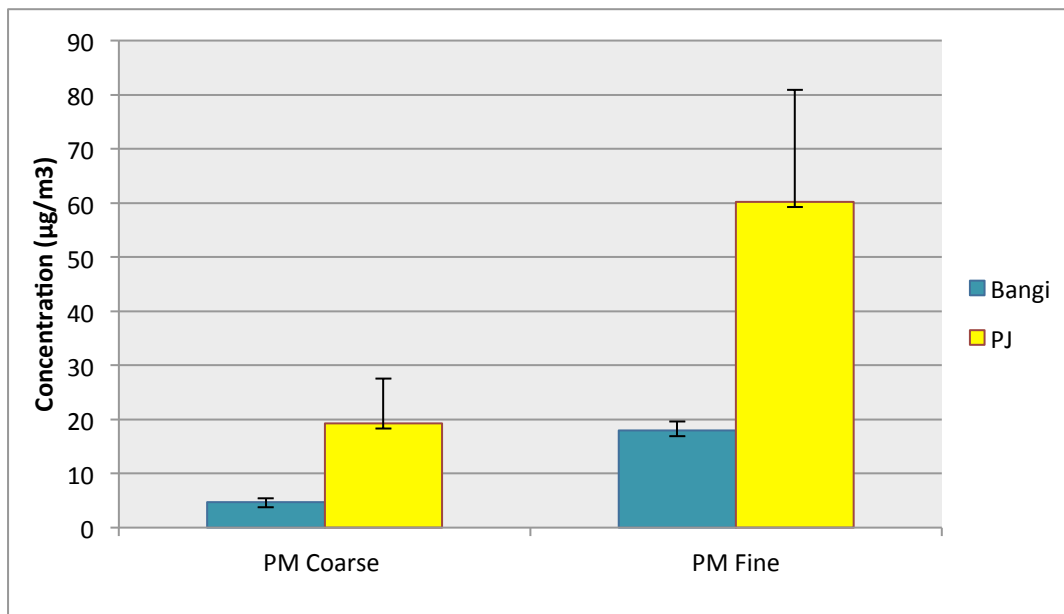


Figure 3.14 Comparison of PM coarse and PM fine in Bangi and Petaling Jaya

Figure 3.15 compares the average mass concentrations of trace elements in particle coarse between Bangi and Petaling Jaya. In the coarse mode aerosols, high concentrations of Cr ($21.88\text{ng}/\text{m}^3$) and Sr($10.96\text{ng}/\text{m}^3$) were found in Bangi. The chemical composition of PM coarse is found to have higher concentration of Sr($18.74\text{ng}/\text{m}^3$), Mn($8.58\text{ng}/\text{m}^3$), Cu($7.94\text{ng}/\text{m}^3$) and Cr ($6.34\text{ng}/\text{m}^3$) than other elements in Petaling Jaya.

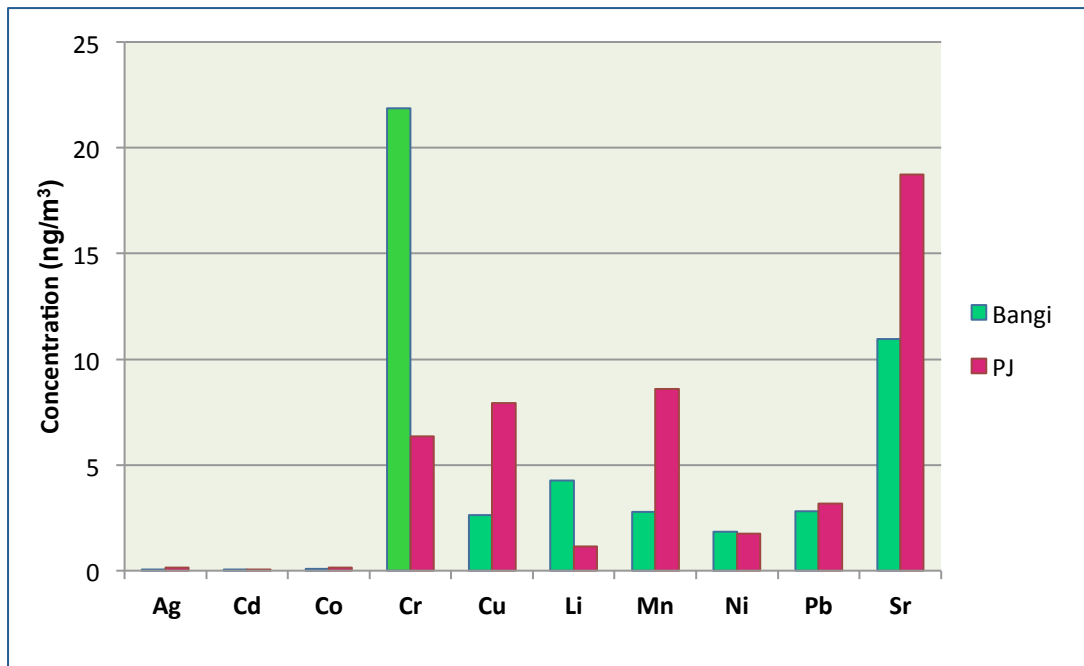


Figure 3.15 Average concentrations of trace elements in PM coarse

In the case of PM fine, the Cr, Sr and Cu showed higher concentration in Bangi with the reading of 32.49ng/m^3 , 8.46ng/m^3 and 7.75ng/m^3 ; respectively (Figure 3.16). In Petaling Jaya, the result also showed abundance of Sr, Cu, and Cr with the recorded concentration 18.05ng/m^3 , 12.27ng/m^3 and 8.31ng/m^3 ; accordingly.

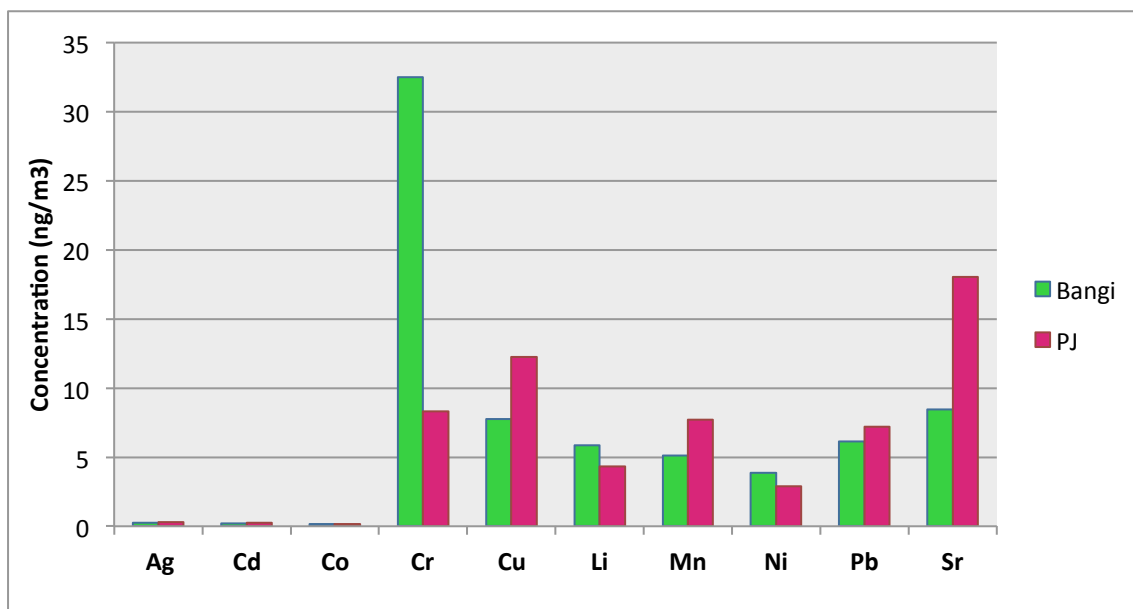


Figure 3.16 Average concentrations of trace elements in PM fine

C. Comparison of Findings with Other Studies

Trace elements concentrations in atmospheric particulate matter in comparison with the various city worldwide are shown in Table 3.6. The present trace elements level in Bangi and Petaling Jaya were comparatively lower than those observed in highly polluted metropolitan cities such as Lahore (Harrison et al., 1997), Karachi (Parekh et al., 1987), Calcutta (Gupta et al., 2007), Delhi (Shridhar et al., 2010), Dhaka (Salam et al., 2003), Tehran (Sohrabpour et al., 1999), Shiraz (Hadad et al., 2003), Beijing (Wang et al., 2001), Bursa (Samura et al., 2003), Bilbao (Aranguiz et al., 2002), Athens (Valavanidis et al., 2006), and Santa Cruz (Quiterio et al., 2004a).

The average level of Cr in the atmospheric particulates of Bangi and Petaling Jaya were lower compared to cities such as Lahore (Harrison et al., 1997), Delhi (Shridhar et al., 2010), Bursa (Samura et al., 2003), Athens (Valavanidis et al., 2006) and Santa Cruz (Quiterio et al., 2004). However, these levels are comparable with those reported from Karachi (Parekh et al., 1987), Faisalabad (Qadir & Zaidi, 2006), Shiraz (Hadad et al., 2003), Won Ju City (Kim, 2004) and Frankfurt (Zereini et al., 2005).

Present levels of Cu and Mn in the particulate atmospheric were found to be lower compared to those observed from Islamabad (Shah & Shaheen, 2008), Lahore (Harrison et al., 1997), Delhi (Shridhar et al., 2010), Bilbao (Aranguiz et al., 2002) and Santa Cruz (Quiterio et al., 2004). Nevertheless, the mean level of Cu and Mn are comparable with those reported from Paris (Ayrault et al., 2010) and Ispra (Rizzio et al., 1999).

Mean level of Pb estimated in the present study showed lower concentration in comparison with the polluted cities of the world, such as Lahore (Harrison et al., 1997), Faisalabad (Qadir & Zaidi, 2006), Kolkata (Gupta et al., 2007), Delhi (Shridhar et al., 2010), Dhaka (Salam et al., 2003), Tehran (Sohrabpour et al., 1999), Shiraz (Hadad et al., 2003), Qingdao (Hao et al., 2007), Beijing (Wang et al., 2001), Cartagena (Moreno–Grau et al., 2000), Bilbao (Aranguiz et al., 2002), Athens (Valavanidis et al., 2006), Pavia (Rizzio et al., 2001a) and Santa Cruz (Quiterio et al., 2004a). Based on this result, it proved that since the leaded petrol has been banned in Malaysia since 1997, the level of Pb in atmospheric has reduced significantly. Even though Malaysia has banned leaded gasoline in early 1997s and with complete phase out in year 2000, the legacy of using leaded gasoline for several years will remain for a long time in the form of dust especially near the roadways or roof-top dust (Abdul Rahman et al., 2011).

Furthermore, the amount of Co and Cd found in present study is lower than the concentration found in Islamabad (Shah & Shaheen, 2008), Beijing (Wang et al., 2001), Delft (Wang et al., 2001), Santa Cruz (Quiterio et al., 2004), Frankfurt (Zereini et al., 2005), Paris (Ayrault et al., 2010) and Pavia (Rizzio et al., 2001).

Table 3.6 Comparison of TSP ($\mu\text{g}/\text{m}^3$) and trace element levels (ng/m^3) in atmospheric particulate matter around the world

	TSP	Cd	Co	Cr	Cu	Mn	Pb
Islamabad, Pakistan (Shah & Shaheen, 2008)	164	4	33	10	306	79	157
Lahore, Pakistan (Harrison et al., 1997)	607	43.4		113	420	350	3920
Karachi, Pakistan (Parekh et al., 1987)				30		80	70
Faisalabad, Pakistan (Qadir & Zaidi, 2006)	550	20.5	5.6	30.9			549
Kolkata, India (Gupta et al., 2007)		39.6		56.0		28.1	159
Delhi, India (Shridhar et al., 2010)	546	10		350	3690	740	440
Dhaka, Bangladesh (Salam et al., 2003)		2.5			54		279
Shiraz, Iran (Hadad et al., 2003)				15	122	53	545
Yokohama, Japan (Khan et al., 2010)	34.2	1.2		4.1	47.7	32.5	27.2

	TSP	Cd	Co	Cr	Cu	Mn	Pb
Beijing, China (Wang et al., 2001)	496	4.44	7.09		154		404
Delft, Netherlands (Wang et al., 2001)	56	0.458	0.147		139		16.64
Won Ju City, Korea (Kim, 2004)		2.1		14.7		33.3	84
Bursa, Turkey (Samura et al., 2003)		1.8		92		992	53
Cartagena, Spain (Moreno-Grau et al., 2000)	200	9.23			50		690
Bilbao, Spain (Aranguiz et al., 2002)	171	8			200	260	1570
Athens, Greece (Valavanidis et al., 2006)	133	4.5		370	700		2700
Frankfurt, Germany (Zereini et al., 2005)		0.3	0.8	16.3	102	35.3	32.6
Paris, France (Ayrault et al., 2010)		0.393	0.208	4.12	18.4	6.95	15.37
Pavia, Italy (Rizzio et al., 2001a)		1.3	2.1	59	54	56	185
Ispira, Italy (Rizzio et al., 1999)		0.51	0.75	6.5	10.5	14	98
Santa Cruz, Brazil (Quiterio et al., 2004a)	87	0.9	1.1	421	335	1216	101

3.4 CONCLUSION

In this study, the analysis of the size and concentration distribution of the airborne particles and associated trace elements were determined from samples collected from urban and semi urban areas in Malaysia.

The results indicated that Petaling Jaya recorded higher mean concentrations for all particles size group compared to Bangi. Similarly, the 24-h TSP levels in Petaling Jaya were higher compared to Bangi. The 24-h TSP level in Bangi is below the guideline set by WHO and USEPA standard value, while the average 24-h TSP in Petaling Jaya was found to be significantly higher than USEPA standard value. In addition, the TSP values obtained for both sampling site in Bangi and Petaling Jaya were still well below the Recommended Malaysian Air Quality Guideline (RMAQG) for TSP. Particles size of $<0.49\mu\text{m}$ contribute more than 50% of total PM concentrations in both locations; which is 68% in Bangi and 55% in Petaling Jaya. The result clearly showed that fine particles dominated the overall of percentage PM concentrations in both locations.

Among the trace metals that were studied, Cr in Bangi and Sr in Petaling Jaya have recorded an outstanding higher concentrations than other trace elements in their groups, in all particle sizes; except for Sr in Petaling Jaya for particle size $<0.49\mu\text{m}$. Cr in Bangi and Sr in Petaling Jaya recorded the highest concentrations for particle sizes of $<0.49\mu\text{m}$ and $0.49\text{--}0.95\mu\text{m}$; respectively. Meanwhile, apart from Cr and Sr; Cu, Li, Mn, Ni and Pb show almost similar trends of moderate concentrations in all particles size groups; except for Cu in particle size $<0.49\mu\text{m}$, which shows relatively higher concentrations for both locations. Other trace elements such as Ag, Co and Cd recorded relatively lower concentrations in all particle sizes compared to other trace elements. The size distributions of elements in atmospheric aerosols may have resulted from a combination of processes including local anthropogenic and natural sources, long-range transport and re-suspension.

In both locations, the average concentrations of fine particles are higher than the coarse particles. In addition, the average concentrations of PM for coarse and finesize in Petaling Jaya are higher compared to Bangi. In the coarse mode aerosols, high concentrations of Cr and Sr were found in Bangi and Petaling Jaya. Similarly, for fine particulate matter, Cr in Bangi and Sr in Petaling Jaya also recorded the highest concentrations among other trace elements in the groups.

CHAPTER 4

PRINCIPAL COMPONENT ANALYSIS (PCA) AND RISK ASSESSMENT OF TRACE ELEMENTS IN ATMOSPHERIC PARTICULATE MATTER

4.1 INTRODUCTION

Particles released into the atmosphere bear specific chemical compositions that can be used to identify their origins. Wind-blown fine dust particles have a similar elemental composition to the earth's crust. Fresh sea-salt aerosol has the same composition as bulk seawater because it is generated by the bursting of bubbles from the surface water layer (Blanchard & Woodcock, 1980).

Traditional approaches such as dispersion models use emission inventories from different sources as inputs in combination with mass balance calculations to identify source impacts on specific sites. However, because of physical and chemical transformations in the atmosphere, such as the conversion of SO₂ to sulfate in fine aerosol, the chemical compositions of particles after release may change as they travel. Even if the dispersion model correctly accounts for these changes, the source emissions which it is based upon may have changed because of improved technologies or they may subject to progressive changes over time. Also, fugitive emissions such as wind-blown dust and gases are difficult to include in dispersion models because they are not easily inventoried.

To understand the sources and transport of environmental species at the receptor site, factor analysis as a receptor model, is used in this study. Factor analysis uses statistical multi-variate methods to test for correlations among the measured species or parameters. This allows the identification and impact assessment of different sources on a receptor site without prior knowledge of the sources' characteristics (Hopke, 1991; Henry et al., 1984). Unlike chemical mass balance models, which require detailed knowledge of the sources of the particles and/or their possible transport pathways and chemical transformations, factor analysis is capable of evaluating uncharacterized area sources such as fugitive emissions or wind-blown crustal material. The use of factor analysis is therefore extremely useful in many situations for identifying the sources of environmental contaminants.

4.2 METHODOLOGY

Three main component of analysis were used in further assessment of trace elements in this study. The method of analysis used includes the Principal Component Analysis, Trajectory Analysis and also the Health Risk Assessment tools. Risk characterization associated with the assessment of trace elements was quantified separately for non-carcinogenic and carcinogenic effects. Figure 4.1 summarized the methodology used in this analysis.

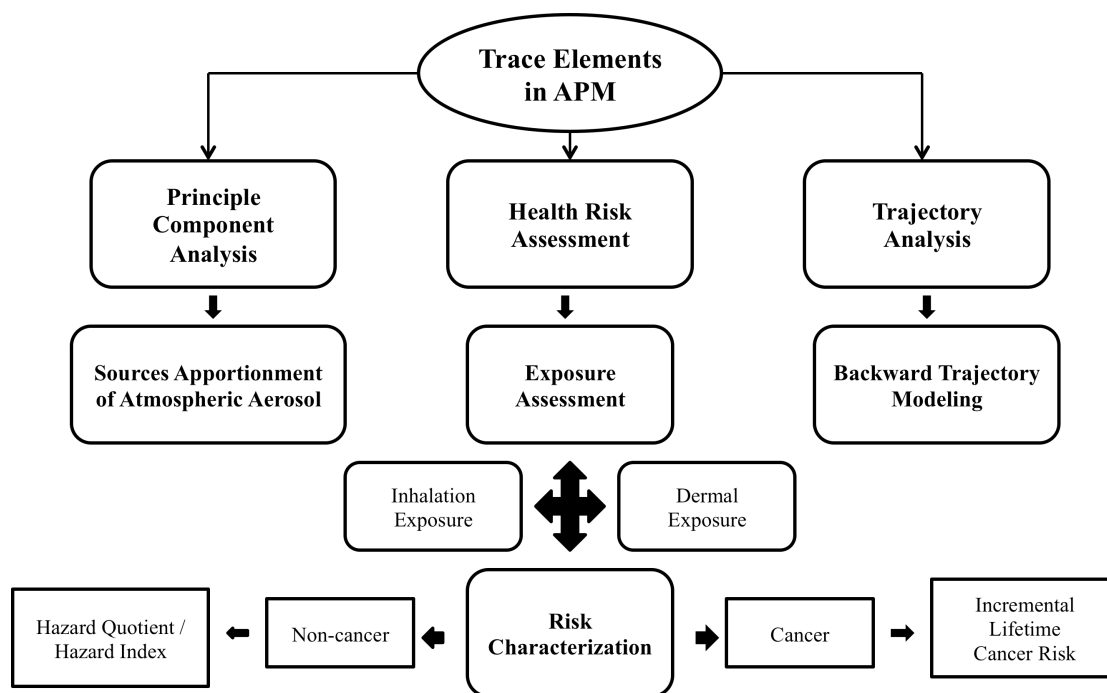


Figure 4.1 Methodology of analysis

4.2.1 Principle Component Analysis (PCA)

PCA was selected for this research, as it is one of the most important multivariate analytical tools. PCA is a pattern recognition technique that reduces data dimensionality by performing a covariance analysis between factors. It is a widely used analytical tool in air quality research studies to extract important information from multivariate databases. In terms of atmospheric studies, multivariate techniques of principle component analysis were used for the source apportionment of TSP and trace elements in the urban particulate samples (Harrison et al., 1997; Bilos et al., 2001; Ragosta et al., 2002; Quiterio et al., 2004a; Arditoglou & Samara, 2005; Shah & Shaheen, 2008).

PCA is one of the most useful exploratory techniques that can be used to display the data structure (Lavine, 2000). This method is designed to compress and reduce the original set of data matrix into a set of new variables, the principal components (PCs), which are orthogonal, linear combinations of the original variables. To apply this method, the data must be arranged into a data matrix which consists of the variables (such as the pollutants) displayed in the columns and the objects (such as the atmospheric pollutant samples) in the rows.

The first PC explains most of the data variance while the second PC accounts for the next highest amount of variance and so on until as many PCs are produced as there are original variables. To aid the visual display of the PCA results, they were presented either as scores plots which show the relationships between the objects, or loadings plots which explain the relationships of the variables with one another. Each object has a score value on each PC, and every variable is also linked with a loading on each PC. Bi-plots combine both the loadings and the scores in the one plot. This is more useful than either the scores or loadings plot because it shows the relation between the objects and the variables in the same plot.

PCA can also be used to examine the importance of particular variables for each PC. If the variables have high positive values or high negative ones, it means that these variables are important. On the other hand low loadings show that the variables are less important. Also the objects can be clustered together or widely dispersed. If they lie in the same direction and the angles between their vectors are less than 90° , then the vectors are to a greater or lesser extent correlated. However, if the angles between the variables vectors are equal to 90° , the vectors are independent, while they are opposite each other if the angles between the vectors are about 180° .

Seinfeld and Pandis (1998) have listed several assumptions on application of PCA to source apportionment purposes:

- The composition of emission sources is constant.
- Chemical species used in PCA do not interact with each other and their concentrations are linearly additive.
- Measurements errors are random and uncorrelated.
- The variability of the concentrations is dominated by changes in source contributions.
- The effect of processes that affect all sources equally (e.g. atmospheric dispersion) is much smaller than the effect of processes that influence individual sources (e.g., wind direction).
- There are many more samples than source types.
- The extracted factors and rotations are physically meaningful.

Table 4.1 presents an array of ions and metals that are abundant in various sources. Examples of markers include an abundance of potassium (K) for biomass source, aluminium (Al) and silicon (Si) for fugitive dust source, sulfate ions (SO_4) for coal and diesel combustion, which can be further differentiated with other ion and metal fractions in the source profiles. In addition, particles from different sources and emission processes are often distinguished by their physical size, as highlighted for total suspended particles (TSP) in Figure 4.2. Thus, the ratio between two fractions of PM is simple; although crude, indicator of the amount of particulate matter originates from different types of sources.

Table 4.1 Typical markers elements and ions associated with PM sources

Emission Sources	Marker Elements
Natural	
Soil	Al, Si, Sc, Ti, Fe, Sr, Ca, OC
Sea spray	Na, Cl
Secondary PM	NH_4^+ , Na, NO_3^- , SO_4^{4-} , OC, WSOC
Anthropogenic	
Road dust	Al, Si, Ti, Fe, Sr, Ca, K, OC, EC
Diesel vehicles	EC, OC, NO_3^- , SO_4^{4-} , Cu, Fe, Zn
Gasoline vehicles	OC, EC, Ca
Refuse incineration	K, Zn, Pb, EC, OC
Cement industry	Ca, Si, Al, Fe
Biomass burning	OC, EC, K, Cl ⁻ , NH_4^+
Ferrous industry	Fe, Cr, Zn
Nonferrous industry	Zn, Cu, Pb, Al

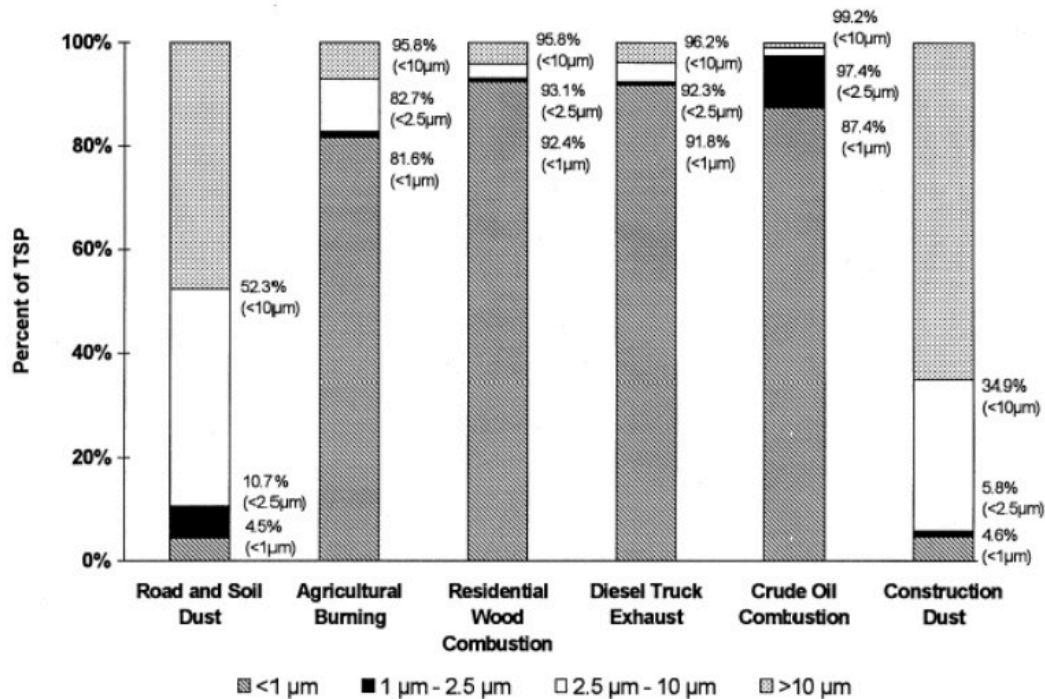


Figure 4.2 Size distributions of several TSP sources emissions
(Adapted from Watson & Chow (eds), 2000)

4.2.2 Backward Trajectory Analysis

HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model is one of the atmospheric transport and dispersion models most frequently used in large-scale research. It was developed by the Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA). The model features a trajectory model calculating simple trajectories and a concentration model simulating complex dispersion and disposition of pollutants. This study focuses on the trajectory model only.

A backward trajectory model represents the recent history of an air mass. An air mass trajectory can provide information about the source regions that impact a given site (Dutkiewicz et al., 2006). The backward trajectories provide Lagrangian path of air parcels in the chosen time scale, which could be used to identify the potential source regions and transport pathways of pollutant.

The particle is assumed to be passively following the wind, so that the computation of trajectories is just the integration of the particle position vector in space and time. A trajectory is computed from the time integration of the three-dimensional vector P , where V is the horizontal velocity vector in infinitesimally small space and time.

$$dP / dt = V(x, y, z, t)$$

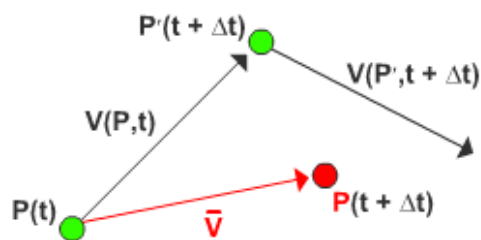


Figure 4.3 Trajectory computation method of HYSPLIT trajectory model

$$P'(t + \Delta t) = P(t) + V(P, t) \Delta t \quad (\text{First-guess position})$$

$$P(t + \Delta t) = P(t) + 0.5 [V(P, t) \Delta t + V(P', t + \Delta t) \Delta t] \quad (\text{Final position})$$

In other words, a first-guess position $P'(t + \Delta t)$ is calculated using the wind vector at the initial point $P(t)$, and then the final position $P(t + \Delta t)$ is computed by the velocity vector $\bar{V}$, which is the average of the wind vector at the initial position $P(t)$ and the first-guess position $P'(t + \Delta t)$.

4.2.3 Health Risk Assessment Method

A. Exposure Assessment

In order to assess the health risk due to atmospheric elemental particulate matter for both the children and the adults, the generally recognized methods described by US Environmental Protection Agency (USEPA) have been applied. This method has been widely used around the world (Ferreira-Baptista & De Miguel, 2005; Chen & Liao, 2006; Hu et al., 2007; Shi et al., 2011).

With high population density, all people living in the study areas (Bangi and Petaling Jaya) are considered as receptors of atmospheric deposition. Because of their susceptibility, the behaviors and body systems function differently, thus the subjects were divided into two groups: children and adults. In this study, the health risk assessments for both inhalatory and dermal exposures of trace metals were calculated. Although exposure to environmental trace metals has been based on the assumption that inhalation was the primary route, dermal contact is increasingly taken into account.

Exposure level is expressed in terms of a daily dose and was calculated separately for each trace metal and for each exposure pathway by formulas displayed in Table 4.2 (Equation 4.1 and Equation 4.2). In addition, the formulas used in calculating the carcinogenic assessment for the trace elements are illustrated in Table 4.3 (Equation 4.3 and Equation 4.4). Exposure parameter values used in the current study are listed in Table 4.4.

Table 4.2 Mathematical models in the exposure assessment of trace elements

Exposure Models for Inhalation Route →	Eq. 4.1
$DD_{Inh} = \left(\frac{C_g * ET * EF}{AT_{noncarc}} \right) * \left(\frac{InhR * ED}{BW} \right) adult / children * CF$	
▪ DD_{inh} = daily dose associated with the inhalation (mg/ kg/d) ▪ C_g = the gas phase atmospheric concentration of each individual metal (ng/m³) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ $InhR$ = inhalation rate (m³/h) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ $AT_{noncarc}$ = average timing for non carcinogenic health effects (d) ▪ cf = conversion factor	

Exposure Models for Dermal Route →	Eq. 4.2
$DD_{der} = \left(\frac{C_p * ET * EF * ABS}{AT_{noncarc}} \right) * \left(\frac{SA * AF_d * ED}{BW} \right) adult / children * CF$	
▪ DD_{der} = daily dose associated with dermal exposure (mg/ kg/d) ▪ C_p = the particulate phase concentration of each individual metal (µg/g) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ ABS = dermal adsorption fraction (dimensionless) ▪ SA = skin surface area exposed (cm²) ▪ AF_d = particle-to-skin adherence factor (mg/cm²/event) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ $AT_{noncarc}$ = average timing for non carcinogenic health effects (d) ▪ cf = conversion factor	

Table 4.3 Mathematical models in the carcinogenic assessment of trace elements

LADD for Carcinogens (Inhalation) →	Eq. 4.3
$LADD_{inh} = \left(\frac{C_g * ET * EF}{AT_{carc}} \right) * \left(\frac{InhR * ED}{BW} \right) adult / children * CF$	
▪ $LADD_{inh}$ = lifetime average daily dose associated with the inhalation (mg/ kg/d) ▪ C_g = the gas phase atmospheric concentration of each individual metal (ng/m³) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ $InhR$ = inhalation rate (m³/h) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ AT_{carc} = average timing for carcinogenic health effects (d) ▪ cf = conversion factor	

LADD for Carcinogens (Dermal) →	Eq. 4.4
$LADD_{der} = \left(\frac{C_p * ET * EF * ABS}{AT_{carc}} \right) * \left(\frac{SA * AF_d * ED}{BW} \right) adult / children * CF$	
▪ $LADD_{der}$ = lifetime average daily dose associated with dermal exposure (mg/ kg/d) ▪ C_p = the particulate phase concentration of each individual metal (µg/g) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ ABS = dermal adsorption fraction (dimensionless) ▪ SA = skin surface area exposed (cm²) ▪ AF_d = particle-to-skin adherence factor (mg/cm²/event) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ AT_{carc} = average timing for carcinogenic health effects (d) ▪ cf = conversion factor	

Table 4.4 Exposure parameter values used in the risk assessment calculations

Variable	Adult	Children	Reference
ET (h/d)	8		USEPA, 2004
EF (d/y)	350		USEPA, 2004
ED (y)	30	6	USEPA, 2004
BW (kg)	70	15	USEPA, 2004
AT _{carc} (d)	70 x 365		USEPA, 2004
AT _{noncarc} (d)	ED x 365		USEPA, 2004
InhR (m ³ /h)	0.83	0.32	USEPA, 1989
ABS	0.001		USEPA, 2004
SA (cm ²)	5700	2800	USEPA, 2004
AF _d (mg/cm ² /event)	0.07	0.2	USEPA, 2004

B. Risk Characterization

Non-cancer

The potential for non-cancer health effects is evaluated by comparing the estimated exposure level of a receptor at the site over a specific time period to a reference threshold that represents an exposure level below which it is unlikely for even sensitive populations to experience adverse health effects. The resulting ratio is known as the Hazard Quotient (HQ). EPA defines an HQ as “the ratio of a single substance exposure level of a specified time period (e.g., subchronic) to a reference dose for that substance derived from a similar exposure period” (USEPA, 1989). If an HQ exceeds one, there is a possibility that some non-cancer effects may occur. Generally, larger HQs indicate greater levels of concern. If the HQ is less than one, it is believed that there is no increased risk of non-cancer health effects at a site.

In order to evaluate non-cancer effects due to inhalation and dermal contact of trace metals, time-weighted daily dose was divided with the reference dose. The reference dose (mg/kg/day) is an estimation of the maximum permissible risk on human population through daily exposure, taking into consideration a sensitive group during a lifetime. The threshold value of RfD can be used to indicate whether there was an adverse health effect during a lifetime.

To assess the overall potential of non-carcinogenic effects posed by more than one route, the HQ is calculated as a Hazard Index (HI) (USEPA, 1989): $HI = HQ_1 + HQ_2 + \dots + HQ_n$. The total risk HI is the sum of the risks associated with the each exposure route. The approach assumes that the magnitude of the adverse effect is proportional to the sum of ratios of the simultaneously subthreshold exposure to acceptable exposure for each chemical (USEPA, 1989). If the value of HI is less than one, it is believed that there is no significant risk of non-carcinogenic effects. If HI exceeds one, then there is a chance that non-carcinogenic effects may occur, with a probability which tends to increase as the value of HI increases (USEPA, 2001).

Table 4.5 Mathematical models in non-cancer risk for trace elements

Hazard Quotient Based on Non-cancer Risk →	Eq. 4.5
$HQ = IR / RfD$	
▪ HQ = hazard quotient ▪ $IR = IR_{inh}(DD_{inh}) / IR_{der}(DD_{der})$ ▪ RfD = specific reference dose	

Hazard Index Based on Non-cancer Risk →	Eq. 4.6
$HI = \sum HQ_i$	
▪ HI = hazard index ▪ HQ_i = hazard quotient	

For the health effects of the metals are similar, HQ can be added which generated a Hazard Index (HI) to estimate the risk of mixed contaminants; where i corresponds to different contaminants (Equation 4.6). $HI \leq 1$ indicated no adverse health effects and $HI > 1$ indicated likely adverse health effects (Guney et al., 2010; Zheng et al., 2010a).

Cancer

The excess risk of cancer over a lifetime as a result of exposure to a particular contaminant is expressed in terms of a probability of developing cancer due to that exposure. EPA considers cancer risks between $1E-06$ (i.e., 1 in 1,000,000) and $1E-04$ (i.e., 1 in 10,000) to be generally acceptable (USEPA, 1991b). However, EPA evaluates this on a case-by-case basis and risks below $1E-04$ may not be considered sufficiently protective and many warrant remedial action (USEPA, 2009a).

According to the USEPA, a one in a million chance of additional human cancer over a 70 year lifetime ($ILTCR = 10^{-6}$) is the level of risk considered acceptable or inconsequential, since this compares favorably with risk levels from several 'normal' human activities such as diagnostic X-rays; whereas a lifetime risk of one in a thousand or greater ($ILTCR > 10^{-3}$) is considered serious and is a high priority for attention.

For carcinogens, the daily value was multiplied by the corresponding slope factor (SF) to produce an estimate of cancer risk (Zheng et al., 2010b; Kong et al., 2012). The incremental lifetime cancer risk (ILTCR) for Co, Ni, Pb, Cr and Cd inhalation exposure route was used for cancer risk assessment by Equation 4.5 (Table 4.5).

Table 4.6 Mathematical models in the cancer risk for trace elements

Incremental Lifetime Cancer Risk Model →	Eq. 4.7
$ILTCR_i = LADD_i \cdot CSF_i$	
▪ $ILTCR_i$ = incremental lifetime cancer risk for an exposure route ▪ $LADD_i$ = lifetime average daily dose for an exposure route ▪ CSF_i = cancer slope factor for an exposure route	

Table 4.7 Relative toxicity values used in this study

	Inhal. RfD	Dermal RfD	Inhal. SF
Ag		9.00E-04	
Cr (Non-cancer)	2.86E-05	6.00E-05	
Cr (Cancer)			4.10E+01
Mn	1.43E-05	1.84E-03	
Co (Non-cancer)	5.71E-06	1.60E02	
Co (Cancer)			9.80E+00
Ni (Non-cancer)	2.00E-02	5.40E-03	
Ni (Cancer)			8.40E-01
Cu	4.00E-02	1.20E-02	
Cd (Non-cancer)	1.00E-03	1.00E-05	
Cd (Cancer)			6.30E+00
Pb (Non-cancer)	3.50E-03	5.25E-04	
Pb (Cancer)			4.20E-02
Sr		1.20E-01	

4.3 RESULT & DISCUSSION

4.3.1 Sources Apportionment of Atmospheric Aerosol

In the present study, the statistical program XLSTAT is used for varimax rotated principal component analysis. The 10 trace metals at each site were considered variables for factor analysis. The results of PCA of trace metal composition data set are tabulated in Table 4.8 and Table 4.9. The result revealed that two factors explain the main part of the data varians.

Table 4.8 Varimax rotated factor loading for Bangi

	F1	F2
Ag	0.994	0.066
Cd	0.967	0.148
Co	0.978	-0.141
Cr	0.986	-0.105
Cu	0.995	0.074
Li	0.993	0.101
Mn	0.988	0.110
Ni	0.997	-0.066
Pb	0.986	-0.068
Sr	-0.424	-0.903
Eiganvalue	8.947	0.909
Variability %	89.472	9.090
Cumulative %	89.472	98.562

In Bangi, the result shows two possible factor representing different contributing sources for airborne elements. Factor 1 explain by 89.4% of total varians of the data; has high loading for Ag (0.994), Cd (0.967), Co (0.978), Cr (0.986), Cu (0.995), Li (0.993), Mn (0.988), Ni (0.997) and Pb (0.986), which can be identified as vehicles emission/oil combustion, re-suspended dust/brake emission and industry emission.

The presence of Cr and Pb was considered the major component of the vehicle tailpipe emissions (Vassilakos et al., 2007; Kong et al., 2012; Li et al., 2012). Since Malaysia already banned the use of Pb, the presence of Pb reflects the influence of re-suspended dust. According to Geller et al. (2006) high loading of Li is associated with emission form automobiles particularly diesel vehicles.

Mn and Co have been linked to re-suspended dust with high traffic densities (Kong et al., 2012), and Cu could point to brake emission (Xie et al., 2008). In addition to re-suspended dust, the presence of Mn might showed the methylcyclopentadienyl manganese tricarbonyl (MMT, $C_9H_7MnO_3$) has been used as an anti-knock agent, particularly, with the advent of unleaded gasoline, as an alternative to lead alkyls. Trace elements of Cr and Mn might also indicated brake lining dusts. The brake linings that are subject to wear are composed of several metallic, inorganic and organic materials. Composition is dependent on the manufacturer and lining type but metals that have been linked with brake wear is Cu that can be present in significant amounts as well as Cr and Mn. High loading for Cd suggesting an influence from industrial processes (Fang et al., 2010). Particulate Ni in ambient air may originate from oil combustion (Zoller et al., 1974; Kowalczyk et al., 1982).

The factor 2 with 9.01% of total varians is solely related to Sr (0.903); indicated their origin from soil as it is contain typical elements from crustal origin. This is consistent with the lack of correlation found between Sr and the rest of the elements in this study. This may suggest that crustal soil is the dominant source for Sr in atmospheric particulate matter at this location; either due to episodic presence of crustal substances brought to the area from distant sources or re-suspended local soil.

Table 4.9 Varimax rotated factor loading for Petaling Jaya

	F1	F2
Ag	0.989	-0.146
Cd	0.951	-0.306
Co	0.891	0.451
Cr	0.993	-0.010
Cu	0.994	0.044
Li	0.987	-0.155
Mn	0.789	0.606
Ni	0.988	-0.145
Pb	0.836	-0.535
Sr	-0.955	-0.278
Eiganvalue	8.838	1.096
Variability %	88.378	10.964
Cumulative %	88.378	10.964

In Petaling Jaya, 88.38% variances of the data was observed in factor 1. High loading of Ag (0.989), Cd (0.951), Co (0.891), Cr (0.993), Cu (0.994), Li (0.987), Mn (0.789), Ni (0.988), Pb (0.836) and Sr (-0.955) indicates that the contributing sources in factor 1 of Petaling Jaya are similar to the factor 1 of the Bangi site. Previous study showed that Ni is regarded as an indicator of emission from fossil fuel combustion and vehicles exhaust (Zheng et al. 2011).

High loading of Cu, Mn, Pb, Co, Cd and Li considered that this element originated from vehicles emissions and re-suspended road dust from urban areas with high traffic densities (Samara & Voutsas, 2005; Shah et al., 2006b; Viana et al., 2008). In addition, Cu is a marker of automobile brake pads and worn tires (Garg et al., 2000; Sternbeck et al., 2002; Gietl et al., 2010). Sr on the other hand is associated with re-suspension sources. At the study site, high re-suspension of particles due to the turbulence induced by vehicle movement (vehicle wake effect) as well as wind fluctuations (natural turbulence) is expected.

Together, these results indicate that road dust can act as a repository for elements from anthropogenic sources, and that re-suspension could at certain locations contribute to the atmospheric concentration of these elements. The plausibility of this theory is supported by studies where it has been shown that larger particles are more easily re-suspended by wind and traffic, and that deposited materials are more likely to become re-suspended if they are associated with larger host particles (Nicholson & Branson, 1990).

Factor 2 with total variances 10.96% and considerable contributions from Co, Mn and Pb may be due to industrial/re-suspension. Previous study showed that the presence of Co might be originated from industrial emission (Shah et al., 2012). Both natural and anthropogenic sources emit Mn (Kowalczy et al., 1982; Marcazzan et al., 2001; Chao et al., 2002). Ny & Lee (2011) indicated that Mn in ambient atmosphere could be the influence of industry. There are significant numbers of small industries that are involved in metal works scattered around Klang Valley and the main industrial area located about 15 to 20km to the southern/southwestern side of the sampling site. The industries include iron and steel, paint, aluminum fabrication, pharmaceutical, rubber glove production, as well as food industries (Abdul Rahman et al., 2011). Pb has been added traditionally to gasoline as anti-knock agents to raise its octane level. At present, only unleaded fuel is supplied in Malaysia. Therefore, the presence of Pb in ambient environment at the study site is might be from the bulk matrix of road dust or re-suspension.

4.3.2 Backward Trajectory Modeling

The transport distance at the regional scale or mesoscale is always within 1 km for approximately 2 to 3 days at the boundary layer. Thus, a backward trajectory length of 72 hours was chosen. The 72 hours backward trajectories were obtained using HYSPLIT4, available online at <http://www.arl.noaa.gov/ready/hysplit4.html>.

The backward trajectories provide Lagrangian path of air parcels in the chosen time scale, which could be used to identify the potential source regions and transport pathways of pollutants. The trajectory starts from Bangi (latitude of 2°55' 24.1"N and longitude of 101°46' 50.7" E) and Petaling Jaya (latitude of 3°06' 09.5" N and longitude of 101°38' 41.2" E) at 4:00 UTC (Coordinated Universal Time) each day, which is equivalent to 12:00 (noon) Malaysia local standard time (LST). Three-dimensional 6 hours backward trajectories arriving at the receptor site 1000 m above ground level (AGL) were calculated every 6 hour using HYSPLIT-4.9.

In order to minimize the friction effect from the Earth's surface and to represent wind in the lower boundary layer (Begum et al., 2005), the arriving level of air masses is fixed at 1000 m above ground level (AGL). This is the average daytime mixing height for the Klang Valley, which was estimated based on the mixing height data obtained from the Malaysia Meteorological Department. The mixing height is the variation value of the atmosphere height above the ground where the vertical mixing takes place due to mechanical or convection turbulence.

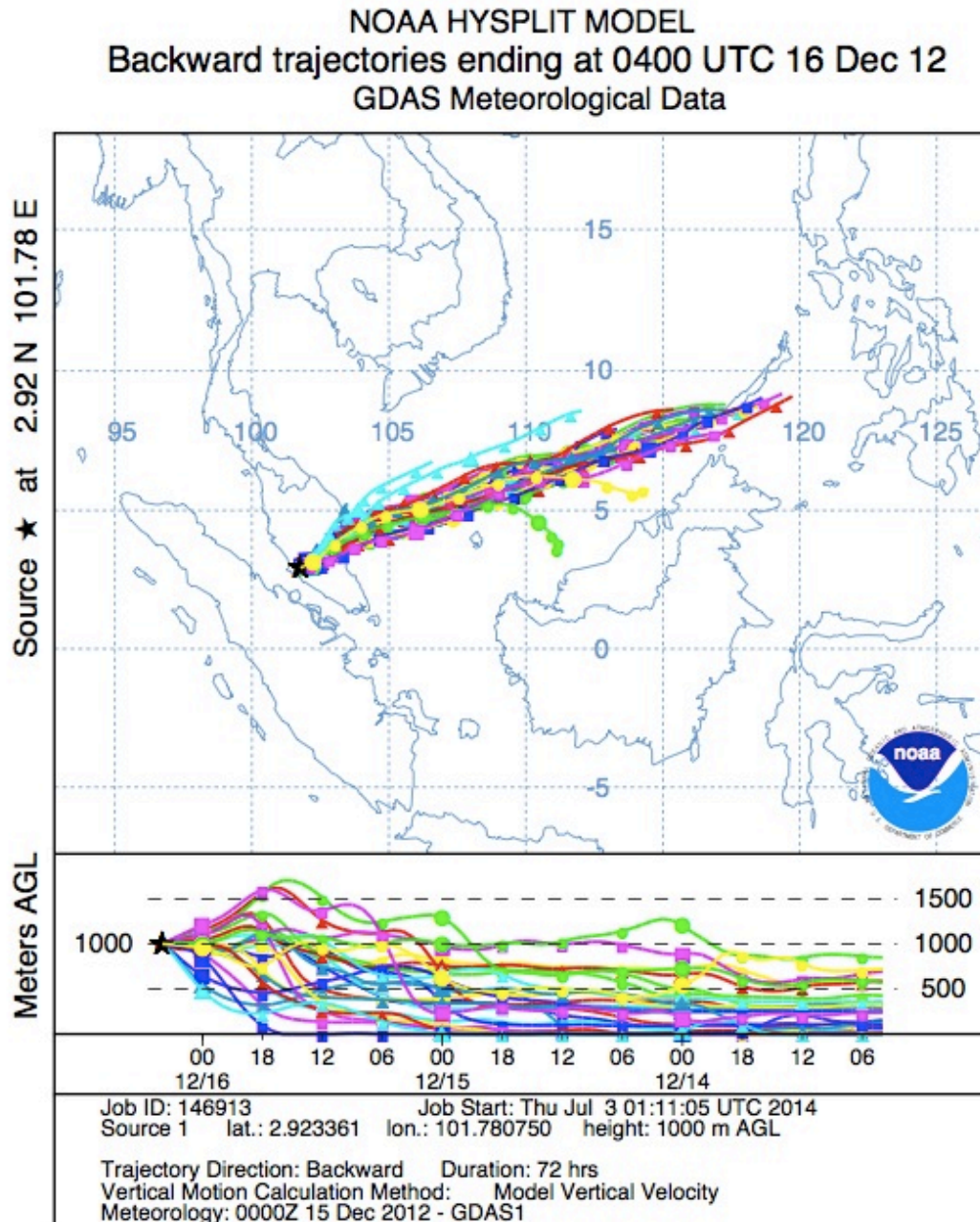


Figure 4.4 Backward trajectories of Bangi

In Figure 4.4, the trajectories mostly start over the Pacific Ocean and directly move westward through the South China Sea, passing the Sulu Sea before arriving to the south of Klang Valley (Bangi). Sometimes, air masses within this cluster normally originate over the East and South China Sea. This cluster usually occurs in the period from November to May with higher frequencies from February to April. Due to its main pathway over the ocean, the trajectory vertical position does not change much along the trajectory. During this period of the year, the influence of the northeast monsoon is reduced, while the influence of the tropical depression in the Pacific Ocean is increased. Based on its pathway and origin, this air mass is expected to bring in relatively clean air from the Pacific Ocean to the Klang Valley.

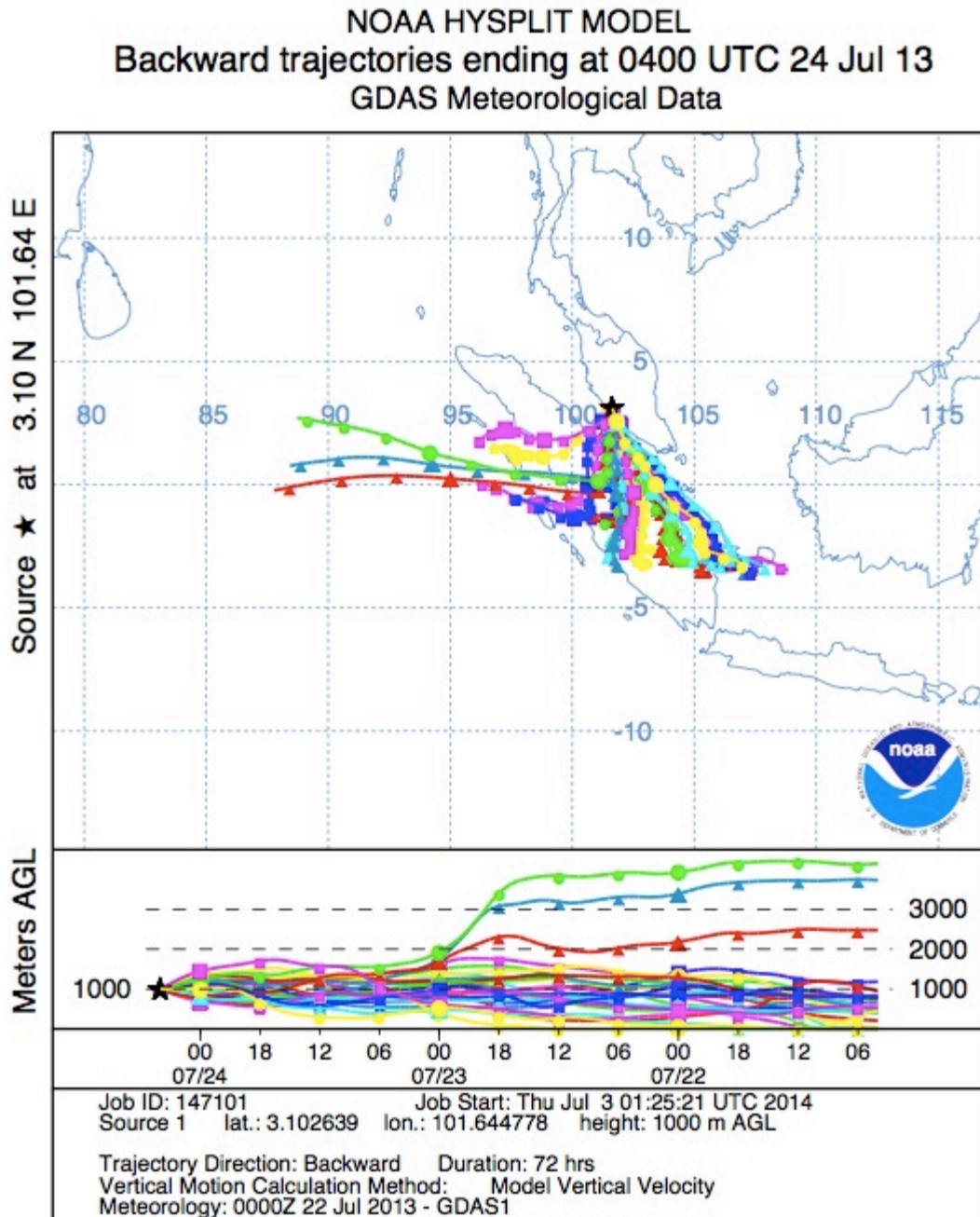


Figure 4.5 Backward trajectories of Petaling Jaya

Figure 4.5 demonstrated that in 3 days backward, most of the wind came from the Malacca Straits during southwest monsoon. Peninsular Malaysia has been affected by severe smoke haze due to forest fires in the region periodically. With its pathways above the populated areas, and short passages over the sea, these air masses have a potential to bring in the long-range transport air pollution to the Malaysia. The low wind speed observed during southwest monsoon would limit the horizontal transport/dilution of locally emitted air pollution and enhance high air pollution build-up levels, especially with low efficiency of wet removal.

4.3.3 Health Risk Assessment

A. Non-Cancer

The estimates of daily dose exposure for the inhalation and dermal routes are given in Tables 4.10 and 4.11, respectively. The daily dose values calculated were later used to derive Hazard Quotient (HQ) and Hazard Index (HI) which were based on non-carcinogenic risk for trace metals involved.

The daily dose exposure for inhalation and dermal routes show relatively higher values in children compared to adult; in both locations and for both particle sizes. The higher daily dose exposure values for children suggest that they might be more susceptible to exposure to trace metals exposure through inhalation and dermal contact, compared to adult people.

The highest inhalation daily dose exposure value for children in Bangi was recorded for Cr (5.32E-06 mg/kg/d) while in Petaling Jaya, Sr was the highest with 3.07E-06 mg/kg/d. Similarly, the highest inhalation daily dose in Bangi and Petaling Jaya among adult were also held by Cr and Sr with values of 2.96E-06 mg/kg/d and 1.70E-06 mg/kg/d; respectively. However, the highest inhalation daily dose value for Cr in Bangi was shown in fine mode particle size while in Petaling Jaya, the highest inhalation daily dose value was recorded for Sr in coarse mode particle size. Apart from Cr, other trace elements including Sr, Cu, Li, Mn and Pb also recorded relatively higher inhalation daily dose values for both adult and children in Bangi, with the range between 2.39E-07mg/kg/d to 1.79E-06mg/kg/d. Similarly, in Petaling Jaya, Cr, Cu, Mn, Li and Pb also have higher inhalation daily dose values for groups of adult and children in range between 1.03E-07mg/kg/d to 2.01E-06mg/kg/d.

In contrast to inhalation daily dose exposure values, Li recorded the highest dermal daily dose exposure values for adult and children in both locations for fine mode with respective values of 9.03E-07mg/kg/d, 5.92E-06mg/kg/d, 6.70E-07mg/kg/d and 4.39E-06mg/kg/d. However, for coarse mode particle size, Li has the highest dermal daily dose values for adult and children in Bangi (6.59E-07mg/kg/d and 4.31E-06mg/kg/d); while in Petaling Jaya Sr recorded the highest dermal daily dose values with 2.29E-07mg/kg/d and 1.50E-06mg/kg/d, for adult and children correspondingly. Other than Li, the second highest dermal daily dose value in Bangi was held by Cr with reading of 4.50E-07mg/kg/d, 2.95E-06mg/kg/d, 6.68E-07mg/kg/d and 4.38E-06mg/kg/d in correspond of coarse and fine mode particle size. Li and Mn in Petaling Jaya for coarse mode recorded almost the same dermal daily dose values with 1.75E-07mg/kg/d, 1.15E-06mg/kg/d, 1.67E-07mg/kg/d and 1.09E-06mg/kg/d; for adult and children respectively. For fine mode particle size in Petaling Jaya, the dermal daily dose values stand in descending orders of Li > Sr > Cu > Cr > Mn > Ni > Pb > Ag > Co > Cd.

Table 4.10 Calculated daily dose (mg/kg/d) for inhalation exposure route

Location	Particle Size	Metals	Adult	Children
Bangi	Coarse Mode	Ag	5.89E-09	1.06E-08
		Cd	5.18E-09	9.32E-09
		Co	7.86E-09	1.41E-08
		Cr	1.99E-06	3.58E-06
		Cu	2.39E-07	4.30E-07
		Li	3.89E-07	6.99E-07
		Mn	2.53E-07	4.55E-07
		Ni	1.67E-07	3.00E-07
		Pb	2.56E-07	4.60E-07
		Sr	9.96E-07	1.79E-06
	Fine Mode	Ag	2.23E-08	4.02E-08
		Cd	1.99E-08	3.58E-08
		Co	1.68E-08	3.02E-08
		Cr	2.96E-06	5.32E-06
		Cu	7.05E-07	1.27E-06
		Li	5.33E-07	9.59E-07
		Mn	4.63E-07	8.34E-07
		Ni	3.50E-07	6.30E-07
		Pb	5.57E-07	1.00E-06
		Sr	7.69E-07	1.38E-06
Petaling Jaya	Coarse Mode	Ag	1.22E-08	2.19E-08
		Cd	4.59E-09	8.26E-09
		Co	1.39E-08	2.51E-08
		Cr	5.77E-07	1.04E-06
		Cu	7.22E-07	1.30E-06
		Li	1.03E-07	1.86E-07
		Mn	7.81E-07	1.40E-06
		Ni	1.58E-07	2.85E-07
		Pb	2.87E-07	5.17E-07
		Sr	1.70E-06	3.07E-06
	Fine Mode	Ag	2.58E-08	4.63E-08
		Cd	2.15E-08	3.88E-08
		Co	1.27E-08	2.29E-08
		Cr	7.56E-07	1.36E-06
		Cu	1.12E-06	2.01E-06
		Li	3.96E-07	7.12E-07
		Mn	7.03E-07	1.26E-06
		Ni	2.63E-07	4.74E-07
		Pb	6.57E-07	1.18E-06
		Sr	1.64E-06	2.95E-06

Table 4.11 Calculated daily dose (mg/kg/d) for dermal exposure route

Location	Particle Size	Metals	Adult	Children
Bangi	Coarse Mode	Ag	6.42E-10	4.20E-09
		Cd	5.42E-10	3.55E-09
		Co	1.57E-09	1.03E-08
		Cr	4.50E-07	2.95E-06
		Cu	4.43E-08	2.90E-07
		Li	6.59E-07	4.31E-06
		Mn	5.41E-08	3.54E-07
		Ni	3.34E-08	2.19E-07
		Pb	1.45E-08	9.51E-08
		Sr	1.34E-07	8.76E-07
	Fine Mode	Ag	2.43E-09	1.59E-08
		Cd	2.08E-09	1.36E-08
		Co	3.35E-09	2.19E-08
		Cr	6.68E-07	4.38E-06
		Cu	1.30E-07	8.54E-07
		Li	9.03E-07	5.92E-06
		Mn	9.92E-08	6.49E-07
		Ni	7.01E-08	4.59E-07
		Pb	3.16E-08	2.07E-07
		Sr	1.03E-07	6.76E-07
Petaling Jaya	Coarse Mode	Ag	1.33E-09	8.70E-09
		Cd	4.80E-10	3.15E-09
		Co	2.78E-09	1.82E-08
		Cr	1.30E-07	8.54E-07
		Cu	1.34E-07	8.76E-07
		Li	1.75E-07	1.15E-06
		Mn	1.67E-07	1.09E-06
		Ni	3.17E-08	2.08E-07
		Pb	1.63E-08	1.07E-07
		Sr	2.29E-07	1.50E-06
	Fine Mode	Ag	2.81E-09	1.84E-08
		Cd	2.25E-09	1.48E-08
		Co	2.54E-09	1.66E-08
		Cr	1.71E-07	1.12E-06
		Cu	2.06E-07	1.35E-06
		Li	6.70E-07	4.39E-06
		Mn	1.50E-07	9.86E-07
		Ni	5.28E-08	3.46E-07
		Pb	3.73E-08	2.44E-07
		Sr	2.20E-07	1.44E-06

Table 4.12 and Table 4.13 displayed the non-carcinogenic risk assessment results for adult and children in Bangi and Petaling Jaya, according to exposure to particulate metals. The risk assessment was calculated for Hazard Quotient (HQ) and Hazard Index (HI). Based on the result, it was found that inhalation is an important pathway of for exposure to trace elements in the circumstance of particulate matter in Bangi and Petaling Jaya. HQ for non-cancer risk due to dermal contact of particulate matter is in lower magnitude and it is unlikely that this exposure route would pose a higher risk than inhalation.

For both sampling location Bangi and Petaling Jaya the same trend of result were observed. Inhalation of particles appeared to have much higher risk for Cr, Co and Mn; which were one to three orders of magnitude higher than the corresponding risks of the dermal exposure route. In contrast for Cr compared to other elements, dermal contact showed some tendency to be the main exposure route that might results in some risk. The highest non-carcinogenic risk of inhalation appeared to occur for Cr, followed by Mn and Co.

Regarding to non-cancer effects, all trace elements exhibit Hazard Index lower than safe level (1), except for Ag and Sr as their HI could not be calculated. Ambient exposure especially to Cr and Mn could trigger adverse health effects for both adult and children. However, compared to children, adult health risk due to the certain trace elements from ambient air is generally lower.

Health risk is especially high for children because of their low tolerance to toxins (Ljung et al., 2005; Acosta et al., 2009). Pollutant metals are usually non-degradable and there is no known homeostasis mechanism for them. Thus, any high levels of heavy metals will threaten biological life (Tong & Lam, 2000). They may accumulate in the fatty tissues of our body and affect our central nervous system, or they may be deposited in our circulatory system and disrupt the normal functioning of our internal organs, or they may act as cofactors in other diseases (Nriagu, 1988).

In comparison to the children and adult cases, the inhalation and dermal exposure route has higher values for children than that for adult and hence the overall values of risk are higher than adult. The children living surrounding the Bangi sampling site might be affected by the non-cancerous health hazard of Cr for both coarse and fine mode, as the risk of this element as the values approach to the safe level (HI=1) that is 1.74E-01 and 2.59E-01 respectively. In case for adults, the value of overall hazard quotient regarding the non-carcinogenic, calculated for Cr is somehow high for fine mode (1.14E-01) but is well below the recommended threshold value of risk (HI=1) compared to coarse mode (7.70E-02). The safe limits are found for the non-carcinogenic effects of Co, Pb, Ni, Cd and Cu when calculated for adult and children.

Table 4.12 Hazard quotient and hazard index for non-cancer risk in Bangi

Location	Particle Size	Group	Metals	HQ _{inh}	HQ _{dermal}	HI = $\sum HQ_i$
Bangi	Coarse Mode	Adult	Ag		7.13E-07	
			Cd	5.18E-06	5.42E-05	5.93E-05
			Co	1.38E-03	9.80E-08	1.38E-03
			Cr	6.96E-02	7.50E-03	7.70E-02
			Cu	5.98E-06	3.69E-06	9.67E-06
			Mn	1.77E-02	2.94E-05	1.77E-02
			Ni	8.34E-06	6.19E-06	1.45E-05
			Pb	7.31E-05	2.77E-05	1.01E-04
			Sr		1.11E-06	
		Children	Ag		4.67E-06	
			Cd	9.32E-06	3.55E-04	3.64E-04
			Co	2.48E-03	6.42E-07	2.48E-03
			Cr	1.25E-01	4.91E-02	1.74E-01
			Cu	1.08E-05	2.42E-05	3.49E-05
			Mn	3.18E-02	1.93E-04	3.20E-02
			Ni	1.50E-05	4.05E-05	5.56E-05
			Pb	1.32E-04	1.81E-04	3.13E-04
			Sr		7.30E-06	
	Fine Mode	Adult	Ag		2.71E-06	
			Cd	1.99E-05	2.08E-04	2.28E-04
			Co	2.94E-03	2.09E-07	2.94E-03
			Cr	1.03E-01	1.11E-02	1.14E-01
			Cu	1.76E-05	1.09E-05	2.85E-05
			Mn	3.24E-02	5.39E-05	3.25E-02
			Ni	1.75E-05	1.30E-05	3.05E-05
			Pb	1.59E-04	6.02E-05	2.19E-04
			Sr		8.60E-07	
		Children	Ag		1.77E-05	
			Cd	3.58E-05	1.36E-03	1.40E-03
			Co	5.28E-03	1.37E-06	5.28E-03
			Cr	1.86E-01	7.29E-02	2.59E-01
			Cu	3.17E-05	7.12E-05	1.03E-04
			Mn	5.83E-02	3.53E-04	5.86E-02
			Ni	3.15E-05	8.51E-05	1.17E-04
			Pb	2.86E-04	3.95E-04	6.81E-04
			Sr		5.63E-06	

Table 4.13 Hazard quotient and hazard index for non-cancer risk in Petaling Jaya

Location	Particle Size	Group	Metals	HQ _{inh}	HQ _{dermal}	HI = $\sum HQ_i$
Petaling Jaya	Coarse Mode	Adult	Ag		1.48E-06	
			Cd	4.59E-06	4.80E-05	5.26E-05
			Co	2.44E-03	1.74E-07	2.44E-03
			Cr	2.02E-02	2.17E-03	2.23E-02
			Cu	1.81E-05	1.11E-05	2.92E-05
			Mn	5.46E-02	9.08E-05	5.47E-02
			Ni	7.92E-06	5.88E-06	1.38E-05
			Pb	8.21E-05	3.11E-05	1.13E-04
			Sr		1.91E-06	
		Children	Ag		9.66E-06	
			Cd	8.26E-06	3.15E-04	3.23E-04
			Co	4.39E-03	1.14E-06	4.39E-03
			Cr	3.63E-02	1.42E-02	5.05E-02
			Cu	3.25E-05	7.30E-05	1.05E-04
			Mn	9.82E-02	5.95E-04	9.88E-02
			Ni	1.42E-05	3.85E-05	5.27E-05
			Pb	1.48E-04	2.04E-04	3.51E-04
			Sr		1.25E-05	
	Fine Mode	Adult	Ag		3.12E-06	
			Cd	2.15E-05	2.25E-04	2.47E-04
			Co	2.23E-03	1.58E-07	2.23E-03
			Cr	2.64E-02	2.85E-03	2.93E-02
			Cu	2.79E-05	1.72E-05	4.51E-05
			Mn	4.92E-02	8.18E-05	4.92E-02
			Ni	1.32E-05	9.77E-06	2.29E-05
			Pb	1.88E-04	7.10E-05	2.59E-04
			Sr		1.84E-06	
		Children	Ag		2.04E-05	
			Cd	3.88E-05	1.48E-03	1.51E-03
			Co	4.00E-03	1.04E-06	4.01E-03
			Cr	4.76E-02	1.87E-02	6.62E-02
			Cu	5.02E-05	1.13E-04	1.63E-04
			Mn	8.85E-02	5.36E-04	8.90E-02
			Ni	2.37E-05	6.40E-05	8.77E-05
			Pb	3.38E-04	4.65E-04	8.03E-04
			Sr		1.20E-05	

In Petaling Jaya, the health risk values for non-cancerous for Mn showed the highest but are within the safe limit both in case of adults and children for both coarse and fine mode particles. Therefore, those who are residents of the surrounding areas may be at higher risk for non-carcinogenic effects of Mn. On the other hand, the result also indicated the potential health risk from Cr is the second highest HI recorded for both coarse and fine mode but is within the safe limits. The health risk hazard of Co, Pb, Ni, Cd and Cu are within the recommended safe level as calculated during non-cancerous health risk assessment for both adult and children in coarse and fine mode.

Though, HI for Mn is lower for adult and children, chronic inhalation exposure of humans to manganese results primarily in effects on the nervous system. Therefore, Mn exposure to the ambient particulate matter cannot be overlooked, and its health implications need further detailed investigations. Knowledge about human exposure levels to manganese and health effects from this exposure is needed in order to ensure that a repeat of the lead-additive experience would not occur, i.e., the impairment of cognitive development in children at very low lead levels of exposure. Neurological effects have been observed in adults at occupational levels of manganese; however, little is currently known about the effect on children's cognitive development from environmental exposure levels to manganese. The toxicological studies strongly suggest that transition metals such as Cr, Mn, Ni and Cu are components in particulate matter with toxic capability based on their potential for oxidative activity and the production of reactive oxygen species (Schlesinger et al., 2006).

In addition, the result also showed that the fine mode particle are likely to exhibit more potential health effects compared to coarse mode for all trace elements in both sampling side. The proportion of fine particles has two important implications on the health effects of re-suspended dust episodes. Firstly, fine particles can remain in suspension much longer than coarse particles and it can result in larger spatial impact by re-suspended PM, and secondly, the fine fraction of re-suspended particulate matter is more likely to comprise anthropogenic constituents that are potentially more toxic than the fine particles of pure crustal origin. This study was in agreement with the reviews done by Pope & Dockery (2006) and Schlesinger et al., (2006) which conclude that there tends to be a stronger relation between fine particles, $PM_{2.5}$ and most health effects than between PM_{10} and effects on health.

B. Cancer

The LADD carcinogenic values for inhalation and dermal exposure routes are displayed in Table 4.14 and Table 4.15, respectively. The values were later used to calculate the Incremental Lifetime Cancer Risk (ILTCR) for inhalation exposure route. The cancer risk was estimated for Cd, Co, Cr, Ni and Pb.

Table 4.14 Calculated LADD (mg/kg/d) for inhalation exposure route

Location	Particle Size	Metals	Adult	Children
Bangi	Coarse Mode	Cd	2.22E-09	7.98E-10
		Co	3.37E-09	1.21E-09
		Cr	8.52E-07	3.07E-07
		Ni	7.15E-08	2.57E-08
		Pb	1.10E-07	3.95E-08
	Fine Mode	Cd	8.54E-09	3.07E-09
		Co	7.19E-09	2.59E-09
		Cr	1.27E-06	4.56E-07
		Ni	1.50E-07	5.40E-08
		Pb	2.39E-07	8.59E-08
Petaling Jaya	Coarse Mode	Cd	1.97E-09	7.08E-10
		Co	5.97E-09	2.15E-09
		Cr	2.47E-07	8.89E-08
		Ni	6.79E-08	2.44E-08
		Pb	1.23E-07	4.43E-08
	Fine Mode	Cd	9.23E-09	3.32E-09
		Co	5.45E-09	1.96E-09
		Cr	3.24E-07	1.17E-07
		Ni	1.13E-07	4.06E-08
		Pb	2.82E-07	1.01E-07

The LADD values through inhalation exposure for adult in Bangi range between 2.22E-09mg/kg/d to 1.27E-06mg/kg/d; while for children, the LADD values stand between 7.98E-10mg/kg/d and 4.56E-07mg/kg/d. For both adult and children in Bangi, Cr in fine mode recorded the highest values; while the lowest reading of LADD holds by Cd in coarse mode. Particularly, almost the same pattern was observed in Petaling Jaya. The lowest values were recorded by Cd in coarse mode for both adult and children. However, the highest LADD values for adult and children in Petaling Jaya were hold by Pb and Cr in fine mode, accordingly. The LADD values through inhalation exposure for adult in Petaling Jaya range between 1.96830E-09mg/kg/d to 2.82E-07mg/kg/d; while for children, the LADD values stand between 7.08E-10mg/kg/d and 1.17E-07mg/kg/d.

For LADD values through dermal exposure, the same patterns were observed for all carcinogens in Bangi and Petaling Jaya; for both particle sizes and groups. The estimated LADD values stand in descending orders of Cr > Ni > Pb > Co > Cd. In Bangi, the LADD values for adult range between 2.32E-10 mg/kg/d to 2.86E-07 mg/kg/d; while for children, the values range between 3.04E-10 mg/kg/d to 3.75E-07 mg/kg/d. Similarly, in Petaling Jaya, the LADD values for adult stand between 2.06E-10 mg/kg/d and 7.33E-08 mg/kg/d; as for children, the LADD values were between 2.70E-10 mg/kg/d to 9.60E-08 mg/kg/d.

Table 4.15 Calculated LADD (mg/kg/d) for dermal exposure route

Location	Particle Size	Metals	Adult	Children
Bangi	Coarse Mode	Cd	2.32E-10	3.04E-10
		Co	6.72E-10	8.80E-10
		Cr	1.93E-07	2.53E-07
		Ni	1.43E-08	1.88E-08
		Pb	6.22E-09	8.15E-09
	Fine Mode	Cd	8.93E-10	1.17E-09
		Co	1.43E-09	1.88E-09
		Cr	2.86E-07	3.75E-07
		Ni	3.01E-08	3.94E-08
		Pb	1.36E-08	1.78E-08
Petaling Jaya	Coarse Mode	Cd	2.06E-10	2.70E-10
		Co	1.19E-09	1.56E-09
		Cr	5.59E-08	7.32E-08
		Ni	1.36E-08	1.78E-08
		Pb	6.99E-09	9.16E-09
	Fine Mode	Cd	9.66E-10	1.26E-09
		Co	1.09E-09	1.42E-09
		Cr	7.33E-08	9.60E-08
		Ni	2.26E-08	2.96E-08
		Pb	1.60E-08	2.09E-08

Table 4.16 summarized the estimated incremental lifetime cancer risk (ILTCR) values for inhalation exposure route. The values were derived from Equation 4.7 (Table 4.6) by multiplying the LADD inhalation values with corresponding slope factor to produce an estimate cancer risk.

The relative toxicity values used in the analysis were summarized from the literature as shown in Table 4.7 (Man et al., 2010; Zheng et al., 2010a, b). Ni, Cu, Cd and Pb toxicity values considered for the inhalation route were substituted by the corresponding oral reference doses with the assumption that, after inhalation, the absorption of the particle-bound toxicants will result in similar health effects as if the particles had been ingested.

Table 4.16 Incremental lifetime cancer risks for inhalation exposure route

Location	Particle Size	Metals	Adult	Children
Bangi	Coarse Mode	Cd	1.40E-08	5.03E-09
		Co	3.30E-08	1.19E-08
		Cr	3.50E-05	1.26E-05
		Ni	6.01E-08	2.16E-08
		Pb	4.61E-09	1.66E-09
	Fine Mode	Cd	5.38E-08	1.94E-08
		Co	7.04E-08	2.53E-08
		Cr	5.19E-05	1.87E-05
		Ni	1.26E-07	4.53E-08
		Pb	1.00E-08	3.61E-09
Petaling Jaya	Coarse Mode	Cd	1.24E-08	4.46E-09
		Co	5.85E-08	2.10E-08
		Cr	1.01E-05	3.65E-06
		Ni	5.70E-08	2.05E-08
		Pb	5.17E-09	1.86E-09
	Fine Mode	Cd	5.82E-08	2.09E-08
		Co	5.34E-08	1.92E-08
		Cr	1.33E-05	4.78E-06
		Ni	9.48E-08	3.41E-08
		Pb	1.18E-08	4.25E-09

Lead exposure occurs through inhalation. Most of inhaled lead is absorbed into the body and can be deposited for a long period of time in some tissues. Lead exposure is the possible source of tumors. USEPA has considered lead to be Group B2 (probable human carcinogen). The toxicity of Cd consists in accumulation in soft tissues (liver and kidneys) and in mineralizing tissues (bones). Key health endpoints include kidney and bone damage and cancer. Chronic exposure from inhalation can cause chronic pulmonary effects. Cadmium exposure has been examined in several studies by reason of its potential carcinogenic risks. The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as Group I (human carcinogens) while USEPA categorized the compounds as Group B1 (probable human carcinogen).

Nickel is one of the metals usually found in PM₁₀ resulted from fossil fuel combustion. The most toxic form of Ni is nickel carbonyl gas. Immediate symptoms of exposure to nickel carbonyl gas contain headache, nausea, weakness, vomiting and, in some cases, death. Inhalation of nickel may lead to nasal and pulmonary tumors. IARC has classified nickel and nickel compounds as Group 1 (human carcinogens) and metallic nickel as Group 2B (possibly carcinogenic to humans). USEPA has classified nickel refinery dust and nickel subsulfide as Group A (human carcinogen) and nickel carbonyl as Group B2 (probable human carcinogen). Chromium exists in the ambient air primarily in the trivalent (Cr(III)) and hexavalent (Cr(VI)) states (Kimbrough et al.,

1999). Cr(III) is considered to be essential to humans in trace concentrations. In contrast, the Cr(VI) is recognized as a pulmonary carcinogen by the International Agency for Research on Cancer and the US Toxicology Program (Barceloux, 1999). Exposure to airborne Cr(VI) has been associated with an increased risk of lung and nasal cancer (Crump et al., 2003).

For cancer risk, only carcinogen risk for inhalation exposure model was considered. In this study, the incremental lifetime cancer risk (ILTCR) for Cr, Pb, Cd, Ni and Co was calculated to see the probability of getting cancer from the exposure of ambient atmospheric particulate matter. The acceptable level of cancer risk is recognized as 1×10^{-6} , which signifies the increase of individual lifetime cancer risk by 1 case of 1 million exposed populations. Generally, environmental exposure to trace metals in both study area posed unacceptable potential of adverse health effects as the magnitude higher than the acceptable risk level 1×10^{-6} .

Cr has the highest ILTCR values among all the carcinogens. In Bangi, the estimate Cr risk values for adult were 3.50×10^{-5} (coarse mode) and 5.19×10^{-5} (fine mode); while for children the values were 1.26×10^{-5} (coarse mode) and 1.87×10^{-5} (fine mode). Similarly, the Cr ILTCR values in Petaling Jaya for adult were 1.01×10^{-5} (coarse mode) and 1.33×10^{-5} (fine mode); as for the children were 3.65×10^{-6} (coarse mode) and 4.78×10^{-6} (fine mode). Therefore, it can be confirmed that exposure to Cr is quite a serious problem in respect for both adult and children population in Bangi and Petaling Jaya. Other carcinogens have estimated ILTCR values in range between 4.46×10^{-9} to 5.82×10^{-8} for Cd; 1.19×10^{-8} to 7.04×10^{-8} for Co; 2.05×10^{-8} to 1.26×10^{-7} for Ni; and 1.66×10^{-9} to 1.18×10^{-8} for Pb.

In Bangi, the probability of developing tumorous diseases from long-term Ni exposure could be regarded insignificant and acceptable among adult and children in the coarse mode. On the other hand, although the probability of developing cancer from Ni exposure among adult and children for fine mode are ranges between limit of acceptability, the cancer risk is slightly increased at 1.26×10^{-7} . In Petaling Jaya, the assessed values of ILTCR among children show that the cancer risk of Ni for both coarse and fine mode could be regarded as acceptable with the rates of 2.05×10^{-8} and 3.41×10^{-8} respectively. Nevertheless, ILTCR values for adult are comparable with children in both coarse and fine mode as the probability developing cancer from long term Ni, Co and Cd exposure could be regarded as insignificant as the value above the level of acceptability. On the other hand, the probability of developing cancer from long term Pb exposure could be regarded as insignificant for both adult and children in both sampling site; in Bangi and Petaling Jaya, during the assessed period.

The risk assessment suggested that there was an acceptable potential adverse health effects for adult and children in both localities (Bangi and Petaling Jaya) caused by particulate metals except for Cr. Environmental exposure to particulate matter bound Cr posed an unacceptable potential cancer risk to both adult and children in Bangi and Petaling Jaya. Although generally probability developing cancer risk is low, it was thus clear that the exposure of resident lived nearby study area to the coarse and fine particles with toxic contents should be of special concern for certain trace elements. However, the increasing population growth rate and hence the increasing number of vehicles and industries in Klang Valley is a threat for healthy environment.

Calculated values of ILTCR can be expected as a little inaccurate in consequence of specific uncertainties. Some of uncertainties of health risk assessment are the following:

- a) The input data are results of some models and approximations.
- b) The impossibility to connect effects of observed pollutants and other undetected pollutants.
- c) Some specific factors are not considered, only general features are reflected on.
- d) The concrete number of population of specific locality is not known.
- e) The exposure scenario assumes that the population is exposed to effects of pollutants almost two thirds of the day and almost the whole year.
- f) The exposure scenario also assumes the average weight (70 kg). It can be supposed that the weight is probably higher than the average weight.

4.4 Conclusion

Analysis from PCA has established two possible factors loading for source apportionment of airborne trace elements composition in Bangi and Petaling Jaya. In Bangi, factor 1 comprises of 89.4% of total varians with high loading of >0.9 for all trace elements except Sr; can be identified as vehicles emission/oil combustion, re-suspended dust/brake emission and industry emission. The factor 2 with 9.01% of total varians is solely related to Sr (0.903); indicated their origin from soil as it is contain typical elements from crustal origin. Similarly, factor 1 in Petaling Jaya with total varians of 88.38% also indicates similar contributing sources as factor 1 in Bangi. Factor 1 in Petaling Jaya recorded high loading for all trace elements with values more than 0.7; except for Sr which is negatively correlated (-0.955). Factor 2 has total varians of 10.96% and considerable contributions from Co, Mn and Pb may be due to industrial/re-suspension.

Backward trajectories of Bangi showed that the trajectories mostly start over from the Pacific Ocean and directly move westward through the South China Sea, passing the Sulu Sea before arriving to the south of Klang Valley (Bangi). Based on its pathway and origin, this air mass is expected to bring in relatively clean air from the Pacific Ocean to Klang Valley. Meanwhile, backward trajectories of Petaling Jaya showed that most of the wind came from the Malacca Straits during southwest monsoon. Peninsular Malaysia has been affected by severe smoke haze due to forest fires in the region periodically. With its pathways above the populated areas, and short passages over the sea, these air masses have a potential to bring in the long-range transport air pollution to the Malaysia.

The non-carcinogenic risk assessment in terms of Hazard Quotient (HQ) and Hazard Index (HI) were calculated according to exposure to particulate bound metals. Based on the result, it was found that inhalation is an important pathway of for exposure to trace elements in the circumstance of particulate matter in Bangi and Petaling Jaya. HQ for non-cancer risk due to dermal contact of particulate matter is in lower magnitude and it is unlikely that this exposure route would pose a higher risk than inhalation. For both sampling location Bangi and Petaling Jaya, the same trend of result was observed. Inhalation of particles appeared to have much higher risk for Cr, Co and Mn, which were one to three orders of magnitude higher than the corresponding risks of the dermal exposure route. In contrast for Cr compared to other

elements, dermal contact showed some tendency to be the main exposure route that might results in some risk. Regarding non-cancer effects, all trace elements exhibit Hazard Index lower than safe level (1). In comparison to the children and adult cases, the inhalation and dermal exposure route has higher values for children than that for adult and hence the overall values of risk are higher than adult.

For cancer risk, the only carcinogen risk for inhalation exposure model was considered. In this study, the incremental lifetime cancer risk (ILCR) for Cr, Pb, Cd, Ni, and Co was calculated the see the probability getting cancer from the exposure of ambient atmospheric particulate matter. Cr has the highest ILTCR values among all the carcinogens. In Bangi, the estimate Cr risk values for adult were $3.50\text{E-}05$ (coarse mode) and $5.19\text{E-}05$ (fine mode); while for children the values were $1.26\text{E-}05$ (coarse mode) and $1.87\text{E-}05$ (fine mode). Similarly, the Cr ILTCR values in Petaling Jaya for adult were $1.01\text{E-}05$ (coarse mode) and $1.33\text{E-}05$ (fine mode); as for the children were $3.65\text{E-}06$ (coarse mode) and $4.78\text{E-}06$ (fine mode). Therefore, it can be confirmed that exposure to Cr is quite a serious problem in respect for both adult and children population in Bangi and Petaling Jaya.

The risk assessment suggested that that there was an acceptable potential adverse health effects for adult and children in both localities (Bangi and Petaling Jaya) caused by particulate metals except for Cr. Although generally probability developing cancer risk is low, it was thus clear that the exposure of resident lived nearby study area to the coarse and fine particles with toxic contents should be of special concern for certain trace elements.

CHAPTER 5

DETERMINATION OF TRACE ELEMENTS IN WHOLE BLOOD

5.1 INTRODUCTION

Minerals are inorganic substances, present in all body tissues and fluids and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life. Minerals are chemical constituents used by the body in many ways. Although they yield no energy, they have important roles to play in many activities in the body (Malhotra, 1998). Every form of living matter requires these inorganic elements or minerals for their normal life processes (Ozcan, 2003). Minerals may be broadly classified as macro (major) or micro (trace) elements. The macro-minerals include calcium, phosphorus, sodium and chloride, while the micro-elements include iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulfur (Soetan et al., 2010). The macro-minerals are required in amounts greater than 100 mg/dl while the micro-minerals are required in amounts less than 100 mg/dl (Murray et al., 2000).

As a result of human exposure to the environment, the elements appearing in the body can be harmful to it and may disturb its functioning. Therefore, the knowledge of the content of various elements in the human body can be helpful in determining its condition. Determination of element concentration is performed in many investigations. Consequently, many physical and chemical methods have been used to determine the concentration of elements in human biological materials.

At present, mainly sequential single element determination techniques are common in investigating body fluids and tissues. More information from these samples could be obtained by using simultaneously multi-element techniques which offer several advantages as suggested by Prange et al., 1989; 1) trace element metabolic interactions may be revealed in disease; 2) unsuspected nutritional depletions may be detected, if a trace metal profile can easily be obtain; 3) smaller volumes of samples, e.g. of blood and tissue, are required which is especially important in medical studies; 4) more economy in time and sample material.

5.2 PRINCIPLE OF TOTAL REFLECTION X-RAY FLUORESCENCE (TXRF) SPECTROSCOPY

Total reflection X-ray fluorescence (TXRF) spectroscopy which is a special modification of energy dispersive X-ray fluorescence (ED-XRF) spectroscopy has gained very big importance for the determination of elements with the atomic number of larger than 11 in the last two decades. In this new design, the sample is placed over the specific sample holder containing smooth surface and a reflector. The beams emitted from X-rays tube are felt over the sample holder with very small angle; therefore almost all of the beams are reflected. Only the sample atoms from the sample holder and emitted fluorescence beams can be reached to the energy dispersive detector, which placed in a vertical position according to the sample holder. Hence, the determination capacity of the system is increased 100-1000 times according to the classical XRF technique. In addition, it is possible to place a few μ l solution or a few mg solid sample over the sample holder, therefore this technique can be used both in microanalysis and trace analysis (Klockenkaemper et al., 1992).

The instrumentation of TXRF is relatively simple in comparison with that of other modern methods of spectroscopy. An excitation unit containing a high voltage generator, an X-ray tube, a total reflection module, a detection unit with semiconductor detector and a multi channel analyser are needed. The operation, the study, the preparation and the enthusing of sample are fairly simple and the operation costs are reasonable. In total reflection X-ray fluorescence (TXRF) analysis, the main principle is based on the excitation of characteristic X-rays in the sample produced by radiation from X-ray tube. In the process of atom radiation interaction, an inner shell electron from an atom in the sample is removed. Such an ionized atom constitutes an unstable system.

Another electron from the outer shell fills a hole and in accordance with the principle of conservation of energy, a photon is emitted. The Moseley law says that its energy is proportional to the atomic number of the atom. Therefore these photons are called characteristic radiation and it allows the identification of element. The main advantage of this method is the possibility to analyze several elements simultaneously in a short time (100 s -1 h) and a small quantity of material is enough for analysis (μl - mg). This makes the TXRF method competitive with chemical methods (Majewska et al., 2014).

TXRF differs from conventional ED-XRF mainly in the excitation geometry. A flat primary X-ray beam is generated by a high power X-ray tube (Mo or W) with a line focus, is filtered by a thin metal foil and sheet like shaped a pair of precisely aligned slits. The polychromatic beam is deflected by a first reflector with may be a simple quartz glass mirror. The primary spectrum is simplified and more or less monochromatized. After passing the first reflector, primary beam hits the sample-carrier as a second reflector under grazing incidence. It is totally reflected here under glancing angle of only 0.1 degree. If loaded with some amount of sample material, the atoms within the sample effectively excited to X-ray fluorescence. Figure 5.1 shows a scheme of the TXRF principle.

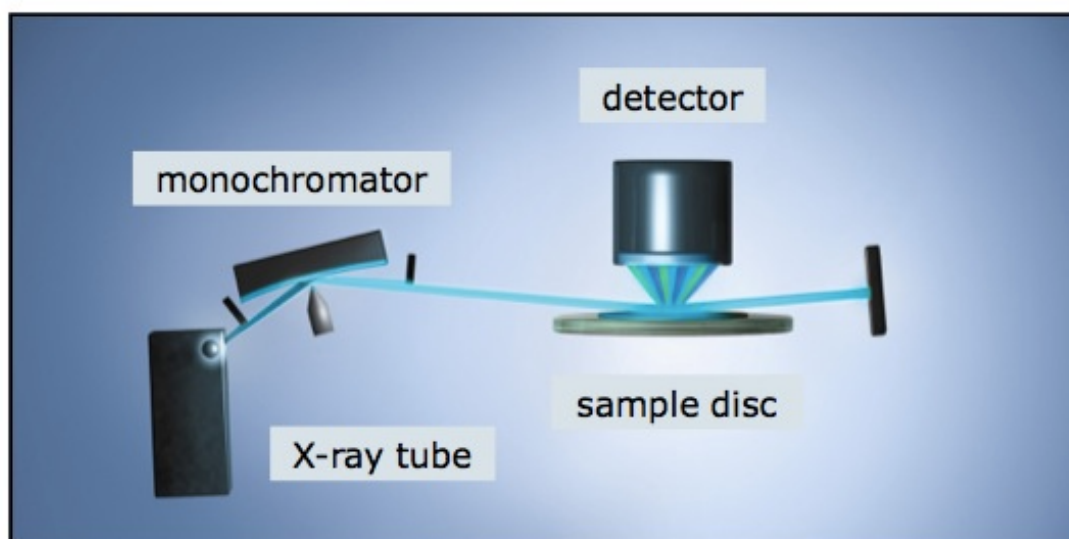


Figure 5.1 Scheme of the TXRF principle

In general all elements starting from Sodium up to Uranium (excluding Niobium, Molybdenum and Technetium) can be analyzed by the TXRF. The analysis of TXRF is based on internal standardization. Therefore, an element, which is not present in the sample, must be added for quantification (Figure 5.2).

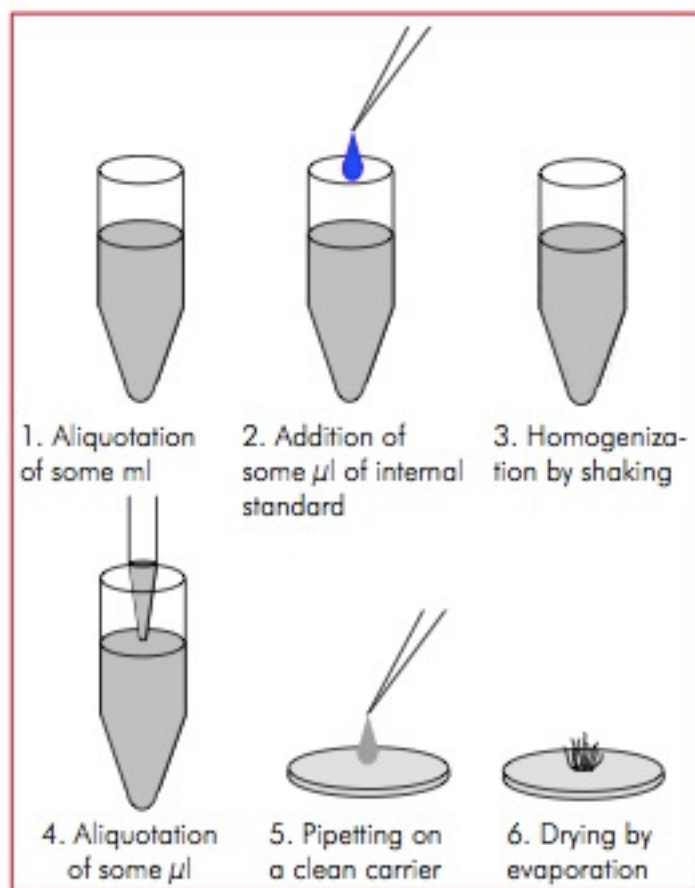


Figure 5.2 Steps for the TXRF analysis of liquids

5.3 METHODOLOGY

5.3.1 Samples Collection

In this study, whole blood samples were obtained among pregnant women who are receiving antenatal care at the Department of Obstetrics & Gynecology University Malaya Medical Center, Kuala Lumpur. The procedures for the study were explained to the participants after whom oral informed consents were obtained. The protocol for the study has been approved by the Ethics and Research Committee of University Malaya Medical Center, Kuala Lumpur. The study is conducted in accordance with this protocol, relevant in house Standard Operating Procedures (SOPs), Malaysian Guidelines for Good Clinical Practice and 'Declaration of Helsinki'. The whole blood was collected once at recruitment during 8:00 – 10:00 hours into EDTA tube to prevent blood samples from coagulation. The whole blood was transported to the laboratory and stored in a freezer at 20°C prior to analysis.

5.3.2 Instrumentation

TXRF measurements were performed by Nanohunter (Rigaku) Benchtop TXRF system. The primary X-rays were generated by an air-cooled low power X-ray tube using a molybdenum anode. The excitation settings were 50 kV and 750 mA. Measurements were performed by signal integration over 1000 s. Quartz glass disks were used as sample carriers. They were cleaned in 1 mol L⁻¹ nitric acid followed by water flushing and dried. The quantification of the analytes is performed by the Nanohunter software and quantification is based on the known quantity of the internal standard vanadium.

5.3.3 Direct Sample Preparation

As the high content of organic matrix would prevent the preparation of an ideal thin layer sample, the samples must be diluted with ultrapure water before preparation. The dilutions, which offer the optimum for preparation and traceability of the elements, were found to be whole blood and H₂O of 1:1. Internal standardization was done by adding a Vanadium solution. To evaluate faster preparation without any digestion, 60 μ L of whole blood were diluted with 60 μ L of ultrapure water (MiliQ Water). This treatment led to the disruption of blood cells by osmotic shock and an almost homogenous suspension for direct preparation on sample carrier. The samples were vortexed and 30 μ L of vanadium were added for internal standardization.

An additional preparation step of crucial importance was found to be the drying process of the sample on the carrier. In general, drying by means of heating plates or vacuum did lead to insufficient results. After applying these preparation techniques, the samples were formed irregularly, in many cases ring-shaped specimens with a low adhesion on the sample carrier. An aliquot of 20 μ L were transferred to a quartz glass sample and subsequently dry the sample in a laboratory oven at temperatures of approximately 50°C. After drying, the sample carriers were inserted into the TXRF instrument and analyzed with an integration time of 600 s each.

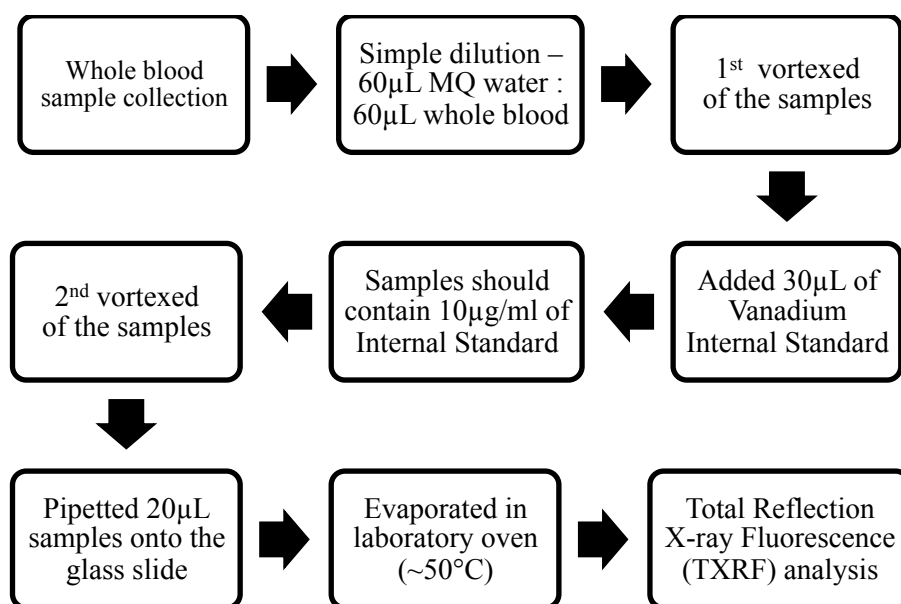


Figure 5.3 Method of analysis

5.4 RESULT AND DISCUSSION

5.4.1 X-ray Spectrum

Figure 5.4 shows a section of TXRF of the human whole blood. The spectrum displayed the intensity of trace elements such as Sulphur (S), Chlorine (Cl), Copper (Cu), Potassium (K), Calcium (Ca), Vanadium (V), Iron (Fe), Zinc (Zn) and Bromine (Br) against the energy emitted.

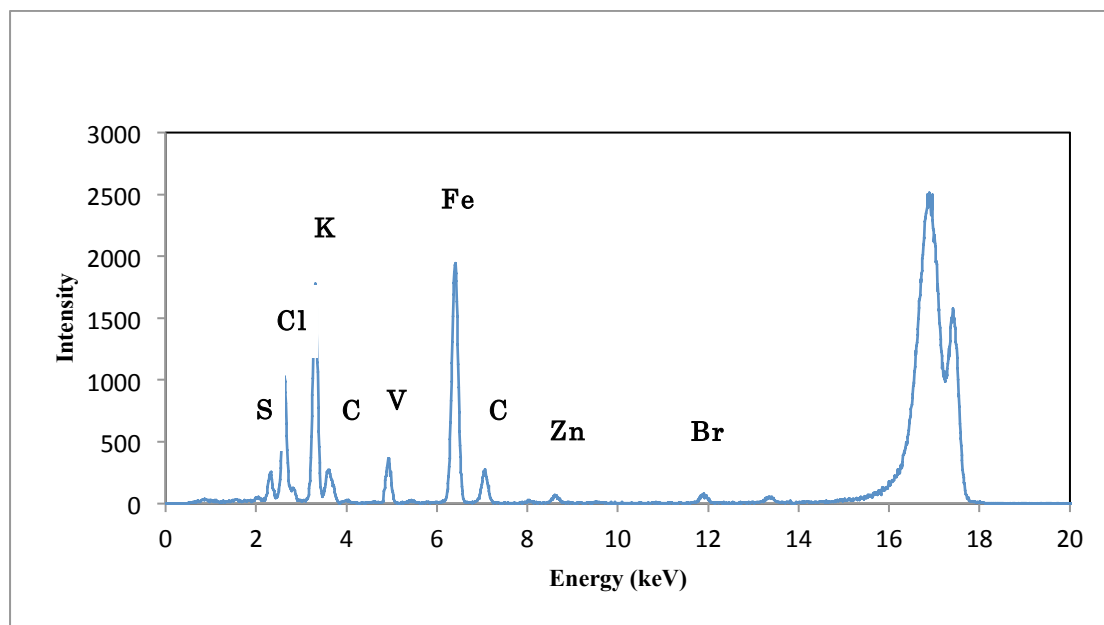


Figure 5.4 X-ray spectrum

5.4.2 Trace Elements in the Whole Blood

Pregnancy is a period of rapid growth and cell differentiation for both the mother and fetus. Consequently, it is a period during which both are vulnerable to changes in dietary supply, especially of those micronutrients that are marginal under normal circumstances. Essential trace elements are involved in various bio-chemical pathways (Mertz, 1981). Their specific and the most important functions are the catalytic role in chemical reactions and in structural function in large molecules such as enzymes and hormones (Black, 2001). Alterations in concentrations and homeostasis of each of these micronutrients in body are well-known contributors in pathophysiology of various disorders and disease (Noura et al., 2014).

It was possible to determine the elemental of S, K, Ca, Fe, Cu, Zn and Br from the sample analysis. The distribution of concentrations data for whole blood samples from 21 pregnant women at University Malaya Medical Center using TXRF is displayed in Figure 5.5. The box plots are enable to show the distributional characteristic of data in the group of trace elements. They include the display of median concentrations and also the range of upper and lower quartile.

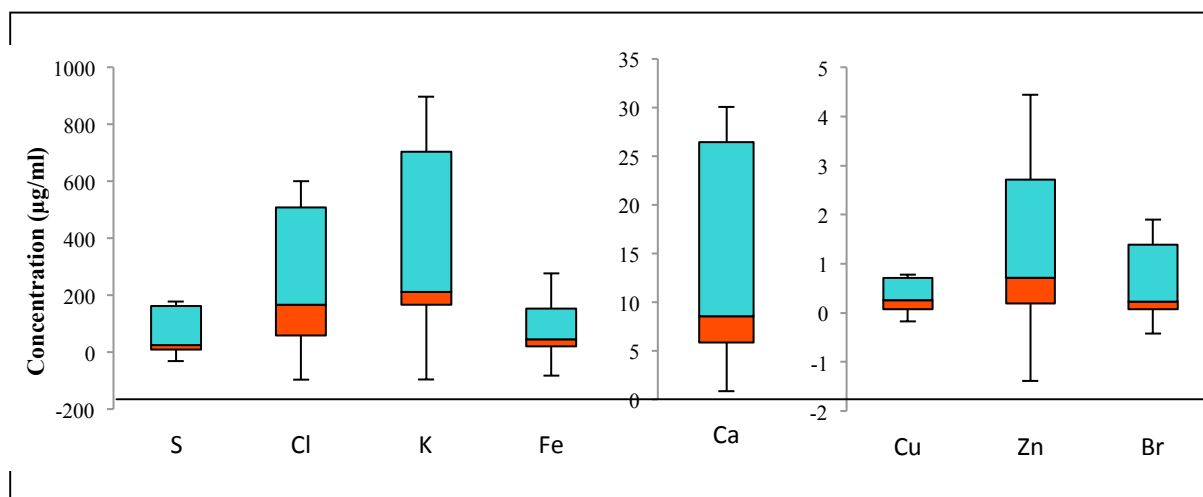


Figure 5.5 Box plots of whole blood concentrations using TXRF

Table 5.1 shows the X-ray fluorescence spectrum of whole blood samples from pregnant women at University Malaya Medical Center using TXRF. Since this study did not have the control sample for non-pregnant women, the concentrations obtained were compared to concentrations ranges given in the literature (Prange et al., 1989; Martinez et al., 2004).

Table 5.1 TXRF result in whole blood in comparison with concentrations given by literature value

Element	Range, µg/ml (Min – Max)	Mean (µg/ml)	Literature value, µg/ml (Prange et al., 1989; Martinez et al., 2004)
S	(95.659 - 176.912)	147.026 (±20.413)	1680-1930
Cl	(183.324 – 599.241)	427.845 (±112.434)	-
K	(229.675 - 897.029)	553.571 (±158.908)	1450-1920
Ca	(11.816 - 30.079)	21.041 (±5.354)	57.5-78.0
Fe	(6.219 - 276.758)	133.767 (±67.575)	301-530
Cu	(0.198 - 0.783)	0.558 (±0.184)	0.64-1.28
Zn	(0.411 - 4.446)	2.334 (±1.049)	4.8-9.3
Br	(0.659 - 1.900)	1.278 (±0.300)	1.7

From the TXRF analysis, no unusual toxic elements have been found in this study that could be due exposure from various environmental pollutants. Only important trace elements that are micronutrients required in the body for its normal function especially through various enzymes, hormones, vitamins etc. where found in the pregnant women in the present study.

It is well established that physiologic, metabolic, and hormonal changes during pregnancy affect the metabolism and body needs for micronutrients and minerals. Deficiency or decreased levels of various minerals and trace elements, such as iron, zinc, and copper, have been shown to be associated with many complications related to pregnancy outcome (Black, 2001; Ladipo, 2000).

As shown in the Table 5.1, whole blood zinc for pregnant women were significantly lower than the literature review value is probably due to several factors, such as increased zinc uptake by the fetus and placenta, increased transfer plasma zinc to maternal erythrocytes, expanded plasma volume, and decreased serum albumin availability for zinc binding during pregnancy (Vir et al., 1981). In addition, zinc transporters such as ZnT that are localized in placenta may play important role in accelerating zinc uptake from the mothers' blood to the developing fetus (Cousins et al., 2000).

Finding pertaining to the copper in whole blood in this study was in close agreement with the results by the literature. During pregnancy, copper level usually higher due to developing babies depends on copper during and beyond pregnancy (Al-Jawadi & Bashi, 2013). Mothers' bodies stock up on the mineral during the final trimester of pregnancy to ensure that copper is available after birth to carry out many metabolic functions. Copper is critical for the optimal formation of a child's brain and nervous system, it is responsible for production and maintenance of myelin, the material that surrounds and protects nerve and brain cells. Copper also plays a role in making neurotransmitters, chemical messengers that foster communication between nerve cells (Al-Jawadi & Bashi, 2013).

A lower concentration of iron was also found compared to the literature value might suggests iron deficiency due to nutritional deficiencies intake of iron and folate during pregnancy. Iron is a primary component of hemoglobin, the part of the blood that supplies mother's cells and baby's cells with oxygen. Iron deficiency anemia during pregnancy is associated with preterm delivery, low birth weight and infant mortality. It is known that the fetus receives iron indirectly from the maternal circulation through a rapid and unidirectional process. Maternal iron is transported to the placenta bound to a protein, maternal transferrin. However this maternal transferrin does not cross the placenta. Hence, the iron will be transferring to placental receptors. Iron then binds to a protein with the same structure, fetal transferrin, and is transported through the bloodstream to fetal tissues (Paiva et al., 2007). In general, iron-related hematological and biological parameters are markedly higher in umbilical cord than maternal blood (Rondo et al., 1995).

In the present study shown that whole blood calcium was 21.041 ± 5.354 ug/mL, which was lower than the literature value. It appears that a significant fall in total calcium occurs in normal human pregnancy when there is also an increased fetal demand and perhaps also a relatively insufficient maternal intake and/or intestinal absorption (Singh et al., 1999). On the other hand, Moheildein et al., (2007) suggests that the low level of maternal total calcium may have a role in the development pregnancy induced hypertension (PIH). The protective effect of calcium on blood pressure can be explained in part by the influence of calcitrophic hormones on intracellular calcium. 1, 25-dihydroxyvitamin D stimulates calcium influx in a variety of cells, including vascular smooth muscle cells. Consequently, low calcium diets, which elicit a 1, 25-dihydroxyvitamin D response, would be expected to increase blood pressure. Therefore, calcium consumption during pregnancy should be encouraged.

Similarly, lower concentration of potassium in whole blood was observed in pregnant women compared to the literature value. Dietary potassium restriction increases both systolic and diastolic blood pressure in subjects with mild essential hypertension (Krishna & Kapoor, 1991). Several factors seem to play a role in mediating the hypertensive effects of potassium depletion. Sodium retention is consistently associated with potassium depletion (Krishna et al., 1989). Sodium retention increases blood pressure by increasing extracellular fluid volume, by altering the pressure-natriuresis relation. Pressure-natriuresis is a phenomenon that increases in arterial pressure would elevate sodium excretion (Hall et al., 1990). In addition, because part of the retained sodium replaces the potassium lost from cells, intracellular sodium concentration must increase during potassium depletion. It was also found that potassium depletion increases urinary excretion of calcium and phosphorus (Krishna & Kapoor, 1991).

Bromine was discuss here as borderline essential element, provided that bromine growth effects have been tested in experimental animals even though it has not been conclusively shown to be involved in any essential function (Martinez et al., 2004; Versieck & Cornelis, 1980). Furthermore, bromine level is considered to be dependent on dietary habits, geographical and environmental factors as well.

5.5 CONCLUSION

Several whole bloods were analyzed by means TXRF after simple dilution. It can be concluded analysis of the nutrition relevant elements by simple dilution with ultrapure water is sufficient. TXRF has advantage of simple quantification of the data by internal standardization since no standard addition or external standards are necessary.

Result from TXRF analysis of blood found no unusual toxic elements that could be due to exposure from various environmental pollutants. Only important trace elements that are categorized as micronutrients required in the body for its normal function such as zinc, copper, calcium and other elements were found in the present study. These trace elements have significant influences on the health of pregnant women and growing fetus. Based on the result, it can be concluded that exposure of pregnant women in Kuala Lumpur from environmental pollutants still in the safe limit.

CHAPTER 6

PAHs COMPOSITION IN ATMOSPHERIC PARTICULATE MATTER

6.1 INTRODUCTION

Particulate matter (PM) air pollution has been linked to increased morbidity and mortality rates, as well as adverse health effects such as respiratory and cardiovascular diseases (Ostro et al., 2007; Pope III et al., 2004). Particles with aerodynamic diameters less than $2.5\mu\text{m}$ ($\text{PM}_{2.5}$) received great attention because, when inhaled, such particles can penetrate and deposit deep in the bronchioles and alveoli of the lungs. In addition, the association of fine particles with mutagenic and carcinogenic chemicals (PAHs) may increase the health effects of such particulates. Polycyclic aromatic hydrocarbons (PAHs) are semi volatile organic compounds and are an important pollutant group because they are toxic organic compounds commonly found in the urban environment (Herngren et al., 2005). Although there are more than hundred different PAHs in the environment, USEPA (1999) found that 16 PAHs are particularly toxic to environmental and human health.

In ambient air, PAHs with 2-3 aromatic rings exist almost exclusively in the gaseous phase, while compounds with 4 or more aromatic rings are primarily associated with the particulate fraction (Eiguren-Fernandez et al., 2004; Re-Poppi & Santiago-Silva, 2005). In addition, it has been reported that particulate PAHs bound predominantly to fine particles, especially in areas with heavy traffic (Cancio et al., 2004; Duan et al., 2005). Because carcinogenic PAHs (e.g. benzo[a]pyrene and benz[a]anthrene) are mostly associated with particulate matter, many studies on PAHs in ambient air have focused on PAHs bound to PM, particularly $\text{PM}_{2.5}$ (Ohura et al., 2004; Bourotte et al., 2005; Sanderson et al., 2004).

6.2 METHOD OF EXTRACTION

6.2.1 Solid Phase Extraction (SPE)

Solid Phase Extraction (SPE) is a sample treatment technique in which a liquid sample was passed through a sorbent. Both the analytes to be determined and the interferences of the samples are retained on the sorbent by different mechanisms. In the first case, the analytes are eluted in a small volume of a solvent; in order to make the analytes to become more concentrated. Consequently, the function of the solid-phase extraction in the second case is to clean the sample. The first case is mainly used for liquid samples; while the second case is for solids, gases or liquids; usually after another sample-treatment technique. Thus, SPE is extremely versatile in the sense that it can be applied to a wide range of samples (Marce & Borruall, 2000).

Time is also another important parameter that must be taken into account considering the huge number of samples collected in environmental studies. SPE saves substantial amount of time. If the sample is not loaded heavily with particles, extraction of a sample does not exceed 1 hour which is one day in the case of Soxhlet Extraction. Considering the trace amount (ng/L) of analytes present in environmental matrices, SPE is very advantageous since it is possible to enrich analytes 1000 times or more.

It is always desirable to extract the samples in situ to avoid decomposition or losses of samples during transport. Samples can be eluted even extracted in the field using SPE. However, it is not always possible to maintain all the laboratory equipment in the field; in that case samples can be eluted through SPE disks or cartridges and brought to laboratory for further steps and analysis. The studies have shown that organics retained on SPE disks or cartridges are stable over 30 days as long as they are stored in dark and cold place.

6.2.2 SPE Procedure

SPE can be used off-line (i.e., the sample preparation is completely separated from the subsequent chromatographic analysis) or online (i.e., it is directly connected to the chromatographic system). In off-line methodologies, samples are treated through a sorbent packed in disposable cartridges or asserted on an inert matrix of a membrane-based extraction disk (Hennion & Pichon, 1994). A typical off-line SPE sequence for cartridges is described below in Figure 6.1. All the procedural steps are same for the SPE disks. In order to show the procedure schematically, cartridges are preferred because of their visual easiness. The SPE procedure can be divided into four main steps: conditioning, application of sample, removal of interferences and water (rinsing) and elution of the sorbed analytes.

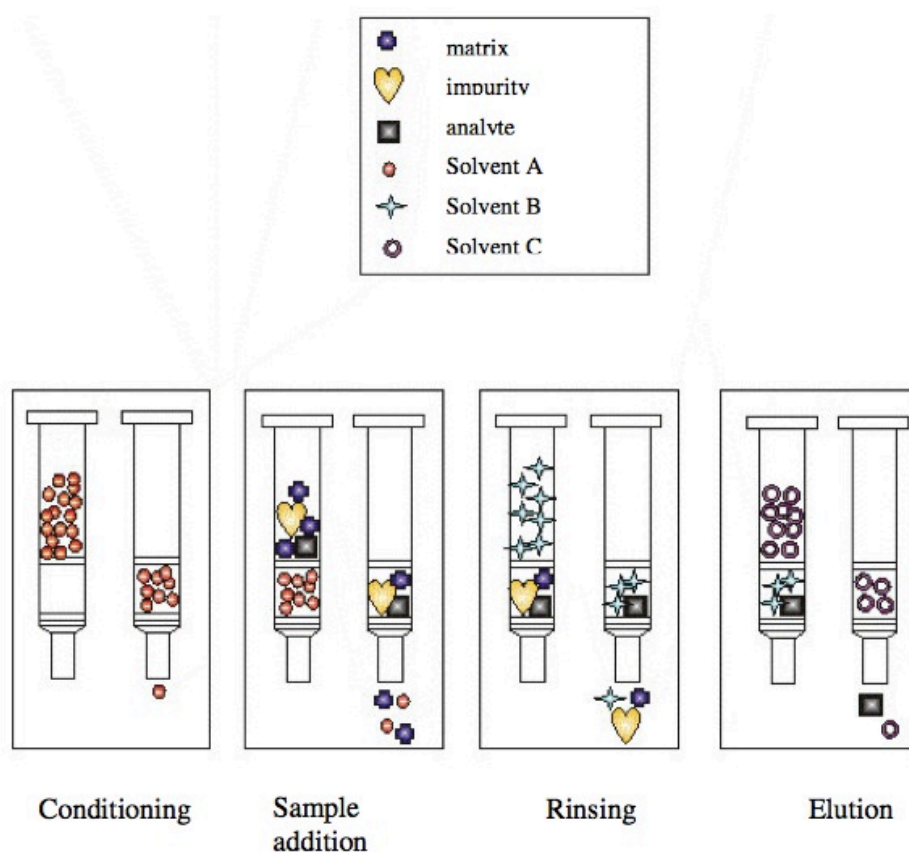


Figure 6.1 Schematic view SPE procedure

Conditioning is usually necessary to prepare the SPE column or disk for the extraction process. For retention of analytes to occur, the bonded phase must be able to interact with the sample matrix. In the dry form of C-18 sorbent, the C-18 chains tend to be coiled up. After application of solvent, these chains will uncoil as shown in Figure 6.2 (Fritz,1999).



Figure 6.2 Activation of C-18 chains with organic solvent

6.3 METHODOLOGY

6.3.1 Sampling Site

In this study, Bangi was chosen to represent a semi urban area. The sampling location is located at Universiti Kebangsaan Malaysia, Bangi Campus, in the state of Selangor, Malaysia; which is about 25km south of Kuala Lumpur's city center. Samples were collected in June (21st – 27th Jun 2013) and July (23rd- 29th July 2013) respectively. Bangi is considered as semi urban with a large number of residential areas. The development of the administrative area of Putrajaya, educational centres and several small medium industrial areas around Bangi has lead to a large increase in traffic volume around Bangi. Since Bangi itself is located south and downwind Kuala Lumpur, therefore it is influenced by the plume from Kuala Lumpur's city centre during the northeast monsoon (January-March).

6.3.2 Sample Acquisition

Aerosol samples were collected using PM_{2.5} high volume sampler (HVS) (Thermo Fisher). The HVS was fitted with fiberglass filter paper for collection atmospheric particulate matter. All the filter paper were packed in aluminium foil and heated at 500°C in a muffle furnace for 4 hours prior to use in order to pyrolyze and thus remove any adsorbed organic materials. After sampling, all fresh and exposed filter papers were placed in desiccators for 24 hours before being weighed with an electronic balance and stored in a refrigerator (4°C) until analysis. The sampling was carried out for 24 hours with a flow rate of 1.13m³/ min.

6.3.3 Sample Extraction and Fractination

A. Ultrasonication Extraction

The fiber glass filter papers were cut into pieces and be put into 15mL centrifuge tube. 10mL of Dichloromethane (DCM) were added respectively. The tubes were then sonicated in ultrasonic bath for 10 minutes. The tubes were shaken to remove any gasses. The filters were extracted three times. The extraction solutions were then centrifuged at 3000 rpm for 10 minutes and the supernatant around 5mL were put into tubes. The extracts were further reduced to 200ul using Nitrogen gas and the DCM is replaced with 800ul of n-hexane. These processes were repeated 3 times.

B. Fractination

InertSep C18 500mg/6mL Cartridge were conditioned with 5mL methanol and 10mL ultrapure water to prepare the column for the cleaning up process. 1mL of the extraction solution was loaded through each cartridge under gentle vacuum. The extraction tubes were rinsed by 5mL of ultrapure water and loaded through the cartridge. The column cartridges were dry up with vacuum for 10 minutes to remove any excess water. The cartridges were sequentially eluted with 5mL of methanol at flowrate of 1 mL/min. The elutes were then collected into 15mL centrifuged tubes and were gently evaporated under Nitrogen gas to 200ul. 25ul of internal standard were added into the elutes. Finally, the elutes were reconstituting with Toluene until up to 0.5mL.

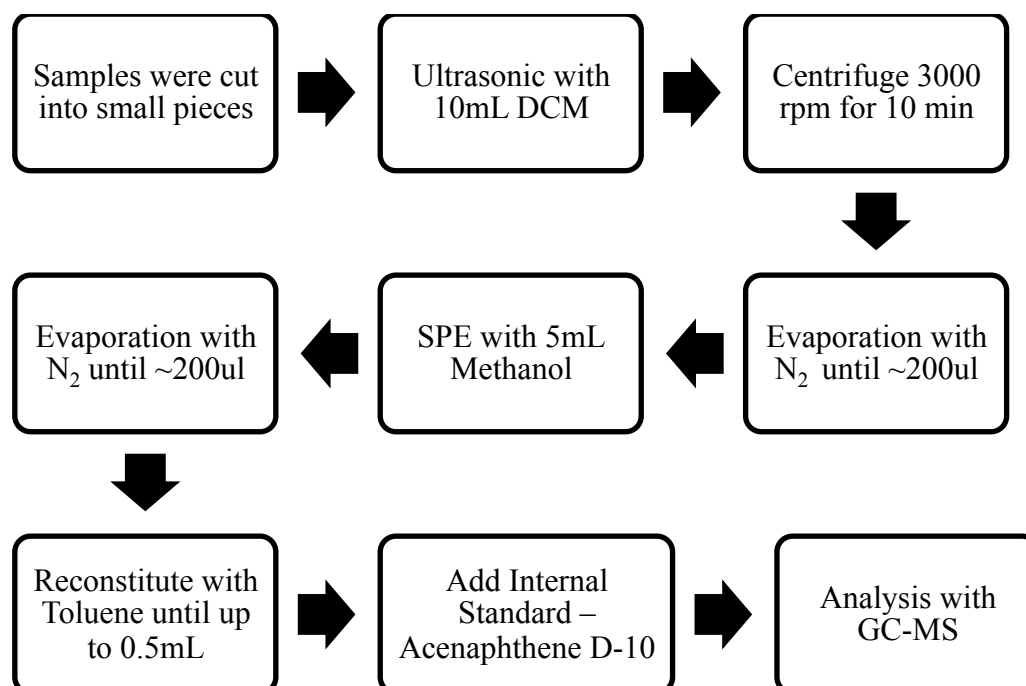


Figure 6.3 Diagram of PAHs extraction

6.3.4 Sample Analysis

The analysis were carried out on a Gas Chromatography 17A coupled with QP 5050A. Method development was to detect all target PAHs with a uniquely identifiable peak in the chromatogram. It was found that temperature programming was one of the most important methods to achieve good separation of PAHs. Injection port temperature was set at 230°C. Several temperature programs were experimented to obtain the best resolution of PAHs and the one given in Table 6.1 was found to be optimum and later used for determination of PAHs in atmospheric particulate matter.

Table 6.1 Operating conditioned of GC-MS for PAHs analysis

GC-MS	GC-MS 17A –QP 5050A
Column	DB-5 ms (Length 30 m, thickness 0.25 μ m, diameter 0.25 mm)
Inlet mode	Splitless
Column oven temperature	90°C (2 min) $\rightarrow$ (5.0 °C/min) $\rightarrow$ 310 °C (12min)
Carrier gas	Helium
Control mode	Constant linear velocity (54.8 cm/sec)
Column Injection Pressure	150 kPa
Injection rate	1.0 μ L
Interface temperature	300°C
Injection temperature	230°C
Solvent cut time	3.5 min
Measurement mode	SIM
Sampling time	1.5 min
Programmed time	60 min

SIM mode improves sensitivity by limiting the mass of the ions detected to one or more specific fragment ions of known mass. As a consequence, it is highly selective and eliminates a large portion of the noise inherent in full scan detection mode. The most popular method of spectral interpretation and identification remains the comparison of sample spectra with collections of reference spectra (Ragunathan et al., 1999). The presence of a target compound was established when two criteria were met. The first criteria are the retention time; while the second criteria are the ratios of the ions monitored. The retention time of the compound in the sample should match with the retention time in the standard. In addition, the ion ratios of the compound in the sample should be the same with the one in the library database spectra (Table 6.2).

Table 6.2 Quantitation ion and retention time for PAHs

	Abbreviation	Quantitation Ion (m/z)	Retention Time (min)
Naphthalene	NAP	128.2	6.1
Acenaphthylene	ACY	152.1	12.1
Acenaphthene	ACE	154.1	12.9
Fluorene	FLU	166.2	13.0
Phenanthrene	PHE	178.2	15.3
Anthracene	ANTH	178.2	19.8
Fluoranthene	FLA	202.3	20.0
Pyrene	PYR	202.3	25.6
Benzo(a)anthracene	B(a)An	228.3	26.6
Chrysene	CHR	228.3	32.6
Benzo(b)fluoranthene	B(b)Fl	252.3	32.8
Benzo(k)fluoranthene	B(k)Fl	252.3	37.6
Benzo(a)pyrene	B(a)P	252.3	37.7
Indeno(1,2,3-cd)pyrene	InPy	276.3	38.9
Dibenz(a,h)anthracene	DiB(a,h)An	276.3	43.2
Benzo(g,h,i)perylene	B(ghi)P	276.3	44.1

6.4 RESULTS AND DISCUSSION

6.4.1 PAHs in Atmospheric Particles

The concentration of PAHs in association with airborne particles was investigated during a haze period of June 2013 and July 2013 in Bangi, Selangor. The analysis of PAH was performed on samples of PM_{2.5}, which is recognized to be more appropriate indicator of adverse health effects than total suspended particles. The gas phase was not investigated because higher molecular weight PAHs, like target PAHs concerned in this study are present in air almost exclusively as particle bound compounds.

The limit of detection (LOD) and limit of quantification (LOQ) are terms used to describe the smallest concentration of an analyte that can be reliably measured by an analytical procedure. The LOD and LOQ obtained were listed in Table 6.3. Meanwhile the recovery of multi-step procedure for PAHs is listed in Table 6.4. The recovery rates of these compounds ranged from 70% to 97%. Atmospheric particles were spiked with Anthracene –d10 and the recovery was found to be 95%. Appropriate corrections were made to the measured concentrations. Due to their recoveries and poor reproducibility; Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), and Anthracene (ANTH), could not be accurately identified by this method.

Table 6.3 LOD and LOQ for calculated PAHs

PAHs	LOD (ng/ml)	LOQ (ng/ml)
NAP	5.0	16.7
ACY	0.3	1.1
ACE	0.2	0.6
FLU	1.4	4.7
PHE	0.1	0.5
ANTH	0.7	2.4
FLA	1.7	5.7
PYR	2.8	9.3
B(a)An	1.7	5.5
CHR	1.0	3.2
B(b)Fl	4.0	13.5
B(k)Fl	1.7	5.8
B(a)P	3.9	13.0
InPy	28.2	94.1
DiB(a,h)An	23.5	78.2
B(ghi)P	48.1	83.9

Table 6.4 Recovery rate for PAHs during the study

PAH	Relative Molecular Weight	Rings	Carcinogenic Potency*	% Recovery
Fluoranthene	202.26	4	D	75%
Pyrene	202.26	4	D	79%
Benz[a]anthracene	228.3	4	B2	79%
Chrysene	228.3	4	B2	70%
Benzo[b]fluoranthene	252.32	5	B2	91%
Benzo[k]fluoranthene	252.32	5	B2	72%
Benzo[a]pyrene	252.32	5	B2	81%
Dibenz[a,h]anthracene	278.35	5	B2	83%
Benzo[ghi]perylene	276.34	6	D	89%
Indeno[1,2,3-cd]pyrene	276.34	6	B2	97%

* US EPA carcinogenic classification 16

B2: Probable human carcinogen; D: Not classifiable as to human carcinogenicity

The data of PAHs concentrations in June and July obtained in this study were presented using box plots in Figure 6.4 and 6.5. In these figures, the box represents the distribution of 25% - 75% (lower quartile and upper quartile), inter-quartile range (50%) and median of the concentrations values. In addition, the upper and lower whiskers also correspond to the minimum and the maximum value of the PAHs concentrations during the sampling period.

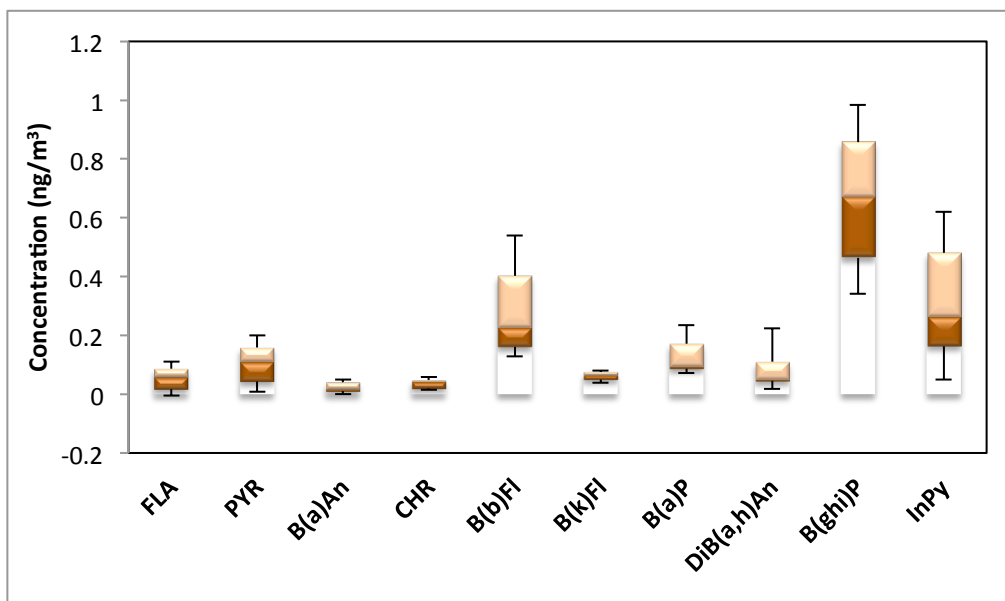


Figure 6.4 Box plots of PAHs concentrations in June

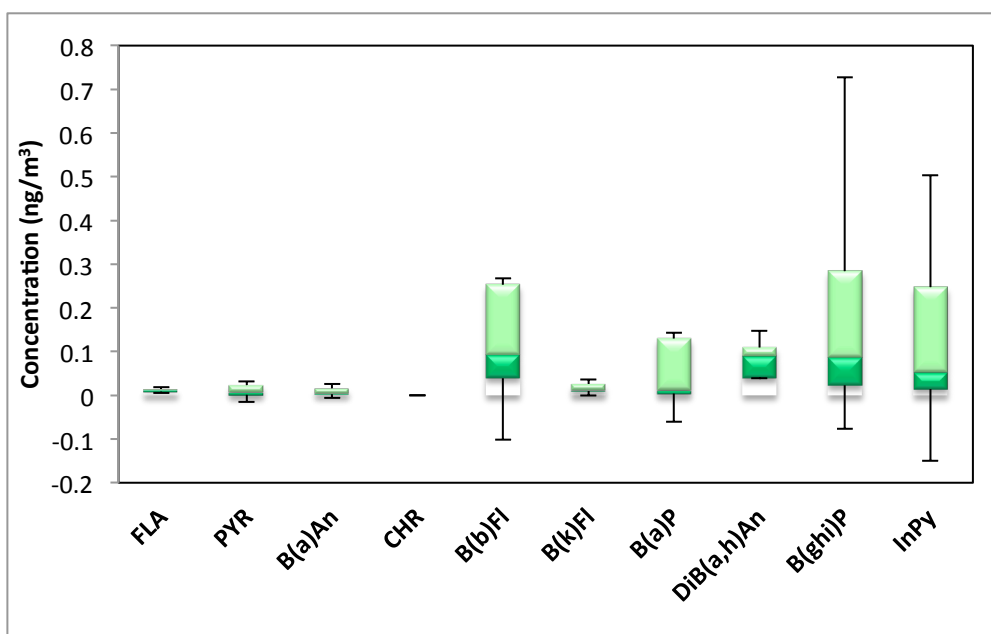


Figure 6.5 Box plots of PAHs concentrations in July

Polycyclic aromatic hydrocarbons can be formed by the thermal decomposition of many organic materials containing carbon and hydrogen. There are two main mechanisms in the formation of PAHs: (1) hydrolysis and incomplete combustion, and (2) carbonization process. The average concentrations (ng/m³) of the 10 PAHs identified in this study are displayed in Table 6.5 for month of June and July. The average Σ PAH concentrations for June and July were recorded at 1.63 $\pm$ 0.16ng/m³ and 0.99 $\pm$ 0.11ng/m³; respectively. It can be seen that the Σ PAH concentrations in June was higher than July, with a total difference of 0.64ng/m³ between the two months. This finding could be caused by an impact of first haze episode in June, which was the peak of haze in Malaysia; together with the influences of localize emission from motor vehicles.

Table 6.5 Mean ($\pm$ SD) PAH concentrations and percentage of total PAH

Month	PAHs Compound	Mean $\pm$ SD (ng/m ³)	% of Total PAH
June	Fluoranthene	0.06 $\pm$ 0.04	2.2
	Pyrene	0.11 $\pm$ 0.07	4.1
	Benz[a]anthracene	0.03 $\pm$ 0.01	1.2
	Chrysene	0.04 $\pm$ 0.03	0.9
	Benzo[b]fluoranthene	0.30 $\pm$ 0.17	11.4
	Benzo[k]fluoranthene	0.05 $\pm$ 0.04	1.5
	Benzo[a]pyrene	0.13 $\pm$ 0.07	4.8
	Dibenz[a,h]anthracene	0.09 $\pm$ 0.07	3.6
	Benzo[ghi]perylene	0.51 $\pm$ 0.39	19.3
	Indeno[1,2,3-cd]pyrene	0.35 $\pm$ 0.19	13.3
	Σ	1.63 $\pm$ 0.16	62.3
July	Fluoranthene	0.01 $\pm$ 0.01	0.3
	Pyrene	0.02 $\pm$ 0.01	0.7
	Benz[a]anthracene	0.01 $\pm$ 0.01	0.6
	Chrysene	ND	0.0
	Benzo[b]fluoranthene	0.18 $\pm$ 0.10	7.0
	Benzo[k]fluoranthene	0.02 $\pm$ 0.01	0.7
	Benzo[a]pyrene	0.11 $\pm$ 0.03	4.4
	Dibenz[a,h]anthracene	0.07 $\pm$ 0.06	2.8
	Benzo[ghi]perylene	0.31 $\pm$ 0.24	12.0
	Indeno[1,2,3-cd]pyrene	0.24 $\pm$ 0.17	9.2
	Σ	0.99 $\pm$ 0.11	37.7
		2.62 $\pm$ 0.14	

Haze has been attributed to agricultural bush burning as well as changes in land-use practices in some areas on the Island of Borneo, Indonesia. Biomass combustion is an important primary source of many trace substances that are reactants in atmospheric chemistry and of soot particulate matter that decreases visibility and absorbs incident radiation (Crutzen & Andreae, 1990; Levine, 1991; Lobert et al., 1990; Seiler and Crutzen, 1980). Chemically, biomass smoke particles contain thermally unaltered and partially altered biomarker compounds from the major vegetation burned.

However, in urban atmosphere like Klang Valley, the particles during a haze event are expected to be comprised of both inputs from biomass combustion as well as vehicular emissions. This is understandable since motor vehicles contributed as much as 74% of air pollutants in Malaysia (DOE, Malaysia, 1998). Furthermore, Malaysia had an estimated value of more than 21 million registered cars, motorcycles, trucks, buses and commercial vehicles on its roads and the value is highest in the big city in Malaysia such as Kuala Lumpur, Johor Bahru and Penang.

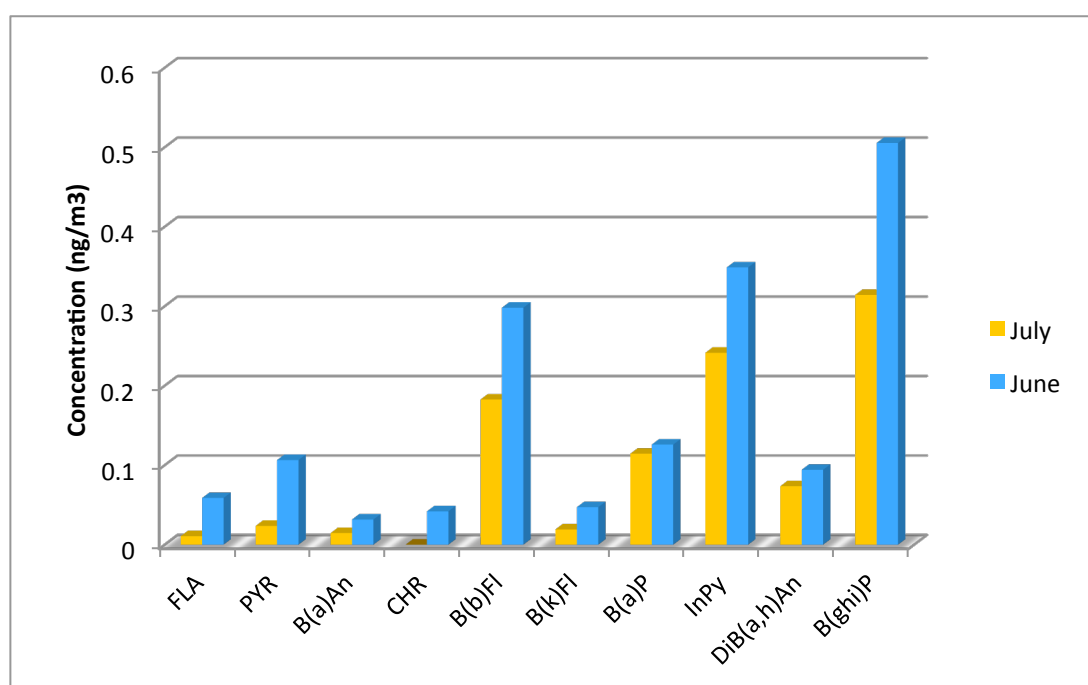


Figure 6.6 Average concentration of PAHs compounds

Figure 6.6 illustrates the average concentration of different PAHs compounds during the sampling period. In general, three PAHs compounds displayed relatively higher concentrations compared to other PAHs compounds. B(ghi)P contribute the highest percentage of total PAHs concentrations with readings of 0.51ng/m^3 (19.3%) in June and 0.31ng/m^3 (12.0%) in July. This indicated that Benzo (g,h,i) perylene could be contributed from diesel or gasoline powered vehicles. The increasing of vehicles ownership with heavy traffic density has lead to contribution of Benzo(g,h,i) perylene in the study area. Other two PAHs compounds with slightly higher concentrations are InPy and B(b)Fl with readings of 0.35ng/m^3 and 0.24ng/m^3 ; 0.30ng/m^3 and 0.18ng/m^3 ; in June and July, accordingly.

In addition, the minimum concentrations of Chrysene were detected in both sampling time. It could be suggested that, other factor such as meteorological condition during sampling time influences the degradation rates of the compound. With a total percentage of 18.3% in June and 9.5% in July; all other PAHs compounds recorded concentrations in the range between 0.03ng/m³ – 0.13ng/m³ (June) and 0.00ng/m³ – 0.11ng/m³ (July). The total PAHs concentrations accumulated for the both months during the sampling period were 2.62ng/m³.

6.4.2 Comparison of PAHs Concentrations with Other Studies

The total PAH concentrations acquired in this study is much lower than those measured in urban locations in China (Simoneit et al., 1991), urban Mumbai, India (Kulkarni & Venkataraman, 2000) and urban Heraclion, Island of Crete, Greece (Gogou et al., 1996). However, the concentrations of PAHs in this study are higher than those measured in urban Los Angeles, USA (Simoneit, 1984). In addition, the value obtained during this study period is also lower than previous studies done in Kuala Lumpur (Omar et al., 2002; Fang et al., 1999). The PAHs concentrations obtained in the two previous studies done in Kuala Lumpur show a similar trend of recorded data. The similarities in those values are a reflection of similar emission sources in all sampled areas. Table 6.6 shows total PAHs concentrations found in other cities around the world done in other studies.

Table 6.6 PAHs concentration found in other studies around the world

Locations	Concentration (ng/m ³)	Particle Size	Sampling Period (hours)	References
Urban sites, China	170-490	TSP	24	Simoneit et al., 1991
Urban Mumbai, India	24.5 & 38.8	PM ₁₀	72	Kulkarni and Venkataraman, 2000
Urban Heraclion, Island of Crete, Greece	21.4–59.0	TSP	12-24	Gogou et al., 1996
Urban sites, Malaysia	7 & 9	TSP	24	Fang et al., 1999
Urban Los Angeles, USA	0.02–0.18	TSP	24	Simoneit, 1984
Rural Finocalia, Island of Crete, Greece	0.2–2.0	TSP	20-24	Gogou et al., 1996
Urban Malaysia	6.28	PM ₁₀	48	Omar et al., 2002

The lower concentration found in this study is not only due to smaller quantities being emitted but also due to some physicochemical and meteorological factors, such as:

- a) dilution, which is the more important factor;
- b) photochemical degradations are stronger;
- c) the gas/particle ratio increases with temperature (Masclet et al., 1986)

6.4.3 Comparison of PAHs Distributions in Atmospheric Particles

To assess PAH homolog distribution for each collected samples, PAHs can be classified into three categories; PAHs containing 4 rings, PAHs containing 5 rings, and PAHs containing 6 rings. Furthermore, information from this study indicated that six ringed PAHs were predominant observed followed by five and four ringed forms respectively. Figure 6.7 compares the distribution of PAHs based on their number of aromatic rings classification.

In June, 52 % of PAHs are six ringed, followed by 34% five ringed and 14% of four ringed. Similar trend was observed in July where 56% are six ringed, followed by 40% five ringed and 4% of four ringed. Unfortunately, the predominant five and six ringed are regarded as having the highest carcinogenic potency. This suggests that PAHs residues found in this study may have all originated from the combustion of gasoline and diesel fuel. FLA, PYR and CHR were the dominant for 4 rings PAHs. FLA and PYR are dominant in diesel exhaust particulates, while sources of CHR are more ubiquitous and include vehicle exhausts, coal combustion and wood burning stoves (Mirante et al., 2013).

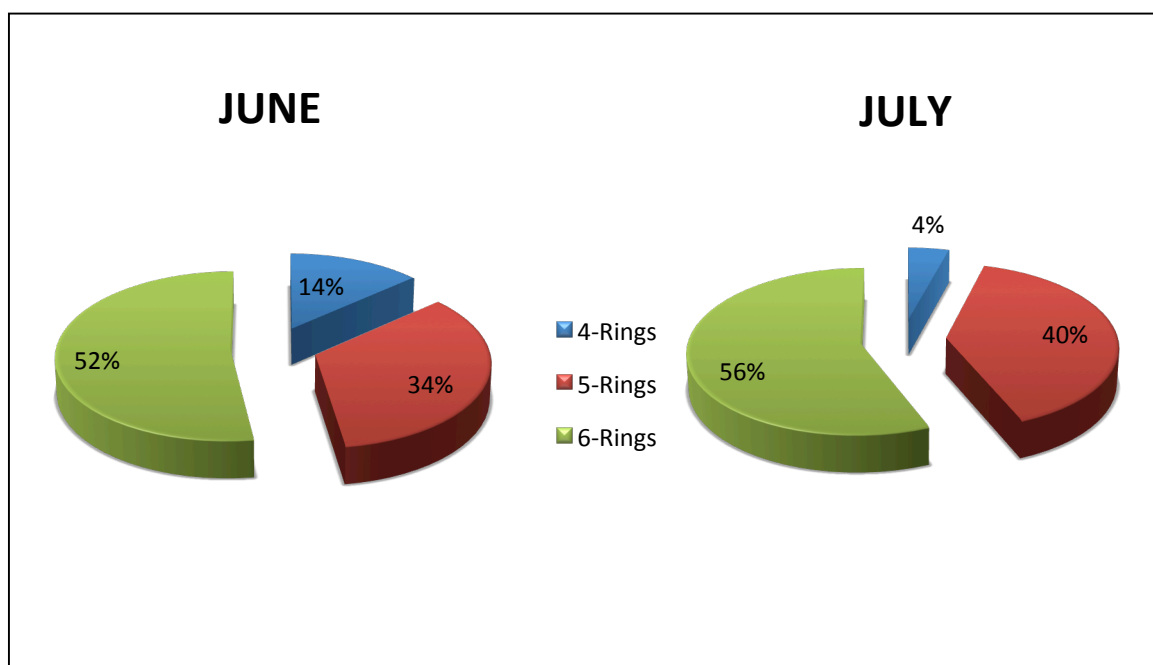


Figure 6.7 Distributions of PAHs based on number of aromatic rings

Figure 6.8 demonstrates the PAHs concentrations based on number of aromatic rings during the sampling period. Predominantly, the total concentrations for PAHs compounds in July are outnumbered by total concentrations in June for all groups of different aromatic rings. As mentioned earlier, the six ringed PAHs with the highest percentage of 52% in June and 56% in July; have accumulated the total concentrations of 0.85ng/m^3 and 0.56ng/m^3 , accordingly. The five ringed PAHs are the second highest of total PAHs concentrations with 0.56ng/m^3 and 0.39ng/m^3 for June and July, respectively. The lowest among the groups of aromatic rings were the four ringed PAHs. In June, the four ringed PAHs recorded the total concentrations of 0.22ng/m^3 , while in July; the total concentrations are locked only at 0.04ng/m^3 .

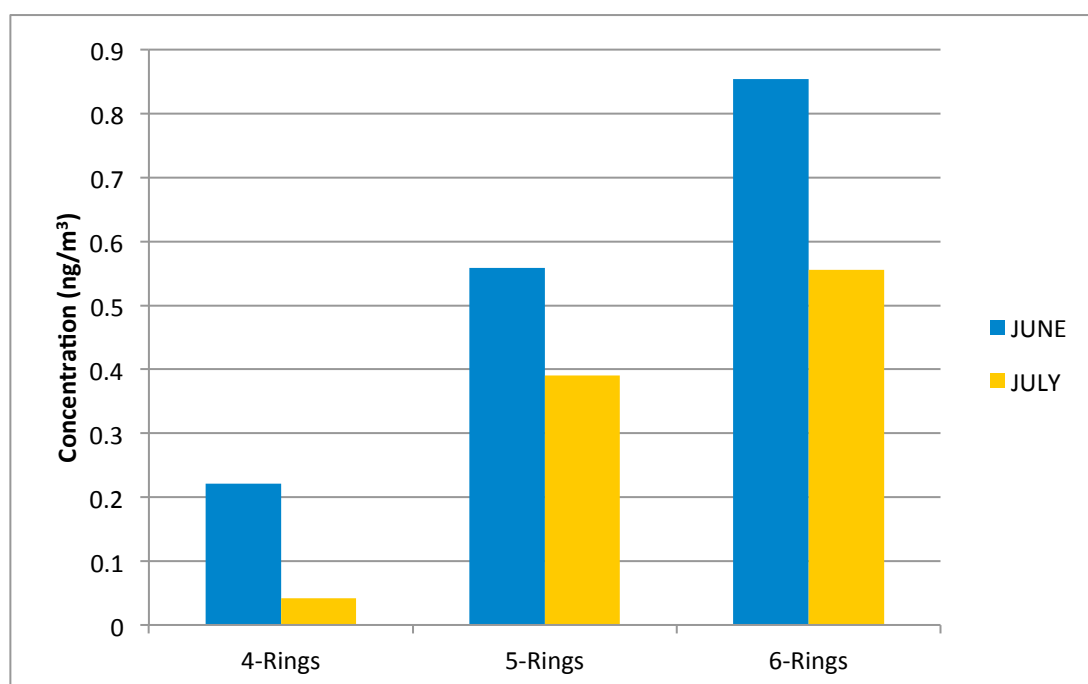


Figure 6.8 Concentrations of PAHs based on number of aromatic rings

In general, low-weight PAHs (i.e., with two, three) are more volatile (with low temperatures of condensation) and exist mainly in the gas phase (Kameda, 2011). Although the lighter PAH compounds are considered to be less toxic, they are able to react with other pollutants (such as ozone, nitrogen oxides, and sulfur dioxide) to form diones, nitro- and dinitro-PAHs, and sulfuric acids, respectively of which toxicity may be more significant (Park et al., 2001).

PAHs with four or more rings show insignificant vaporization under all environmental conditions (Kameda, 2011). Most of the heavier PAHs therefore occur mainly in the particulate phase in the atmosphere due to their low vapor pressure (Kameda et al., 2005). Heavier molecular weight of PAHs such as Benzo(g,h,i)perylene, Benzo[b]fluoranthene, Indeno[1,2,3-cd]pyrene, Chrysene, Benzo[a]pyrene, Fluoranthene, Pyrene, Benzo[a]anthracene, Benzo[k]fluoranthene and Dibenz[a,h]anthracene that mostly adsorb on small inhalable size particles were found in higher concentrations. A similar observation was also reported in study of PAHs in Thailand (Oanh et al., 2000).

Furthermore, considering that several PAHs compounds are known as human carcinogens, PAHs were also classified into two categories depending on their carcinogenicity; such as carcinogen (Benz[a]anthracene, Benzo[b]fluoranthene, Chrysene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, and Indeno[1,2,3-cd]pyrene) and non-carcinogenic (Fluoranthene, Pyrene and Benzo (g,h,i) perylene). This is indicated that 61% of the total PAHs found in this study area for June and July are carcinogenic PAHs whereas 39% are non-carcinogenic PAHs (Figure 6.9). Compared to other study, carcinogenic compounds found in present study was higher. Halek et al. (2008) reported that seven carcinogenic PAHs accounted for 13.5–23.8% of the total particulate PAHs in Tehran.

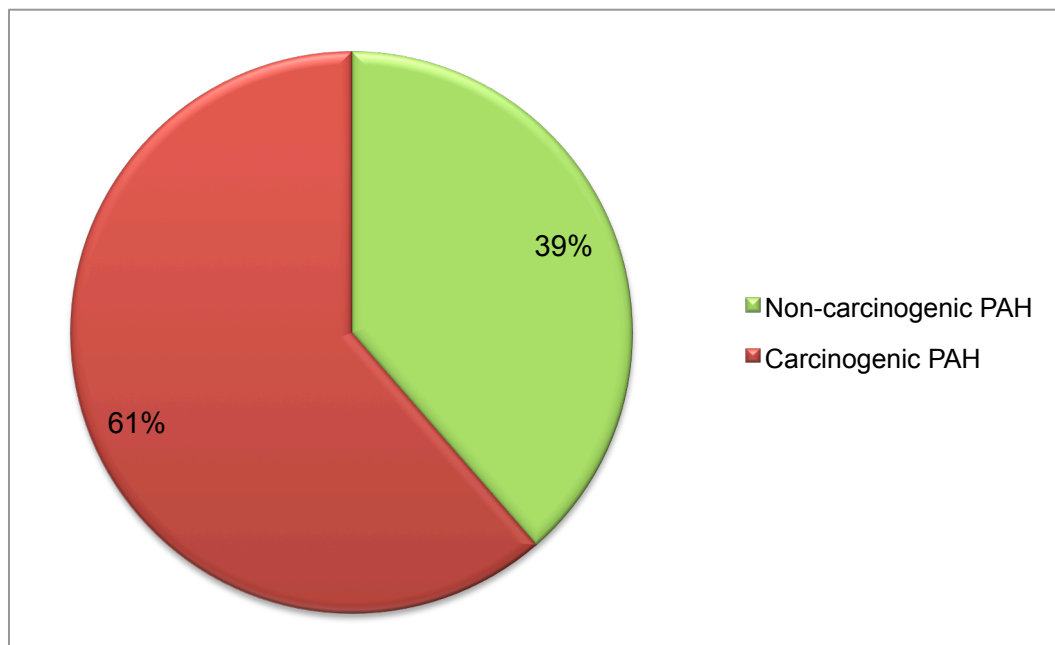


Figure 6.9 Percentage distributions of carcinogenic and non-carcinogenic PAHs

B(a)P is considered one of the most potent carcinogenic PAH (Callén et al., 2013; Chen et al., 2012). Nevertheless, this PAH can underestimate the carcinogenic character of the particulate matter (Wickramasinghe et al., 2012). The average values for B(a)P in this study were lower than those previously reported in other cities (Castellano et al., 2003; Panther et al., 1999; Vasconcellos et al., 2003). Several studies from European cities reported higher B(a)P concentrations than were recorded in this study. They ranged between a mean concentration of 4.4ng/m^3 in winter in Copenhagen, Denmark (Nielsen et al., 1996), and 1.38ng/m^3 in Rome, Italy (Menchini et al., 1999). However, the result was similar to those found in Leipzig (Rehwagen et al., 2005) with the mean concentration ranged between 0.01 and 0.22ng/m^3 .

The results from other studies are obtained in locations with different climates; demonstrate the requirement of considering the meteorological conditions for a comparison of various regions. Apart from local sources, meteorological conditions may significantly affect the abundance and specification of PAHs in aerosols (Guo et al., 2003).

The summertime conditions, such as higher temperature and more intensive solar radiation, as well as the higher ozone concentration, could have reduced the B(a)P concentration (Saarnio et al., 2008). Thus, it seems that B(a)P is not a good representative marker for the refractory carcinogenic PAHs due to its short half-life and high reactivity, especially in summertime. Pufulete et al. (2004) questioned the suitability of B(a)P as an indicator of carcinogenic PAHs by new findings on the presence of more potent PAHs such as dibenzo[a,h]pyrene. Okona-Mensah et al. (2005) estimated that this PAH may have a carcinogenic potency approximately 100 times higher than B(a)P. PAHs are oxidized into oxygenated derivatives (Oxy-PAHs) by UV-light, O₃, NO_x and reactive oxygen species. There are studies which show us that particulate matter emitted from vehicles contain higher amounts of Oxy-PAHs than particulate matter found in the atmospheric air (Tong et al., 1984; Schuelze et al., 1984; Oda et al., 1998).

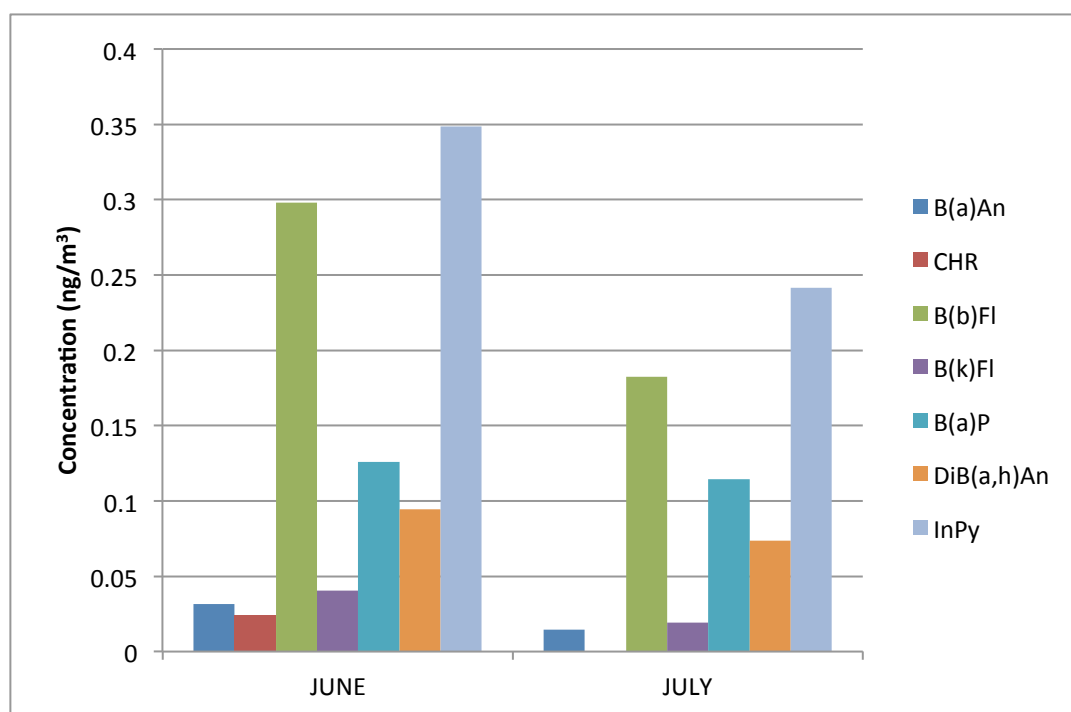


Figure 6.10 Average concentrations of carcinogenic PAHs compounds

Figure 6.10 and 6.11 showed the average concentration of carcinogenic and non-carcinogenic compound of PAHs. For carcinogenic compound of PAHs, Indeno[1,2,3-cd]pyrene indicated the highest concentrations for both June and July with $0.35 \pm 0.19 \text{ ng/m}^3$ and $0.24 \pm 0.17 \text{ ng/m}^3$, respectively. Meanwhile, for non-carcinogenic, Benzo(g,h,i)perylene showed the highest concentration for both June and July with the concentrations $0.51 \pm 0.39 \text{ ng/m}^3$ and $0.31 \pm 0.24 \text{ ng/m}^3$, respectively. The relatively high concentration Benzo(g,h,i)perylene on airborne particle are also reported by many investigators which is similar in the present study (Oanh et al., 2000; Ruchirawat et al., 2002). The abundance of Benzo(g,h,i)perylene among the identified PAHs at sampling sites indicates the high contributions from gasoline powered vehicles (Nielsen, 1996; Harrison et al., 1996) to the PAH concentration levels in Bangi. In addition, considerable contribution of

Benzo[b]fluoranthene in June and July suggested they may be originated from oil combustion or vehicle emissions (Shi et al., 2010).

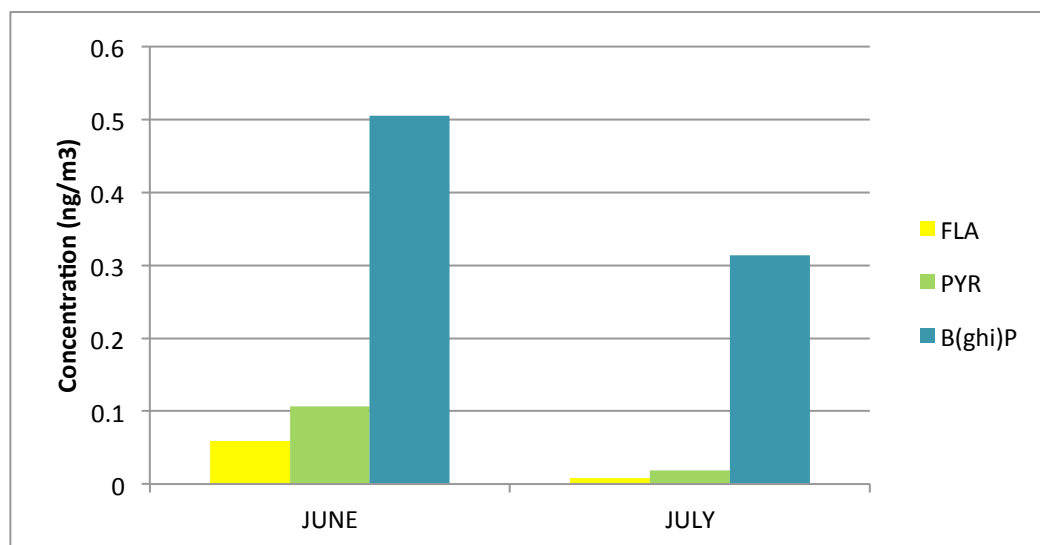


Figure 6.11 Average concentrations of non-carcinogenic PAHs compounds

The Fluoranthene and Pyrene are more volatile PAHs than other non-carcinogenic compounds determined in this study. Therefore, they will be distributed between the gas- and particle-phase and will also be subject to losses from the filter during sampling (Arey et al., 1987; Su et al., 2006). The gas/particle phase partitioning of PAHs depends strongly on temperature, because of the variation of vapor pressures of the condensing compounds with temperature (Seinfeld & Pankow, 2003). The high average temperature in Bangi suggests that the majority of the Fluoranthene will be in the gas phase. Therefore, the Fluoranthene and Pyrene concentrations given in Figure 6.11 are lower limits to the actual concentrations.

6.4.4 Comparison with Ambient Standards

Currently, there are no ambient air quality standards for PAHs in Malaysia. In Europe, Netherlands had introduced an interim goal of reducing the annual average Benzo(a)pyrene concentration to below 5ng/m³ (Smith & Harrison, 1998), while a guideline of 10ng/m³ for the annual average Benzo(a)pyrene has been proposed by the German Federal Environmental Agency (Smith & Harrison, 1998).

Recently, the Dutch National Institute of Public Health and the Environment (DNIPHE) had established the values of maximum permissible concentrations (MPCs) and negligible concentrations (NCs) for about more than 200 toxic compounds including some PAHs (RIVM, 1999a). The MPCs and NCs represent risk limits of the substances in different compartments of the environment: surface water, soil, air, groundwater and sediment, and are calculated from available ecotoxicological data. These risk limits are used to derive environmental quality standards in Netherlands (RIVM, 1999b).

Of the seven PAHs in the Dutch report, only Benzo(a)pyrene had ecotoxicological data available for air. Thus MPCs and NCs for air were not available for the other six PAHs. However, the DNIPHE assigned a critical concentration value in air to each of them (Table 6.7). Critical concentrations (CritConc) are normally calculated for air and/or rainwater. They are theoretically derived steady-state concentrations of the pollutants in air and/or rainwater that will not lead to exceed the MPC value for soil (RIVM, 1999a).

Calculated MPCs, NCs and critical concentrations of PAHs reported in the DNIPHE report (RIVM, 1999a) are compared to the highest concentrations determined in Bangi (Table 6.7). Therefore, only the concentration in June was taken as representative considered. Sampling in June had the highest average concentration of Benzo(a)pyrene detected in Bangi. The Benzo(a)pyrene concentrations in Bangi (0.13ng/m^3) was lower than the DNIPHE maximum permissible concentration.

Table 6.7 Average concentrations of some PAHs in Bangi compared to the DNIPHE of MPCs, NCs and CritConc

PAH	Average 24-h concentration in Bangi (ng/m^3)	MPC [air] (ng/m^3)	NC [air] (ng/m^3)	CritConc [air] (ng/m^3)
Anthracene	-	-	-	8,600
Benz[a]anthracene	0.03	-	-	200
Benzo[a]pyrene	0.13	1.0	0.01	-
Benzo[k]fluoranthene	0.05	-	-	200
Fluoranthene	0.06	-	-	1300
Naphthalene	-	-	-	140,000
Phenanthrene	-	-	-	33,000

6.5 Conclusion

The average Σ PAH concentrations in June were higher than July with reading of 1.63ng/m^3 and 0.99ng/m^3 ; respectively. This finding could be caused by an impact of first haze episode in June, which was the peak of haze in Malaysia; together with the influences of localize emission from motor vehicles. These concentrations are on the lower side compared to the data of PAHs concentrations obtained from other places.

Benzo(g,h,i)perylene contribute the highest percentage of total PAHs concentrations with readings of 0.51ng/m^3 (19.3%) in June and 0.31ng/m^3 (12.0%) in July. This indicated that the abundance of B(ghi)P could be contributed from diesel or gasoline powered vehicles. Other PAHs compounds with literally higher concentrations include Indeno[1,2,3-cd]pyrene, Benzo[b]fluoranthene and Benzo[a]pyrene.

Present study indicated that six ringed PAHs were predominantly observed followed by five and four ringed forms. Similar trend was observed during the sampling period as there were 52% and 56% of six ringed PAHs, followed by 34% and 40% of five

ringed and 14% and 4% of four ringed; in June and July, respectively. This suggests that PAH residues found in this study may have all originated from the combustion of gasoline and diesel fuel. In addition, results also indicated that 61% of total PAHs found in this study are carcinogenic PAHs whereas 39% are non-carcinogenic PAHs. The highest concentrations for carcinogenic PAHs compounds is hold by Indeno[1,2,3-cd]pyrene; while Benzo(g,h,i)perylene shows the highest concentrations among non-carcinogenic PAHs compounds.

At present, there are no ambient air quality standards for PAHs in Malaysia. Therefore, the concentration of PAHs mainly Benzo(a)pyrene was compared the Dutch National Institute of Public Health and the Environment (DNIPHE) guideline. It was found that, the Benzo(a)pyrene concentrations in Bangi (0.13ng/m^3) was lower than the DNIPHE maximum permissible concentration.

CHAPTER 7

DIAGNOSTIC RATIO AND RISK ASSESSMENT OF PAHs IN ATMOSPHERIC PARTICULATE MATTER

7.1 INTRODUCTION

PAHs are mainly produced by incomplete combustion and pyrolysis of organic material (Manahan, 2009). Their occurrence in urban atmospheres is largely the result of anthropogenic emissions, such as mobile emissions (vehicular, shipping and flying), domestic heating, oil refining, waste incineration, industrial activities, asphalt production and agricultural burning of biomass (Marchand et al., 2004; Ravindra et al., 2008). Generally, PAHs occur in the atmosphere as complex mixtures of congeners with different molecular weights: lighter PAHs (2/3 aromatic rings) are present almost exclusively in the vapor-phase, whereas PAHs with higher molecular weights (4 rings) are almost totally adsorbed on the particulate matter. As many of the heaviest PAHs are carcinogenic (IARC, 2010), and were, in particular categorized as human carcinogens (class 1), probable (class 2A) or possible human carcinogens (class 2B) by the International Agency for Research on Cancer (IARC, 2012). The quantification of particle-phase PAHs is a key tool to assess health risks for humans exposed to airborne pollutants.

PAHs are widely distributed in the atmosphere and were one of the first atmospheric pollutants designated as a suspected carcinogen. The PAHs entering the atmosphere can be transported over long distances before deposition through atmospheric precipitation onto soils, vegetation or waters (Ravindra et al., 2008). As molecular weight increases, the carcinogenicity of PAHs also increases with reducing acute toxicity. The most potent PAH carcinogens have been identified to include Benzo[a]anthracene, Benzo[a]pyrene, and Dibenzo[ah]anthracene (Armstrong et al., 2004; Bach et al., 2003; CCME, 2010).

As every congener has its individual toxicity, several approaches have been developed to discriminate individual contributions in a PAH mixture. Toxicity equivalency factors (TEF) and mutagenic equivalency factor (MEF) were used to evaluate the carcinogenicity and mutagenicity of PAHs compound. The experimental evidences in rats suggest that human exposures to PAHs, especially B[a]P are high risk factors for carcinogenic and mutagenic effects (Loli et al., 2004; Wester et al., 2012). Several epidemiological meta-analyses highlight that heavy exposures to mixtures of PAHs entail a substantial risk to developmental neurotoxicity (Hood et al., 2011; Qiu et al., 2011; Crepeaux et al., 2012). For this reason, the monitoring of PAHs in environmental media is a reasonable approach to assess the risk for adverse health effects.

7.2 METHODOLOGY

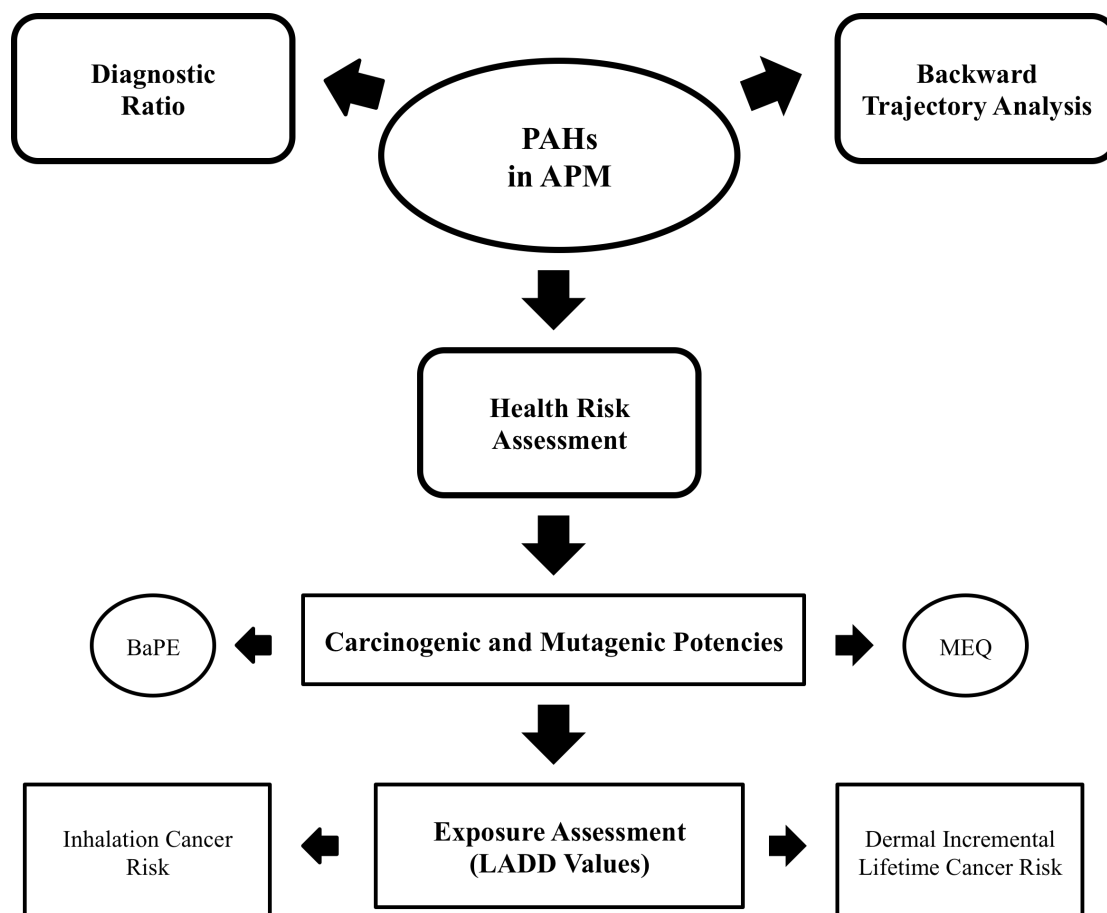


Figure 7.1 Methodology of Analysis

7.2.1 PAHs Diagnostic Ratio

It is suggested that the concentrations of some PAH marker compounds and their ratios can give some indication about the impact of different sources of airborne compounds (Guo et al., 2003). Atmospheric PAH profile can be affected by meteorological variables such as UV light and temperature. Besides, the half-lives of these compounds in the atmosphere vary.

For decades, PAHs have been used as a “chemical proxy” to distinguish the anthropogenic source and biogenic source in marine sediment (Cantwell et al., 2007; Christensen et al., 1996; Fang et al., 2009; Tobiszewski & Namiesnik, 2012). They can be categorized as anthropogenic combustion sources (i.e. oil spill, automobile exhaust and street runoff) and as natural combustion sources (i.e. forest fires and volcano eruption) by using PAHs diagnostic ratios (Yunker et al., 2002, 2011; Yunker & Macdonald, 2003). PAHs of molecular mass 178, 202 and 258 are commonly used to distinguish between pyrogenic (combustion-derived) and petrogenic (unburned petroleum-derived) sources.

The PAHs of petrogenic (petroleum derived residues) origins are characterized by the predominance of 2- and 3-ring or low molecular weight (LMW), while PAHs from pyrogenic (combustion derived) origins are characterized with high proportion of above 4-ring or high molecular weight (HMW) PAHs. LMW_{PAHs} are generated at low to moderate temperatures such as during biomass combustion while the HMW_{PAHs} are generated at high temperature combustion such as vehicle emissions (Mastral & Callen, 2000). This gives different ratio of LMW_{PAHs} to HMW_{PAHs} in soil depending upon the sources.

7.2.2 Health Risk Assessment

The Benzo[a]pyrene equivalent (BaPE) dose for each PAH is calculated by multiplication of the measured concentrations by the respective toxic equivalent factor (TEF). The TEF values were taken from Nisbet and LaGoy (1992) who presented a compilation of data based on the literature (Table 7.1). BaPE is then calculated as a sum to express the carcinogenicity of the mixture:

$$BaPe = \sum PAHi * TEF$$

Table 7.1 Toxic Equivalency Factors for PAHs relative to B(a)P

PAHs	TEF (Data from Nisbet & LaGoy, 1992)
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benzo(a)anthracene	0.1
Chrysene	0.01
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Benzo(a)pyrene	1
Indeno(123-cd)pyrene	0.1
Dibenz(ah)anthracene	1
B(ghi)perylene	0.01

Mutagenicity of individual PAH relative to B(a)P also has been assessed using the mutagenic equivalency factor (MEF) proposed by Durant et al., 1996 (Table 7.2). MEF values in combination with measured air concentrations have been used for the calculation of mutagenic equivalents (MEQ, expressed in ng/m³) in environmental samples:

$$MEQ = \sum PAHi * MEFi$$

Table 7.2 Mutagenic Equivalency Factors for PAHs relative to B(a)P

PAHs	MEF (Data from Durant et al.,1996)
Benzo(a)anthracene	0.082
Chrysene	0.017
Benzo(b)fluoranthene	0.25
Benzo(k)fluoranthene	0.11
Benzo(a)pyrene	1
Indeno(123-cd)pyrene	0.31
Dibenz(ah)anthracene	0.29
B(ghi)perylene	0.19

Exposure is expressed in terms of a lifetime average daily dose (LADD) and is calculated separately for each element and for each exposure pathway according to the USEPA framework (USEPA, 2004, 2009). Mathematical models used for the calculations of LADD are given in Table 7.3 (Equation 7.1 and Equation 7.2). In addition, the exposure parameter values used in the current study are listed in Table 7.4. The incremental lifetime cancer risk (ILTCR) was then estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen through dermal contact (Table 7.5) The cancer slope factors (CSFs) for B(a)P used in the present study for the dermal (Chiang et al., 2009) is 30.5 mg/kg/day.

Table 7.3

Mathematical models in the risk assessment of PAHs study

LADD for Carcinogens (Inhalation) →	Eq. 7.1
$LADD_{inh} = \left(\frac{C_g * ET * EF}{AT_{carc}} \right) * \left(\frac{InhR * ED}{BW} \right) adult / children * CF$	
▪ $LADD_{inh}$ = lifetime average daily dose associated with the inhalation (mg/ kg/d) ▪ C_g = the gas phase atmospheric concentration of each individual metal (ng/m³) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ $InhR$ = inhalation rate (m³/h) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ AT_{carc} = average timing for carcinogenic health effects (d) ▪ cf = conversion factor	

LADD for Carcinogens (Dermal) →	Eq. 7.2
$LADD_{der} = \left(\frac{C_p * ET * EF * ABS}{AT_{carc}} \right) * \left(\frac{SA * AF_d * ED}{BW} \right) adult / children * CF$	
▪ $LADD_{der}$ = lifetime average daily dose associated with dermal exposure (mg/ kg/d) ▪ C_p = the particulate phase concentration of each individual metal (µg/g) ▪ ET = the exposure time (h/d) ▪ EF = the exposure frequency (d/y) ▪ ABS = dermal adsorption fraction (dimensionless) ▪ SA = skin surface area exposed (cm²) ▪ AF_d = particle-to-skin adherence factor (mg/cm²/event) ▪ ED = exposure duration (y) ▪ BW = body weight (kg) ▪ AT_{carc} = average timing for carcinogenic health effects (d) ▪ cf = conversion factor	

Table 7.4 Exposure parameter values used in the risk assessment calculations

Variable	Adult	Children	Reference
ET (h/d)	8		USEPA, 2004
EF (d/y)	350		USEPA, 2004
ED (y)	30	6	USEPA, 2004
BW (kg)	70	15	USEPA, 2004
AT _{carc} (d)	70 x 365		USEPA, 2004
InhR (m ³ /h)	0.83	0.32	USEPA, 1989
ABS	0.13		USEPA, 2004
SA (cm ²)	5700	2800	USEPA, 2004
AF _d (mg/cm ² /event)	0.07	0.2	USEPA, 2004

Table 7.5 Mathematical models in the cancer risk of PAHs study

Inhalation Cancer Risk → Eq. 7.3
$CancerRisk = \sum (PAH_i * TEF_i) * URBaP$
- PAH_i = the individual PAHs measured in the air - TEF_i = the TEF of individual PAH - URBaP = the inhalation cancer unit risk factor for B(a)P

Incremental Lifetime Cancer Risk Model for Dermal → Eq. 7.4
$ILTCR_i = LADD_i \cdot CSF_i$
- ILTCR_i = incremental lifetime cancer risk for an exposure route - LADD_i = lifetime average daily dose for an exposure route - CSF_i = cancer slope factor for an exposure route

A point-estimate approach, developed by the Office of Environmental Health Hazard Assessment (OEHHHA) of the California Environmental Protection Agency (CalEPA) (Collins et al. 1998; OEHHHA 2003), was used to estimate the inhalation cancer risk of PAHs during the different periods. The inhalation cancer risk for the PAH mixture was estimated by multiplying the sum of the individual BaPE concentrations by the unit risk (UR) of exposure to BaPE. CalEPA has calculated a URBaP estimate of 1.1×10^{-6} per ng/m³ based on the data for respiratory tract tumors from inhalation exposure in hamsters (OEHHHA 1993, 2005), whereas the World Health Organization (WHO) has estimated URBaP at 8.7×10^{-5} per ng/m³ based on an epidemiology study on coke-oven workers in Pennsylvania (WHO, 2000). In this study, both URBaP values were used to calculate excess PAH-induced inhalation cancer risk.

7.3 RESULT AND DISCUSSION

7.3.1 Diagnostic Ratio

Table 7.6 Ratio of PAHs concentration in June and July

	June	July
FLA / (FLA + PYR)	3.56E-01	3.12E-01
B(a)An / (B(a)An + CHR)	4.30E-01	-
FLA / PYR	5.52E-01	4.54E-01
B(a)P / (B(a)P + CHR)	7.50E-01	-
InPy / (InPy + B(ghi)P)	4.08E-01	4.34E-01
InPy / B(ghi)P	6.90E-01	7.68E-01
B(a)P / B(ghi)P	2.49E-01	3.64E-01

Table 7.6 provides the values of diagnostic ratio for PAHs such as; FLA / (FLA + PYR), B(a)An / (B(a)An + CHR), FLA / PYR, B(a)P / (B(a)P + CHR), InPy / (InPy + B(ghi)P), InPy / B(ghi)P and B(a)P / B(ghi)P; for both June and July. The ratios can be applied to investigate the origin and sources of PAHs in Bangi atmospheric particulate matter. However, the diagnostic ratio for B(a)An / (B(a)An + CHR) and B(a)P / (B(a)P + CHR) in July cannot be determined as the concentrations for CHR could not be detected.

Atmospheric PAH profiles can be affected by meteorological variables such as UV light and temperature. Furthermore, half-lives of these compounds in the atmosphere vary (Martinis et al., 2002). Despite these facts, the ratios between some of these compounds are considered as fingerprints of an emission sources (Khalili et al., 1995). These diagnostic ratios between PAH are used to characterize potential emission sources and distinguish among PAH sources (Park et al., 2002). This diagnosis is fascinated by comparing compound ratios with those reported in the literature as listed in Table 7.7.

The FLA / (FLA + PYR) values were determined to be 3.56E-01 in June and 3.12E-01 in July; suggested that the emissions could be from petrogenic (petroleum derived residues) origin (Hwang et al., 2003). The FLA / PYR ratios obtained in this study were 5.52E-01 in June and 4.54E-01 in July. These values are similar to those for gasoline or diesel vehicles emission (Lee et al., 2005). On the other hand, the InPy / (InPy + B(ghi)P) ratio were 4.08E-01 in June and 4.34E-01 in July, which are in diesel emission range (Kavouras et al., 2001).

In addition, the B(a)An / (B(a)An + CHR) ratio at 4.30E-01 in June which was similar to the value recorded for biomass burning as well as for coal combustion (Hwang et al., 2003). This is suggested the biomass burning contribution to PAHs composition in Bangi from long-range transport of haze from Indonesia. The B(a)P / (B(a)P + CHR) ratio attained in this study was 7.50E-01 in June; suggested that values lies in the range for diesel fuelled emission (Khalili et al., 1995).

The InPy / B(ghi)P ratios were 6.90E-01 and 7.68E-01 (June and July, respectively), which are also in the range of diesel emission (Carrichia et al., 1999). The B(a)P / B(ghi)P ratios obtained in present study were 2.49E-01 in June and 3.64E-01 in July. These values are indicated to those for traffic and vehicles emission (Smith & Harrison, 1996; Moller et al., 1986). Overall, the above PAHs compositional ratios basically indicate the mixed of petrogenic origin, vehicles emission and biomass burning as the main sources of PAHs in Bangi ambient atmospheric particulate matter.

Table 7.7 Diagnostic ratios of individual PAHs concentration for sources diagnosis

PAHs ratios	Value of ratios	Indicative	References
FLA / (FLA + PYR)	<0.4 ≥0.4-0.5 >0.5	Petrogenic Pyrogenic Biomass, coal comb	Hwang et al., 2003 Hwang et al., 2003 Fadzil et al., 2008
B(a)An / (B(a)An + CHR)	<0.2 0.2-0.35 >0.35	Petrogenic Petroleum combustion Biomass, coal comb	Yunker et al., 2002 Hwang et al., 2003
FLA / PYR	<1.0 1.0-1.4	Gasoline, diesel Biomass, coal comb	Lee et al., 1995
InPy / (InPy + B(ghi)P)	0.35-0.7 0.21-0.22 0.33	Diesel Gasoline Coal	Kavouras et al., 2001 Rogge et al., 1993 Khalili et al., 1995
B(a)P / (B(a)P + CHR)	0.49 >0.73 0.07-0.24	Gasoline Diesel Biomass, coal comb	Khalili et al., 1995 Khalili et al., 1995 Chen et al., 2005
InPy / B(ghi)P	≈1.0 0.4	Diesel Gasoline	Carrichia et al., 1999
B(a)P / B(ghi)P	0.39-0.51	Vehicular, traffic	Smith & Harrison, 1996 Moller et al., 1986

7.3.2 Backward Trajectory Analysis

A backward trajectory model represents the recent history of an air mass. An air mass trajectory can provide information about the source regions that impact a given site (Dutkiewicz et al., 2006). The backward air mass trajectories were calculated using the HYS-PLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory, Version4) model of the ARL (Air Resources Laboratory) of NOAA (National Oceanic and Atmospheric Administration). The trajectory starts from Bangi (latitude of 2°55' 24.1" N and longitude of 101°46' 50.7" E) at 4:00 UTC (Coordinated Universal Time) each day, which is equivalent to 12:00 (noon) Malaysia local standard time (LST). Three-dimensional 6 hours backward trajectories arriving at the receptor site 1000 m above ground level (AGL) were calculated every 6 hour using HYSPLIT-4.9.

Between June and early October, the Southeast Asian region experiences the Southwest Monsoon season, with the low level prevailing winds generally blowing from the southwest. This is also the traditional dry season in Brunei, Indonesia, Malaysia, Singapore and southern Thailand. During the Southwest Monsoon season, smoke haze that originates from widespread land and forest fires is a perennial problem that affects many areas of southern Southeast Asia. Most of these fires are due to land-clearing activities in some parts of the region. The resulting smoke is blown by the prevailing winds towards other parts of the region including Malaysia, and is visible as moderate to dense haze. In the second week of June 2013, drier atmospheric conditions prevailed across large parts of the Indonesian island of Sumatra, Peninsular Malaysia, and Singapore (Figure 7.2).

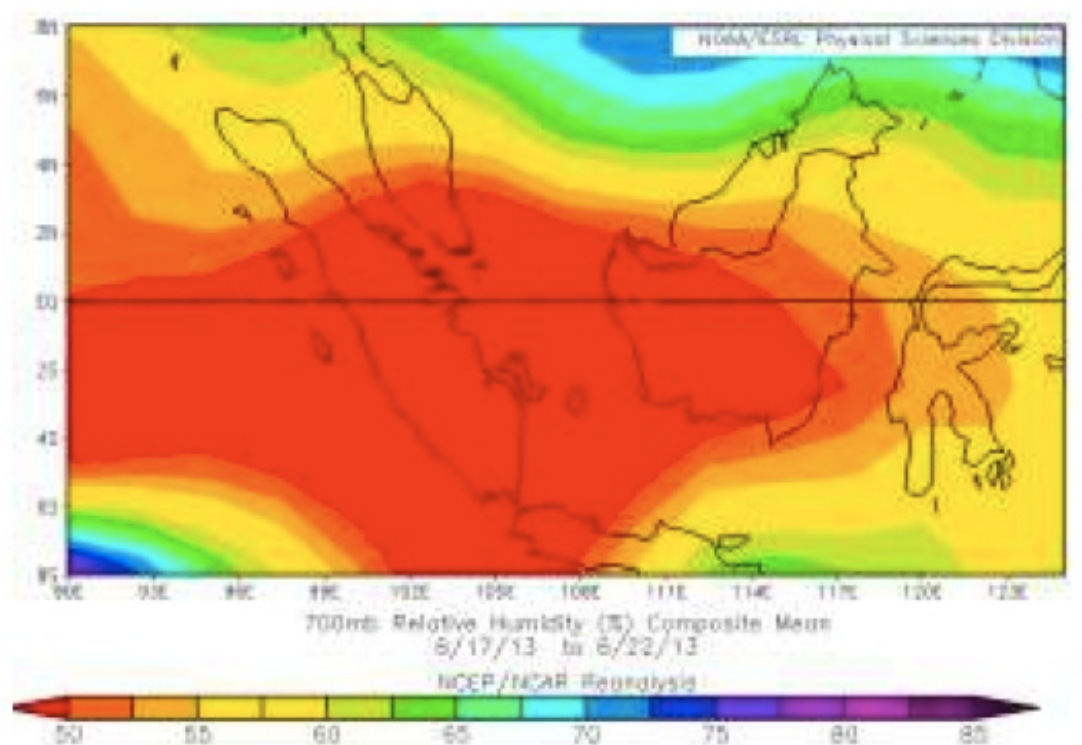


Figure 7.2 Relative humidity over Southern Asean
(Sources: World Meteorological Organization June 2013)

Figure 7.3 shows the hotspot and the biomass burning that occur in Sumatra, which lead to the haze condition in Malaysia. Haze is traditionally an atmospheric phenomenon where dust, smoke and other dry particles obscure the clarity of the sky. Haze has been an annual and a serious recurring problem in Malaysia and Singapore since 1980. The first and most publicly identifiable regional environmental crisis in the South East Asia is the transboundary haze (Palanissamy, 2013). The origination of haze is the smoke from peat and forest fires mostly in Sumatra in Indonesia and becomes transboundary when it travels across national boundaries, monsoon winds blew the smoke eastward, creating negative environmental effects on other South East Asian countries (Mayer, 2006).

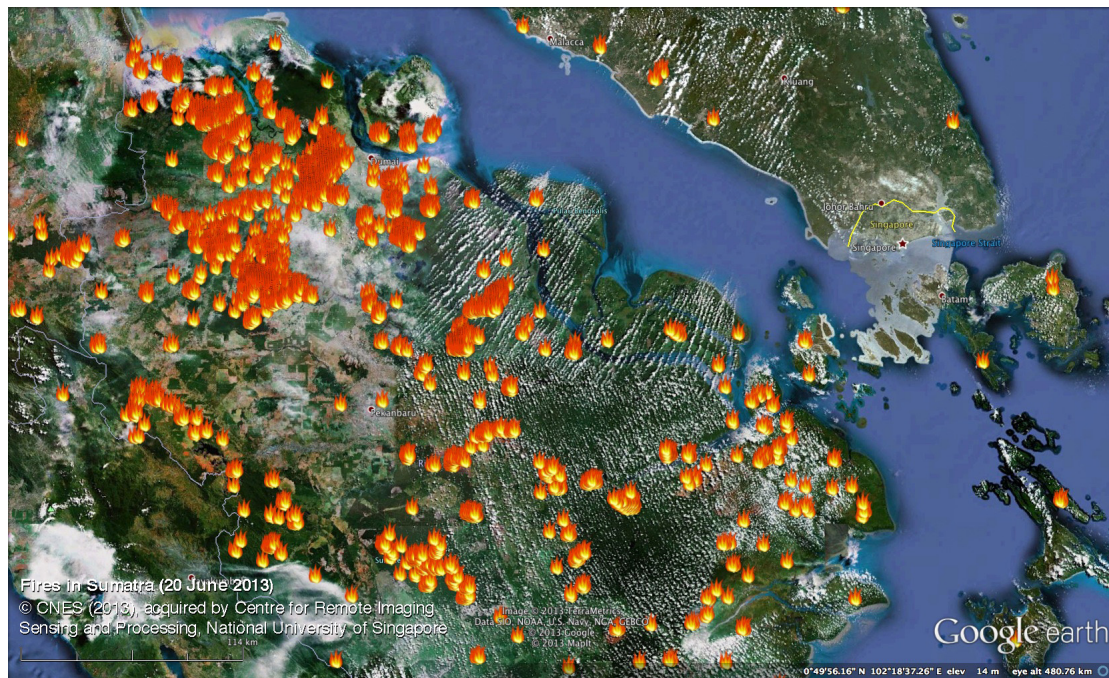


Figure 7.3 Fires in Sumatra (Sources: National Environment Agency, Singapore)

The 72 hours backward trajectories of air masses arriving in Bangi on June and July are shown in Figure 7.4 and 7.5; respectively. During periods of active and intense biomass burning in Sumatra, spells of moderate to dense smoke haze could be expected in the vicinity of the larger fire/hotspot clusters in the affected areas. During the haze event, the origins of air mass are normally located at low latitudes in the Indian Ocean. It follows the southwest monsoon direction through Sumatra, Java Sea and other areas impacted by forest and peat fires before arriving at Malaysia (Figure 7.4 and Figure 7.5). This cluster is predominantly observed in the period from May to September, which coincides with dry season in Malaysia. The mixing height in Klang Valley usually is low, which may be associated with stronger coastal inversion due to enhanced sea breeze the southwest monsoon. Wind speed generally is low and this air mass type is observed with the temperature and highest relative humidity, which show the increase influence of the southwest monsoon.

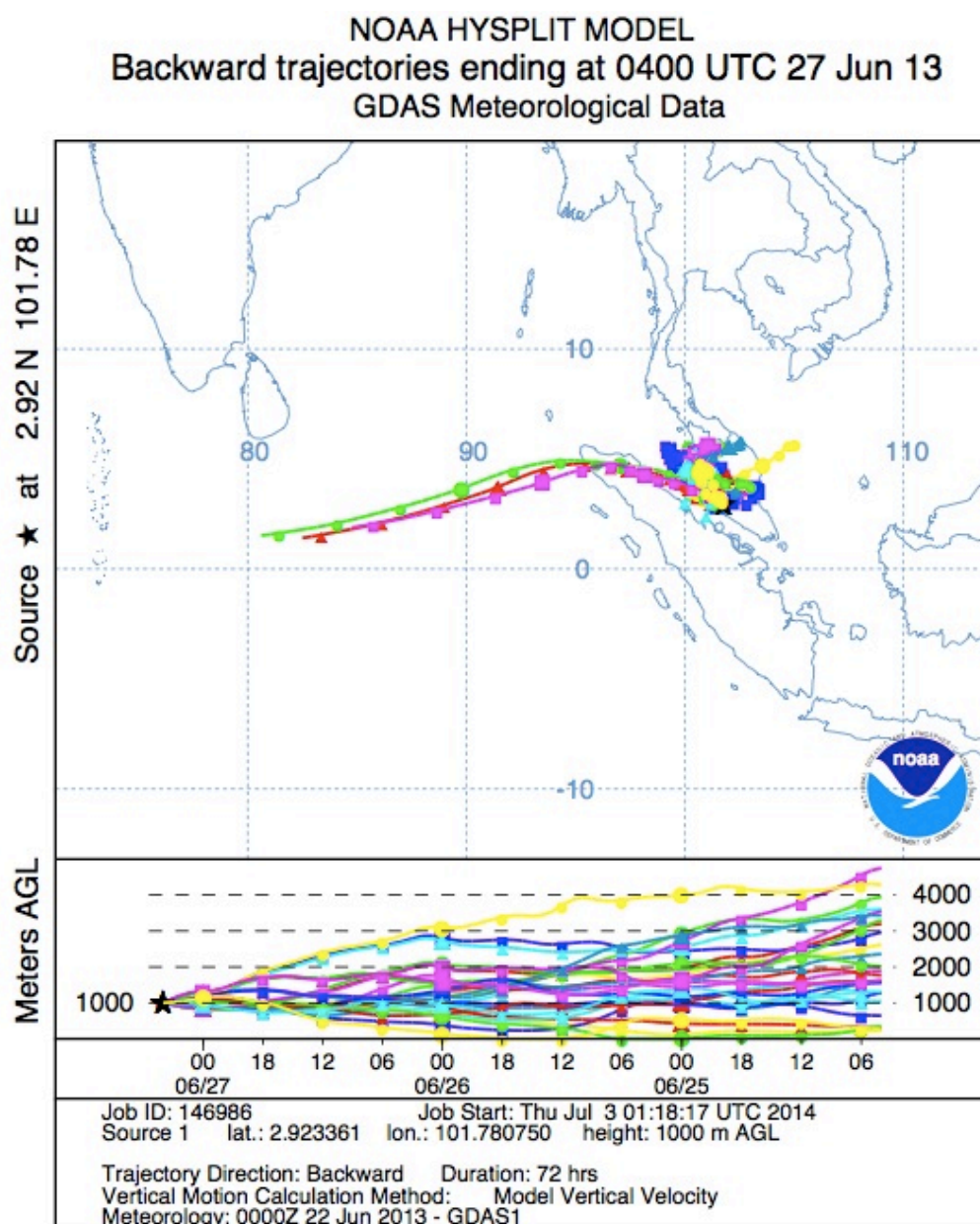


Figure 7.4 Backward trajectories of air masses for sampling site in Bangi on Jun

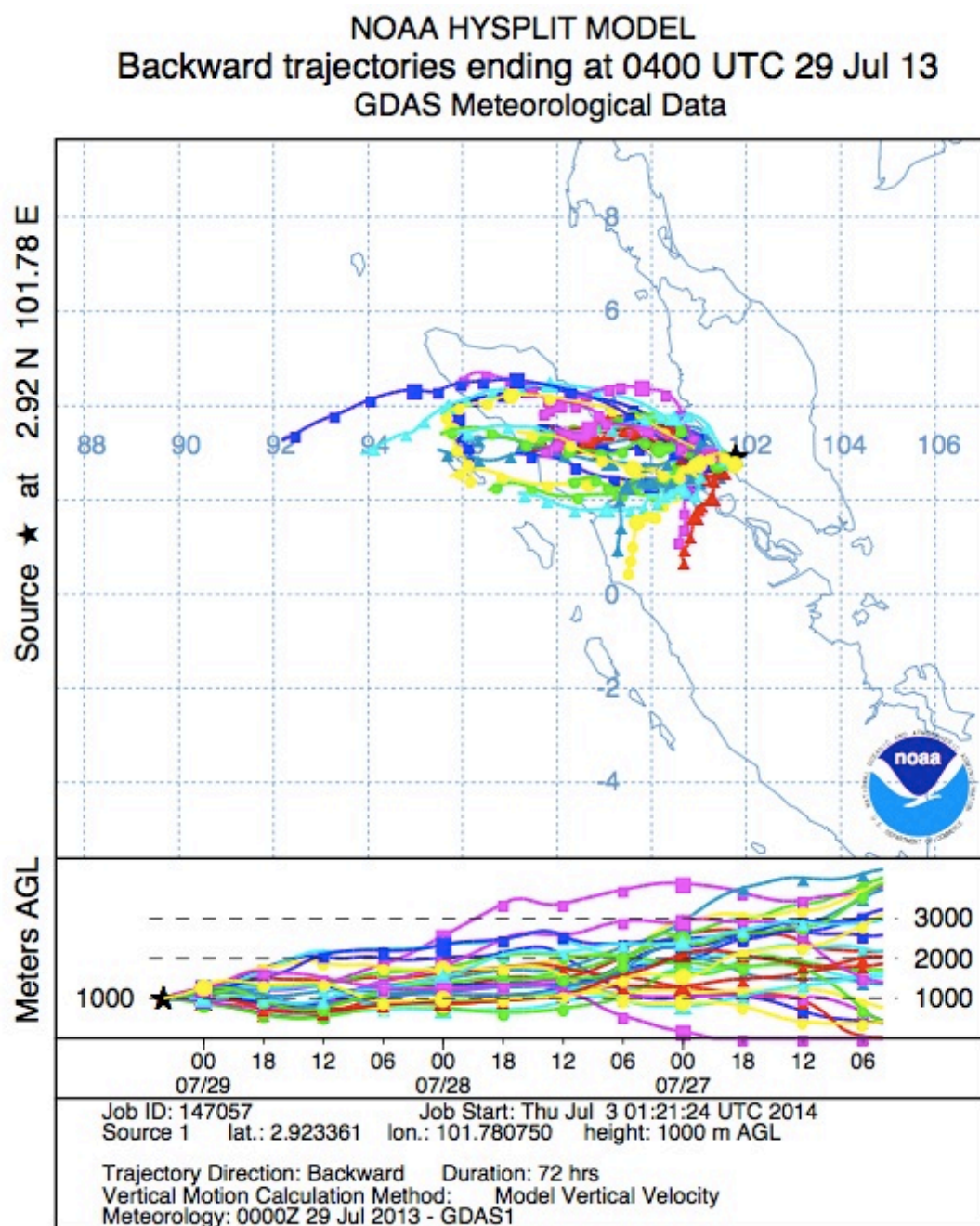


Figure 7.5 Backward trajectories of air masses for sampling site in Bangi on July

7.3.3 Health Risk Assessment

A. Carcinogenic and Mutagenic Potencies

In conventional risk assessments, the carcinogenic potency of a given congener was estimated on the basis of its Benzo(a)pyrene (B(a)P) carcinogenic equivalent concentration (BaPE), assessed by multiplying the ambient concentration of a congener by its Toxic Equivalency Factor (TEF) (Petry et al., 1996; Bostrom et al., 2002; USEPA, 2005). On the basis of these TEF-adjusted concentrations, the total carcinogenic potency $\sum\text{BaPE}$ was estimated as the sum of BaPE for all the congeners in a mixture, assuming that the carcinogenic effects of different congeners are additive (WHO, 2000; Vu et al., 2011). Similarly, just with the replacement of TEF with MEF (Mutagenic Equivalency Factors), the mutagenicity related to B(a)P (BaPMEQ) was calculated as well. Despite the mutagenic activities are associated to some adverse health effects, i.e. pulmonary diseases (DeMarini et al., 2004), they are not uniformly related to cancer (Zeiger, 2001).

The BaPE concentrations were computed applying the modified lists of TEFs provided by Nisbet and LaGoy (1992). The BaPMEQ values were calculated from MEFs proposed by Durant et al. (1996). The BaP-equivalent (BaPE and BaP-MEQ) concentrations calculated for $\sum\text{PAH}$ and individual PAH measured in this study are shown in Table 7.8. Values of $\sum\text{BaPE}$ and $\sum\text{BaPMEQ}$ were significantly higher in June compared to July with the reading of $2.96\text{E-}01\text{ng/m}^3$ and $4.39\text{E-}01\text{ng/m}^3$; respectively. For all sampled study, the largest contribution PAHs to $\sum\text{BaPE}$ in Jun and July were made by B(a)P ($1.26\text{E-}01\text{ng/m}^3$ and $1.15\text{E-}01\text{ng/m}^3$; accordingly). On the other hand, in June, both InPy and B(a)P showed the highest contribution of individual PAH to $\sum\text{BaPMEQ}$ ($1.08\text{E-}01\text{ng/m}^3$ and $1.26\text{E-}01\text{ng/m}^3$). Meanwhile in July, the contribution of B(a)P to $\sum\text{BaPMEQ}$ was substantially higher, making it the dominant compound contributing to $\sum\text{BaPMEQ}$. The results underline and confirm the importance of B(a)P as a surrogate compound for PAH mixture for ambient atmospheric particulate matter in Bangi.

The potential risk of PAHs exposure based on TEF or MEQ may be underestimated if the interactions of some PAHs are synergistic rather than additive. Chemical degradation of PAHs by ambient oxidants (ozone, hydroxyl radical, or nitrogen oxides) in the atmosphere as well as on the filters during sampling could also underestimate the potential risks due to reduced measured PAH levels, as shown in several studies (Schauer et al., 2003; Goriaux et al., 2006). In addition, PAHs collected on the filters may be decomposed through heterogeneous chemical reactions with ozone during an extended sampling period (Schauer et al., 2003; Tsapakis & Stephanou, 2003). Furthermore, nitrated/oxygenated PAH compounds have not been measured in this study, underestimating the full carcinogenic and mutagenic potential of PAHs exposure. Those PAH compounds formed by photochemical/chemical reactions are known to be more toxic than their parent PAH based on tumorigenicity of PAHs in a newborn mouse assay (Collins et al., 1998; Busby et al., 1989).

Table 7.8 BaP-equivalent carcinogenicity and mutagenicity risk assessed in Bangi

Month	PAHs	BaPE	MEQ
June	FLA	5.88E-05	-
	PYR	1.07E-04	-
	B(ghi)P	5.05E-03	9.60E-02
	B(a)An	3.17E-03	2.60E-03
	CHR	2.40E-04	4.07E-04
	B(b)Fl	2.98E-02	7.45E-02
	B(k)Fl	4.05E-03	4.45E-03
	B(a)P	1.26E-01	1.26E-01
	DiB(a,h)An	9.43E-02	2.73E-02
	InPy	3.49E-02	1.08E-01
	Σ	2.98E-01	4.39E-01
July	FLA	8.57E-06	-
	PYR	1.89E-05	-
	B(ghi)P	3.14E-03	5.97E-02
	B(a)An	1.46E-03	1.20E-03
	CHR	ND	ND
	B(b)Fl	1.83E-02	4.57E-02
	B(k)Fl	1.92E-03	2.11E-03
	B(a)P	1.15E-01	1.15E-01
	DiB(a,h)An	7.35E-02	2.13E-02
	InPy	2.41E-02	7.48E-02
	Σ	2.37E-01	3.19E-01

B. Exposure Assessment

The LADD carcinogenic values for inhalation and dermal exposure routes are displayed in Table 7.9 and Table 7.10, respectively. The values were later used to calculate the Incremental Lifetime Cancer Risk (ILTCR) for dermal exposure route.

The total LADD values through inhalation exposure for adult and children in June are 1.19E-08mg/kg/d and 4.960E-09mg/kg/d; respectively. Meanwhile, the total LADD values for adult and children in July are slightly lower than LADD values in June with readings of 9.40E-09mg/kg/d and 3.80E-09mg/kg/d; accordingly. In general, B(a)P recorded the highest LADD values for both adult and children with readings of 4.91E-09mg/kg/d and 1.77E-09mg/kg/d; 4.46E-09mg/kg/d and 1.61E-09mg/kg/d; in June and July respectively. Apart from B(a)P, other PAHs compounds with relatively higher values were DiB(a,h)An, InPy, B(b)Fl and B(ghi)P. Comparison between LADD values among adult and children show relatively higher LADD values in non-carcinogenic PAHs types for children. However, in carcinogenic PAHs types, the LADD values for adult are higher than children for each PAHs compounds.

Table 7.9 Lifetime average daily dose (LADD) (mg/kg/day) for inhalation

Month	Type	PAHs	Adult	Children
June	Non-Carcinogenic	FLA	5.35E-12	9.62E-12
		PYR	9.69E-12	1.74E-11
		B(ghi)P	4.60E-10	8.27E-10
	Carcinogenic	B(a)An	1.24E-10	4.44E-11
		CHR	9.34E-12	3.36E-12
		B(b)Fl	1.16E-09	4.18E-10
		B(k)Fl	1.58E-10	5.68E-11
		B(a)P	4.91E-09	1.77E-09
		DiB(a,h)An	3.67E-09	1.32E-09
		InPy	1.36E-09	4.89E-10
		Σ	1.19E-08	4.96E-09
	Non-Carcinogenic	FLA	7.79E-13	1.40E-12
		PYR	1.72E-12	3.09E-12
		B(ghi)P	2.86E-10	5.14E-10
July	Carcinogenic	B(a)An	5.69E-11	2.05E-11
		CHR	ND	ND
		B(b)Fl	7.12E-10	2.56E-10
		B(k)Fl	7.49E-11	2.70E-11
		B(a)P	4.46E-09	1.61E-09
		DiB(a,h)An	2.87E-09	1.03E-09
		InPy	9.41E-10	3.39E-10
		Σ	9.40E-09	3.80E-09

The LADD values through dermal exposure for adult recorded the total of 6.90E-08 mg/kg/d in June and 5.47E-08 mg/kg/d in July. However, the total LADD values for children are relatively higher than adult with the total of 1.04E-07 mg/kg/d in June and 8.01E-08 mg/kg/d in July. Similar to the LADD values for inhalation exposure route, the highest LADD values through dermal exposure also hold by B(a)P in both months, for adult and children. The LADD values for B(a)P in adult are 2.97E-08mg/kg/d and 2.70E-08mg/kg/d; while for children are 3.90E-08mg/kg/d and 3.54E-08mg/kg/d; in June and July accordingly. In contrast with inhalation exposure routes, the dermal LADD values for children are relatively higher than adult for each of PAHs compounds; for both non-carcinogenic and carcinogenic PAHs types.

Table 7.10 Lifetime average daily dose (LADD) (mg/kg/day) for dermal

Month	Type	PAHs	Adult	Children
June	Non-Carcinogenic	FLA	4.04E-08	2.65E-07
		PYR	7.32E-08	4.80E-07
		B(ghi)P	2.54E-07	1.67E-06
	Carcinogenic	B(a)An	8.27E-09	1.08E-08
		CHR	6.26E-09	8.19E-09
		B(b)Fl	7.04E-08	9.22E-08
		B(k)Fl	9.55E-09	1.25E-08
		B(a)P	2.97E-08	3.90E-08
		DiB(a,h)An	2.02E-08	2.64E-08
		InPy	7.52E-08	9.85E-08
		Σ	6.90E-08	1.04E-07
	Non-Carcinogenic	FLA	5.89E-09	3.86E-08
		PYR	1.30E-08	8.50E-08
		B(ghi)P	1.58E-07	1.04E-06
July	Carcinogenic	B(a)An	3.81E-09	4.99E-09
		CHR	ND	ND
		B(b)Fl	4.31E-08	5.65E-08
		B(k)Fl	4.54E-09	5.95E-09
		B(a)P	2.70E-08	3.54E-08
		DiB(a,h)An	1.57E-08	2.06E-08
		InPy	5.20E-08	6.82E-08
		Σ	5.47E-08	8.01E-08

C. Inhalation Cancer Risk

Two different URBaP values were used in this study to estimate the inhalation cancer risk. One URBaP value (1.1×10^{-6} per ng/m^3) was derived from a rodent study (OEHHA, 1993) and another (8.7×10^{-5} per ng/m^3) was derived from an epidemiology study (WHO, 2000). Table 7.12 shows the estimated lifetime excess inhalation cancer risk per million people due to PAHs exposure during haze episode in Bangi for June and July.

Table 7.11 URBaP values used in this study

URBaP Values	Subjects	Sources
1.1×10^{-6} per ng/m^3	Rodent study	OEHHA, 1993
8.7×10^{-5} per ng/m^3	Epidemiology study	WHO, 2000

Table 7.12 Estimated inhalation cancer risks for PAHs using URBaP value from (OEHHA, 1993) and (WHO, 2000)

Month	PAHs	OEHHA	WHO
June	FLA	6.46E-11	5.11E-09
	PYR	1.17E-10	9.27E-09
	B(ghi)P	5.56E-09	4.40E-07
	B(a)An	3.49E-09	2.76E-07
	CHR	2.64E-10	2.08E-08
	B(b)Fl	3.28E-08	2.59E-06
	B(k)Fl	4.45E-09	3.52E-07
	B(a)P	1.39E-07	1.10E-05
	DiB(a,h)An	1.04E-07	8.20E-06
	InPy	3.84E-08	3.03E-06
	Σ	3.27E-07	2.59E-05
July	FLA	9.42E-12	7.45E-10
	PYR	2.08E-11	1.64E-09
	B(ghi)P	3.46E-09	2.73E-07
	B(a)An	1.61E-09	1.27E-07
	CHR	ND	ND
	B(b)Fl	2.01E-08	1.59E-06
	B(k)Fl	2.11E-09	1.67E-07
	B(a)P	1.26E-07	9.96E-06
	DiB(a,h)An	8.09E-08	6.40E-06
	InPy	2.66E-08	2.10E-06
	Σ	2.61E-07	2.06E-05

Using a URBaP value of 1.1×10^{-6} per ng/m^3 from OEHHA (1993), the average estimated inhalation cancer risk associated with $\Sigma\text{PAH}_{10}\text{-BaPe}$ exposure during haze is $3.27\text{E-}07$ and $2.61\text{E-}07$; in June and July, respectively. Hence, the estimated cancer risk for a lifetime of 70 years is 0.32 cancer cases per million people in June and 0.26 cancer cases per million people in July that will be attributable to inhalation of $\text{PM}_{2.5}$ bound PAHs. Of the individual PAHs, DiB(a,h)An and B(a)P contributed the most to the estimated inhalation cancer risk in June with the reading of $1.04\text{E-}07$ and $1.39\text{E-}07$; respectively. Meanwhile, in July, B(a)P ($1.26\text{E-}07$) contributed the most of the estimated inhalation cancer risk. On the whole, the risk induced by PAHs derivatives should not be neglected, and more research is required to better understanding and control their health effect on human health.

Alternatively, if URBaP value of 8.7×10^{-5} per ng/m³ from WHO (2000) is used, the average estimated inhalation cancer risks due to Σ PAH10-BaPe during June and July period were 2.59E-05 and 2.06E-05; respectively. Thus, the inhalation cancer is 25 cancer cases per million people in June and 20 cancer cases per million people in July for an average lifetime of 70 years. For both all sample studied in June and July, the largest contribution of individual PAHs to the estimated inhalation cancer risk was made by B(a)P. Therefore, when using the value from epidemiology study, the value of inhalation cancer risk greatly increased but still below the health based guideline of 10^{-5} .

It is important to note that the response among various subpopulations to the carcinogenic potential of PAHs is not uniform. This differential response can be the result of genetic factors, such as polymorphisms in glutathione S-transferases that alter the capacity to metabolize PAH compounds (Hecht, 1999) or variants in cytochrome P450 genes (Ishibe et al., 1998). Behavioral factors such as smoking are relevant to individual risk, given the strong association between smoking and PAH-DNA adducts (Shantakumar et al., 2005). Occupation is another important consideration for an individual's cancer risk due to PAH exposure (Boffetta et al., 1997). The carcinogenic risk to individuals or subpopulations that have genetic, behavioral, or occupational issues that increase their susceptibility to PAHs may be underrepresented by this assessment.

Like previous inhalation cancer risk assessments, this assessment has uncertainties and limitations. First, the point-estimate approach assumes additive cancer risk. This approach may not be entirely accurate, but it is the currently accepted approach for assessing inhalation cancer risk due to PAH exposure (Collins et al., 1998; OEHHA, 2003). On top of that, the TEF values used to calculate the BaPE concentration for the individual PAHs are estimates based on toxicology studies that subject from additional uncertainties. In addition, the inhalation cancer risk models used assume a lifetime of exposure. Finally, the result was extrapolated to all of Bangi the PAH concentrations in PM_{2.5} collected from a single, representative site in Bangi.

D. Dermal Incremental Lifetime Cancer Risk (ILTCR)

The incremental lifetime cancer risk for dermal due to exposure to PAHs was shown in Table 7.13. The ILTCR value for dermal contact associated with Σ PAH10-BaPE in June for adult is 2.1 cancer cases per million people, compared with 3.1 cancer cases per million people exposure for children. The dermal cancer risks due to Σ PAH10-BaPE exposure during July were 1.6 cancer cases per million people for adult and 2.4 cancer cases per million people for children respectively. B(a)P contributed the most to the estimated cancer risk due to dermal contact in both adult and children during in the month of June and July. Nevertheless, compared to adults, children are more vulnerable to the effects of dermal contact to particulate matter bound PAHs. This is probably due to the higher skin surface area and more permeable, especially newborns which lead to the higher dermal absorption of PAHs.

All the calculated values for ILTCR due to dermal contact were within the USEPA acceptable level. It also showed that the dermal contact exposure route is one of the major contributor lifetime cancer risks for people in Bangi. Concerning the individual toxicity of the target PAHs, the compounds that contributed most to the total estimated risk was B(a)P, which were associated with vehicular emissions. Thus, the cancer risk associated with the exposure to PAHs emitted from vehicle emissions is not negligible and should be taken into account for health protection in the future.

However, it should be noted that the risk estimates presented are very uncertain. Numerous meteorological and PAHs source type factors may influence the PAHs concentration and profile in different areas of Bangi that would not be reflected in this point-estimate approach. The limitations and assumptions used in this risk assessment model may result in an over- or underestimate of risk to the Bangi population.

Table 7.12 Incremental Lifetime cancer risk (ILCTR) due to dermal contact of PAHs

Month	PAHs	Adult	Children
June	FLA	1.23E-09	8.07E-09
	PYR	2.23E-09	1.46E-08
	B(ghi)P	7.76E-08	5.08E-07
	B(a)An	2.52E-08	3.30E-08
	CHR	1.91E-09	2.50E-09
	B(b)Fl	2.15E-07	2.81E-07
	B(k)Fl	2.91E-08	3.82E-08
	B(a)P	9.07E-07	1.19E-06
	DiB(a,h)An	6.15E-07	8.06E-07
	InPy	2.29E-07	3.01E-07
	Σ	2.10E-06	3.18E-06
July	FLA	1.80E-10	1.18E-09
	PYR	3.96E-10	2.59E-09
	B(ghi)P	4.82E-08	3.16E-07
	B(a)An	1.16E-08	1.52E-08
	CHR	ND	ND
	B(b)Fl	1.32E-07	1.72E-07
	B(k)Fl	1.38E-08	1.81E-08
	B(a)P	8.25E-07	1.08E-06
	DiB(a,h)An	4.80E-07	6.29E-07
	InPy	1.59E-07	2.08E-07
	Σ	1.67E-06	2.44E-06

7.4 Conclusion

Diagnostic ratio of individual PAHs is applied to determine the sources of PAHs in ambient particulate matter. From the result it can be concluded that the concentrations of deposited PAHs and contamination in the study indicate the mixed of petrogenic origin, vehicles emission and biomass burning as the main sources of PAHs in Bangi ambient atmospheric particulate matter. The backward trajectories showed that, during the haze event, the origins of air mass are normally located at low latitudes in the Indian Ocean. It follows the southwest monsoon direction through Sumatera, Java Sea and other areas impacted by peat and forest fires before arriving in Malaysia.

Values of $\sum\text{BaPE}$ and $\sum\text{BaPMEQ}$ were significantly higher in June compared to July with the reading $2.98\text{E-}01\text{ng/m}^3$ to $2.37\text{E-}01\text{ng/m}^3$ and $4.397\text{E-}01\text{ng/m}^3$ to $3.197\text{E-}01\text{ng/m}^3$; respectively. The largest contribution PAHs to $\sum\text{BaPE}$ in Jun and July were made by B(a)P ($1.26\text{E-}01\text{ng/m}^3$ and $1.15\text{E-}01\text{ng/m}^3$; accordingly). On the other hand, both B(a)P and InPy showed the highest contribution of individual PAH to $\sum\text{BaPMEQ}$ with readings of $1.26\text{E-}01\text{ng/m}^3$ and $1.08\text{E-}01\text{ng/m}^3$ (June) and $1.15\text{E-}01\text{ng/m}^3$ and $7.48\text{E-}02\text{ng/m}^3$ (July). The results emphasize and confirm the importance of B(a)P as a surrogate compound for PAH mixture for ambient atmospheric particulate matter in Bangi.

Using a URBaP value of 1.1×10^{-6} per ng/m^3 , the estimated cancer risk for a lifetime of 70 years is 0.32 cancer cases per million people in June and 0.26 cancer cases per million people in July will be attributable to inhalation of $\text{PM}_{2.5}$ bound PAHs. Of the individual PAHs, B(a)P ($1.39\text{E-}07$) and DiB(a,h)An ($1.04\text{E-}07$) in June and B(a)P ($1.26\text{E-}07$) in July contributed the most to the estimated inhalation cancer risks. Alternatively, with URBaP value of 8.7×10^{-5} per ng/m^3 , the inhalation cancer is 25 cancer cases per million people in June and 20 cancer cases per million people in July for an average lifetime of 70 years. For all sample studied, the largest contribution of individual PAHs to the estimated inhalation cancer risk in June and July was made by B(a)P. Thus, when using the value from epidemiology study, the value of inhalation cancer risk greatly increase but within acceptable level of 8.7×10^{-5} .

The ILTCR value for dermal contact associated with $\sum\text{PAH10-BaPE}$ in June for adult is 2.1 cancer cases per million people, compared with 3.1 cancer cases per million people exposure for children. The dermal cancer risks due to $\sum\text{PAH10-BaPE}$ exposure during July were 1.6 cancer cases per million people for adult and 2.4 cancer cases per million people for children respectively. Both B(b)Fl and B(a)P contributed the most to the estimated cancer risk due to dermal contact in both adult and children during in the month of June and July. All the calculated values for ILTCR due to dermal contact were within the USEPA acceptable level.

CHAPTER 8

DETERMINATION OF BENZO(A)PYRENE DIOL EPOXIDE ADDUCTS IN HUMAN PLASMA EXPOSED TO PAHs

8.1 Introduction

PAHs have been of increasing concern in human health due to their wide spread dispersion in the environment and the adverse health effects associated with PAHs exposure such as carcinogenesis and endocrine disruption. Inhaled PAHs are absorbed mainly through the bronchial epithelium. Absorption can be influenced by the size of the particles, with a slower clearance of those adsorbed on particles compared to PAHs in pure crystals (Gastano-Vinyals et al., 2004).

Investigating the significance of specific PAHs in air pollution related lung cancer is very difficult. This is because environmental exposures to PAHs tend to be very low and many potential confounding sources of PAHs are known to exist (e.g. diet and environmental tobacco exposure (ETS), including seasonal variations in air levels). Therefore, the use of biomarkers is very important as they can help to reduce misclassification of exposure, provide information on uptake and early biological changes and ultimately increase the power of epidemiological studies to detect cancer risks at environmental levels. Biomarkers to assess exposure to PAHs at high levels are well studied, but more work is needed to validate these biomarkers when exposure occurs at low, environmental levels.

The most common compound used as a reference substance for carcinogenic PAHs is benzo(a)pyrene (B(a)P). B(a)P was the first PAH recognised to display carcinogenic activity; more importantly, it has a high carcinogenic potency and is present in all environmental media (Gastano-Vinyals et al., 2004). The ultimate carcinogens derived from B(a)P metabolism are the isomeric benzo(a)pyrene-diol-epoxides (BPDEs) which bind to DNA, proteins, and other macromolecules to form adducts. Adducts of the BPDEs accumulate in blood and can be used as biomarkers of exposure to B(a)P and other PAHs from the same source (Tang et al., 2001).

Although DNA adducts of BPDE have been widely investigated in human populations as measures of genetic damage in human cells, adducts of BPDE with human serum albumin (HSA) have also been detected (Lee et al., 1991). This is because HSA is much more abundant than DNA in blood (30 mg HSA/mL opposed to 0.003–0.008 mg DNA/mL). In addition HSA adducts are not repaired, thus HSA adducts have inherent advantages over DNA adducts as measures of exposure for epidemiologic studies (Tornqvist et al., 2002). However, it should be noted here that they may not be strictly proportional to genetic damage in target organs. Furthermore, stable HSA adducts have a mean residence time of 28 days in humans, which is sufficiently long to damp the day-to-day variability in exposure often observed in human studies (Lin et al., 2005). Yet, despite the relative advantages of BPDE-HSA adducts as biomarkers of exposure to PAHs, these adducts have rarely been used in epidemiologic studies.

8.2 Metabolism of Benzo(a)pyrene

PAHs carcinogenicity is dependent on the activation of PAHs compounds by organic enzymes. Once activated, these compounds are able to induce molecular alterations (mutation in target genes) and cellular alterations (chromosomal aberration). Once entering the human body, PAHs are metabolically transformed to carcinogenic forms. Figure 8.1 highlights the critical step in B(a)P activation and detoxification that occurs in human body.

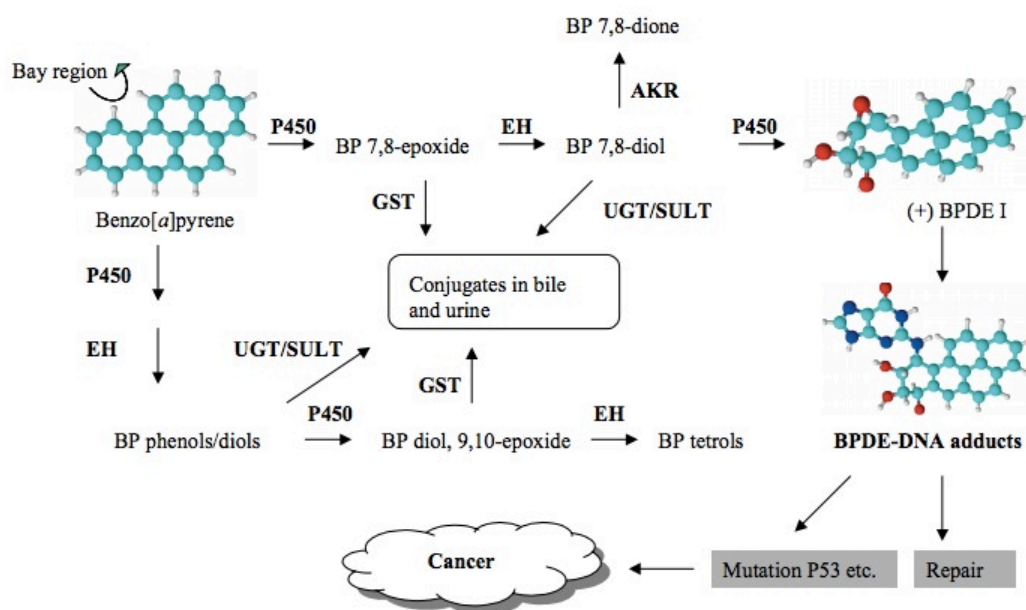


Figure 8.1 Carcinogenic activation and detoxification of benzo(a)pyrene

B(a)P must be bioactivated by enzymes such as cytochrome P-450; which is the essential step in the mechanism in order to acquire its mutagenic and carcinogenic properties (Lieber, 2008; Gelbon, 1980). Cytochrome P450 (CYP) enzymes in a combination with epoxide hydrolase are the major enzymes activating B(a)P to species binding to DNA and protein. The cytochrome P450s (CYPs) superfamily consists of a large number of haem-containing mono-oxygenases that play a pivotal role in the metabolism of many drugs and carcinogens (Nebert & Dalton, 2006). The metabolism of B(a)P is complex as the B(a)P compound has many reactive sites. Oxygen can be substituted in every site forming epoxides. The bay region in the B(a)P molecule is the sterically hindered region formed by the angular benzo ring. The bay-region diol epoxides were found to be more chemically reactive and resistant by hydrolysis by mEH and hence important in DNA/protein binding and tumorigenesis (Conney, 1982; Sayer et al., 1991)

The first step in the metabolic activation of B(a)P is the formation of the B(a)P-7,8-oxide, followed by the microsomal epoxide (mEH) to the benzo(a)pyrene-7R-Trans-7,8 dihydrodiol (7,8 diol) metabolite. This metabolite is further metabolize by P-450 to the mutagenic benzo(a)pyrene-r-7,8-t-dihydrodiol-t-9,10-epoxide, also known as BPDE. These BPDE is extremely reactive and can bind to macromolecules such as DNA, RNA and protein (Kim et al., 1998).

B(a)P is metabolized to various products by the xenobiotic metabolizing enzymes. These enzymes are divided into phase I and phase II enzymes. The microsomal P450 phase I enzymes produce a complex mixture of quinones, phenols, dihydrodiols, triols, pentols but also reactive epoxides (Guengerich, 2000). The phase II enzymes glutathiontransferase, glucuronosyltransferase and sulfotransferase (SULT) will further act on the oxidized products from the phase I step, and form conjugates of glutathione, glucoronide and sulphate. The formation of highly polar and water-soluble metabolites increases the excretion of BP from the body into urine and bile. The conjugated PAHs are not able to bind to DNA and protein. Therefore, the phase II enzymes play important roles in facilitate excretion and protecting the cell from mutation.

8.3 METHODOLOGY

8.3.1 Samples Collection

In this study, whole blood samples were obtained among pregnant women who are receiving antenatal care at the Department of Obstetrics & Gynecology University Malaya Medical Center, Kuala Lumpur. The procedures for the study were explained to the participant after whom oral informed consents were obtained. The protocol for the study has been approved by the Ethics and Research Committee of University Malaya Medical Center, Kuala Lumpur. Only non-smoking pregnant women were included in this study. The study is conducted in accordance with this protocol, relevant in house Standard Operating Procedures (SOPs), Malaysian Guidelines for Good Clinical Practice and 'Declaration of Helsinki'. The whole blood was collected once at recruitment during 8:00 – 10:00 hours into EDTA tube to prevent blood samples from coagulation. The samples were centrifuge for 7 min at 3500 rpm to separate the blood plasma from red blood cells. The blood plasma was collected and stored in a freezer - 20°C prior to analysis.

8.3.2 BPDE Protein Adduct Procedure

A. Assay Principle

In this study, the OxiSelect BPDE Protein Adduct ELISA kit was used as enzyme immunoassay for rapid detection of BPDE protein adducts. Bovine Serum Albumin (BSA) or protein samples are adsorbed onto a 96-well plate for 2 hours at 37°C. The BPDE protein adducts present in the sample or standard are probed with an Anti-BPDE-I Antibody, followed by an HRP Conjugated Secondary Antibody. The BPDE protein adduct content in an unknown sample is determined by comparing with a standard curve that is prepared from predetermined BPDE-BSA standards.

B. Assay Protocol

100 µl of diluted protein samples was added to the 96-well Protein Binding Plate and incubated at 37°C for at least 2 hours or 4°C overnight. After that, the wells were wash with 250µL 1X PBS per well. The last wash, the wells were emptied and microwell strips were tap on absorbent pad or paper towel to removed excess wash solution. Next, 200µL of Assay Diluent was added per well and incubated for 1-2 hours at room temperature on an orbital shaker. The wells after that were washed 3

times with 250µL of 1X Wash Buffer with through aspiration between each wash. Similarly, any excess of wash buffer were removed. 100µL of the diluted Anti-BPDE-I Antibody was added into all well and the plate was incubated again for 1 hour at room temperature on an orbital shaker. Then, the strips were washed 5 times similar with previous step. 100µL of Substrate Solution was added into each well and incubated at room temperature. The incubation period is varying from 2-30 minutes. During this process, if the color change were observed, the reaction was stopped immediately to prevent saturation. Then, 100 µL of Stop Solution was added to each well to stop the enzyme reaction. Soon after that, the absorbance was read immediately using microplate reader at 450nm as the primary wave length.

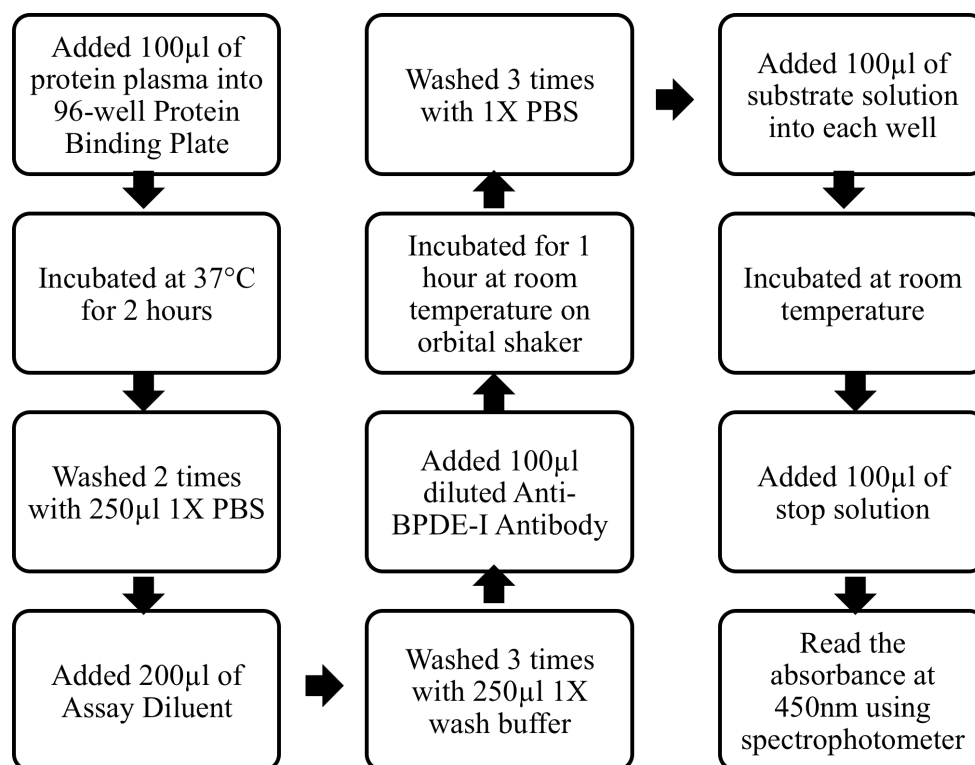


Figure 8.2 Assay protocol

8.4 RESULT AND DISCUSSION

Table 8.1 summarizes the parameters of atmospheric particulate matter (PM) in Klang Valley in June and July 2013. The total PAHs and B(a)P concentrations were calculated based on the average of concentrations of two months period reported from Bangi sampling site.

Table 8.1 Environmental parameters of atmospheric PM in Klang Valley

Parameters	Concentrations
Total PAHs in air ($\mu\text{g}/\text{m}^3$)	1.31
B(a)P in air (ng/m^3)	0.12

Figure 8.3 shows the variation of BPDE-HSA concentration of individual pregnant women participated in the study. Generally, there were two patients which have slightly higher concentration compared to the other patients. The observed highest concentrations were at 16.734 fmol/mg and 11.908 fmol/mg; respectively.

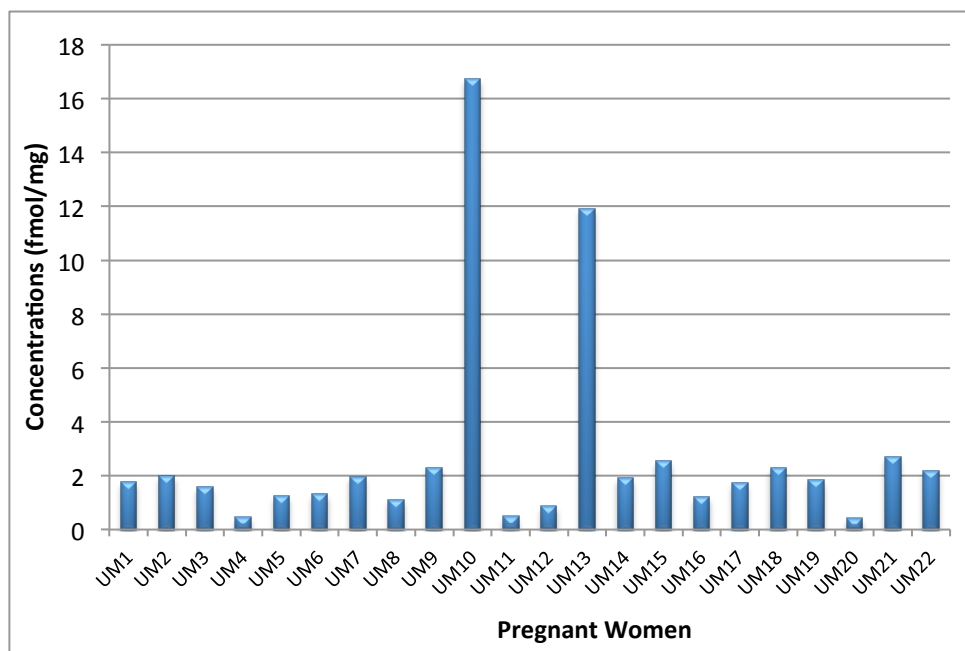


Figure 8.3 Concentrations of BPDE-HSA adduct levels in pregnant women

The two patients who have the highest concentration might be due to the influence of other lifestyle factors (dietary) and other potential confounding factors (second hand smoking). According to Suzuki & Yoshinaga (2007), diet is the main sources of PAHs exposure among individuals not exposed to high levels of tobacco smoke or with occupational sources. In addition to that, the patients might be exposed to PAHs as a second hand smoke from other people such as from their husband or co-workers. A cross sectional study demonstrated that passive smokers have higher levels of enzymes that increase with exposure to reactive oxygen species. Passive smokers had a significant 63% increase in 8-OHdG, a marker of DNA damage resulting from oxidative stress (Howard et al., 1998). On top of that, it was also suggested that inter individual of biotransformation of B(a)P might represent the factor for large range of adduct level found. This was supported by the result of other study who reported large inter individual differences in PAHs transformation by several human tissues such as liver, skin and lung (Harris 1989; Vahakangas & Pelkonen, 1989).

Table 8.2 Concentrations of BPDE-HSA adduct levels in pregnant women

	Range (Min – Max) (fmol/mg)	Median (fmol/mg)	Mean (±SD) (fmol/mg)
Concentrations of BPDE-HSA adduct levels in pregnant women	(0.411 - 16.734)	2.444	2.742 (±3.876)

Table 8.2 explained the concentrations of BPDE-HSA adduct level in pregnant women of Klang Valley. Mean concentration was observed at 2.742 fmol/mg. BPDE-HSA adducts in this study was assumed to integrate exposure over a period of about 24 days based on the half life of human albumin. The result of this study was similar with concentrations observed among control group of study done by Tas et al. (1994). When comparing with the occupational exposure among workers from study done by Tas et al. (1994), the concentration observed in the present were significantly lower. A recent study by Chung et al. (2013) demonstrated that the BPDE-HSA value among healthy female of general population were 10.65 fmol/mg for smoking and 8.65 fmol/mg for non smoking. This result was significantly higher compared to the measured value from the present study. Previous study also observed higher adducts level in male general population including significantly effect of BPDE adduct level in smoking male (Cheng et al., 2013). Thus, it can be suggested that smoking is important sources of B(a)P exposure in the general population. Table 8.3 showed the BDPE-HAS level reported from other study.

A recent study done by Chen & Thilly (1996) demonstrated that the mutational spectra induced by benzo(a)pyrene in human lymphoblastoid cell line cytochrome P450 metabolic activation system was dependent upon the condition of exposure. A low concentration of benzo(a)pyrene and a long exposure time resulted in a different profile of mutations compared to a high concentrations and a short exposure time. These investigations emphasized that mutation studies at low studies are more related to human exposure conditions.

Table 8.3 BDPE-HSA level from other study

Characteristics	Mean (fmol/mg)	References
Occupational exposure		
• Control group	2.27	Tas et al., (1994)
• Exposed group	10.50	
Female general populations		
• Nonsmokers	10.65	Chung et al., (2013)
• Smokers	8.65	
Male general populations		
• Nonsmokers	7.94	Chung et al., (2013)
• Smokers	14.12	

In this study, the airborne PAHs may not contribute more to the concentration of protein adducts. Perhaps PAH exposure from other means such as through diet may contribute significantly to the concentration of protein adducts. However, it should be noted here that, exposure of fetus to environmental PAHs can occur via transplacental from the mother. A study reported by Klopov (1998) of pregnant women in the Russian Arctic region found substantial maternal exposure to PAHs, with PAHs were observed in both cord blood and placenta. The results support the barrier role of the placenta, because levels of many PAH compounds in cord blood were lower than in maternal blood. Nevertheless, these compounds were passing through the placental barrier, at least partially, with the concentrations of some PAHs (anthracene and benzo[a]pyrene) higher in cord blood than in maternal blood. On the other hand,

Autrup et al. (1995) and Autrup & Vestergaard (1996) measured the polycyclic aromatic hydrocarbon-albumin adduct level in serum isolated from the mother and the umbilical cord. It was found that, the median maternal/fetal adduct ratio was approximately 1.3 (maternal blood/umbilical cord blood) and a positive association between the adduct levels in the mother and umbilical cord blood was observed.

8.5 CONCLUSION

In summary, the concentrations of BPDE-HSA adducts found are relatively small compared to the reported value from other studies. Thus, the exposure of airborne B(a)P during haze among is still low among pregnant women in Klang Valley. Although, the BPDE adducts level is lower, no threshold for dose response relationship appears to be exit for PAHs. Therefore, no absolutely safe levels could be established for these compounds.

In addition to that, human populations are commonly exposed to low levels of PAHs carcinogens. Some study, proved that even at low concentrations with long exposure time resulted in mutations cell. Thus, it is to highlight that even at low concentrations of carcinogens/mutagens are more relevant to human exposure.

CHAPTER 9

CONCLUSION AND RECOMMENDATIONS

9.1 CONCLUSION

Concentration and Size Distributions of Atmospheric Particulate Matter

In this study, the analysis of the size and concentration distribution of the airborne particles and associated metals were determined from samples collected from urban and semi urban areas in Malaysia. The results indicate that, Petaling Jaya recorded the higher mean concentrations for all particles size group compared to Bangi. Similarly, the 24-h TSP levels in Petaling Jaya were higher compared to Bangi with the concentrations $79.48\mu\text{g}/\text{m}^3$ and $22.66\mu\text{g}/\text{m}^3$; respectively. The 24-h TSP level in Bangi is below the guideline set by WHO and USEPA standard value, while the average 24-h TSP in Petaling Jaya was found to be significantly higher than USEPA standard value. In addition, the TSP values obtained for both sampling site in Bangi and Petaling Jaya were still well below the Recommended Malaysian Air Quality Guideline (RMAQG) for TSP. Particles size of $<0.49\mu\text{m}$ contribute more than 50% of total PM concentrations in both locations; which is 68% in Bangi and 55% in Petaling Jaya. The result clearly showed that fine particles dominated the overall of percentage PM concentrations in both locations.

Among the trace metals that were studied, Cr in Bangi and Sr in Petaling Jaya have recorded an outstanding higher concentrations than other trace elements in their groups, in all particle sizes; except for Sr in Petaling Jaya for particle size $<0.49\mu\text{m}$. Cr in Bangi and Sr in Petaling Jaya recorded the highest concentrations for particle sizes of $<0.49\mu\text{m}$ and $0.49\text{-}0.95\mu\text{m}$; respectively. Meanwhile, apart from Cr and Sr; Cu, Li, Mn, Ni and Pb show almost similar trends of moderate concentrations in all particles size groups; except for Cu in particle size $<0.49\mu\text{m}$, which shows relatively higher concentrations for both locations. On the other hand, other trace elements such as Ag, Co and Cd recorded relatively lower concentrations in all particle sizes compared to other trace elements. The size distributions of elements in atmospheric aerosols may have resulted from a combination of processes including local anthropogenic and natural sources, long-range transport and re-suspension.

In both locations, the average concentrations of fine particles are higher than the coarse particles. In addition, the average concentrations of PM for size (coarse and fine) in Petaling Jaya are higher compared to Bangi. In the coarse mode aerosols, high concentrations of Cr ($21.88\text{ ng}/\text{m}^3$) and Sr ($10.96\text{ ng}/\text{m}^3$) were found in Bangi. On top of that, the chemical composition of PM coarse is found to have higher concentration of Sr ($18.74\text{ ng}/\text{m}^3$), Mn ($8.58\text{ ng}/\text{m}^3$), Cu ($7.94\text{ ng}/\text{m}^3$) and Cr ($6.34\text{ ng}/\text{m}^3$) than other elements in Petaling Jaya. In the case of PM fine, the Cr, Sr and Cu showed higher concentration in Bangi with the reading of $32.49\text{ ng}/\text{m}^3$, $8.46\text{ ng}/\text{m}^3$ and $7.75\text{ ng}/\text{m}^3$; respectively. Meanwhile in Petaling Jaya, the results indicate the abundance of Sr, Cu, and Cr with the recorded concentration $18.05\text{ ng}/\text{m}^3$, $12.27\text{ ng}/\text{m}^3$ and $8.31\text{ ng}/\text{m}^3$; accordingly.

Principle Component Analysis (PCA) and Risk Assessment of Trace Elements in Atmospheric Particulate Matter

At Bangi sampling site, the observed result show two possible factor representing different contributing sources for airborne elements. Factor 1 explain 89.4% of total varians of the data and has high loading for Ag (0.994), Cd (0.967), Co (0.978), Cu (0.995), Li (0.993), Mn (0.988), Ni (0.997) and Pb (0.986), which can be identified as vehicles emission/oil combustion, re-suspended dust/brake emission and industry emission. The factor 2 with 9.01% of total varians is solely related to Sr (0.903); indicated their origin from soil as it is contain typical elements from crustal origin. At Petaling Jaya sampling site, 88.38% varians of the data was observed in factor 1. High loading of Ag (0.989), Cd (0.951), Co (0.891), Cr (0.993), Cu (0.994), Li (0.987), Mn (0.789), Ni (0.988), Pb (0.836) and Sr (-0.955) indicates that the contributing sources in factor 1 of Petaling Jaya are similar to the factor 1 of the Bangi site. Factor 2 with total varians 10.96% and considerable contributions from Co, Mn and Pb may be due to industrial/re-suspension.

Backward trajectories of Bangi showed that the trajectories mostly start over the Pacific Ocean and directly move westward through the South China Sea, passing the Sulu Sea before arriving to the south of Klang Valley (Bangi). Based on its pathway and origin, this air mass is expected to bring in relatively clean air from the Pacific Ocean to the Klang Valley. Meanwhile, backward trajectories of Petaling Jaya showed that most of the wind came from the Malacca Straits during southwest monsoon. Peninsular Malaysia has been affected by severe smoke haze due to forest fires in the region periodically. With its pathways above the populated areas, and short passages over the sea, these air masses have a potential to bring in the long-range transport air pollution to the Malaysia.

The non-carcinogenic risk assessment in terms of Hazard Quotient (HQ) and Hazard Index (HI) were calculated according to exposure to particulate bound metals. Based on the result, it was found that inhalation is an important pathway of for exposure to trace elements in the circumstance of particulate matter in Bangi and Petaling Jaya. HQ for non-cancer risk due to dermal contact of particulate matter is in lower magnitude and it is unlikely that this exposure route would pose a higher risk than inhalation. For both sampling location Bangi and Petaling Jaya the same trend of result were observed. Inhalation of particles appeared to have much higher risk for Cr, Co and Mn, which were one to three orders of magnitude higher than the corresponding risks of the dermal exposure route. In contrast for Cr compared to other elements, dermal contact showed some tendency to be the main exposure route that might results in some risk. Regarding non-cancer effects, all trace elements exhibit Hazard Index lower than safe level (1). In comparison to the children and adult cases, the inhalation and dermal exposure route has higher values for children than that for adult and hence the overall values of risk are higher than adult.

For cancer risk, the only carcinogen risk for inhalation exposure model was considered. In this study, the incremental lifetime cancer risk (ILCR) for Cr, Pb, Cd, Ni, and Co was calculated the see the probability getting cancer from the exposure of ambient atmospheric particulate matter. Cr has the highest ILTCR values among all the carcinogens. In Bangi, the estimate Cr risk values for adult were 3.50E-05 (coarse mode) and 5.19E-05 (fine mode); while for children the values were 1.26E-05 (coarse

mode) and $1.87\text{E-}05$ (fine mode). Similarly, the Cr ILTCR values in Petaling Jaya for adult were $1.01\text{E-}05$ (coarse mode) and $1.33\text{E-}05$ (fine mode); as for the children were $3.65\text{E-}06$ (coarse mode) and $4.78\text{E-}06$ (fine mode). Therefore, it can be confirmed that exposure to Cr is quite a serious problem in respect for both adult and children population in Bangi and Petaling Jaya.

The risk assessment suggested that there was an acceptable potential adverse health effects for adult and children in both localities (Bangi and Petaling Jaya) caused by particulate metals except for Cr. Although generally probability developing cancer risk is low, it was thus clear that the exposure of resident lived nearby study area to the coarse and fine particles with toxic contents should be of special concern for certain trace elements

Determination of Trace Elements in Whole Blood

Several whole bloods were analyzed by means TXRF after simple dilution. It can be concluded analysis of the nutrition relevant elements by simple dilution with ultrapure water is sufficient. From the TXRF analysis, no unusual toxic elements have been found in this study that could be due exposure from various environmental pollutants. Only important trace elements that are micronutrients required in the body for its normal function especially through various enzymes, hormones, vitamins etc. were found in the pregnant women in the present study.

Generally, all the trace elements detected in this study are lower in concentration compared to the concentration from the literature value. The result is consistent with other researcher that indicates the nutritional level of elements Zn, Cu, Fe, Ca and K are in lower compared to non-pregnant women. The result showed that trace elements such as zinc, copper, calcium and other elements have significant influences on the health of pregnant women and growing fetus. Deficiency of each one gives rise to specific clinical feature. Based on the result, It can be said that exposure of pregnant women in Kuala Lumpur from environmental pollutants still in the safe limit.

PAHs Composition in Atmospheric Particulate Matter

The average Σ PAH concentrations for June and July were recorded at $1.63 \pm 0.16 \text{ ng/m}^3$ and $0.99 \pm 0.11 \text{ ng/m}^3$, respectively. It can be seen that the Σ PAH concentrations in June was higher than July, with a total difference of 0.64 ng/m^3 between the two months. This finding could be caused by an impact of first haze episode in June, which was the peak of haze in Malaysia; together with the influences of localized emission from motor vehicles. These concentrations are on the lower side compared to the data obtained from other places. B(ghi)P contribute the highest percentage of total PAHs concentrations with readings of 0.51 ng/m^3 (19.3%) in June and 0.31 ng/m^3 (12.0%) in July. This indicated that Benzo (g,h,i) perylene could be contributed from diesel or gasoline powered vehicles.

According to present study, indicated that six ringed PAHs were predominant observed followed by five and four ringed forms respectively. In June, 52 % of PAHs are six ringed, followed by 34% five ringed and 14% of four ringed. Similar trend was observed in July where 56% are six ringed, followed by 40% five ringed and 4% of four ringed. This suggests that PAH residues found in this study may have all

originated from the combustion of gasoline and diesel fuel.

The result also indicated that 61% of the total PAHs found in this study area for June and July are carcinogenic PAHs whereas 39% are non-carcinogenic PAHs. For carcinogenic compound of PAHs, Indeno[1,2,3-cd]pyrene indicated the highest concentrations for both June and July with $0.35 \pm 0.19 \text{ ng/m}^3$ and $0.24 \pm 0.17 \text{ ng/m}^3$ respectively. Meanwhile, for non-carcinogenic, Benzo (g,h,i) perylene showed the highest concentration for both June and July with the concentrations $0.51 \text{ ng/m}^3 \pm 0.39$ and $0.31 \pm 0.24 \text{ ng/m}^3$, respectively. The abundance of Benzo (g,h,i) perylene among the identified PAHs at sampling sites indicates the high contributions from gasoline powered vehicles.

At present, there are no ambient air quality standards for PAHs in Malaysia. Therefore, the concentration of PAHs mainly Benzo(a)pyrene was compared the Dutch National Institute of Public Health and the Environment (DNIPHE) guideline. It was found that, the Benzo(a)pyrene concentrations in Bangi (0.13 ng/m^3) was lower than the DNIPHE maximum permissible concentration.

Diagnostic Ratio and Risk Assessment of PAHs in Atmospheric Particulate Matter

Diagnostic ratio of individual PAHs is applied to determine the sources of PAHs in ambient particulate matter. From the result it can be concluded that the concentrations of deposited PAHs and contamination in the study indicate the mixed of petrogenic origin, vehicles emission and biomass burning as the main sources of PAHs in Bangi ambient atmospheric particulate matter. The backward trajectories showed that, during the haze event, the origins of air mass are normally located at low latitudes in the Indian Ocean. It follows the southwest monsoon direction through Sumatera, Java Sea and other areas impacted by forest and peat fires before arriving at Malaysia.

Values of ΣBaPE and ΣBaPMEQ were significantly higher in June compared to July with the reading $2.96\text{E-}01 \text{ ng/m}^3$ and $4.39\text{E-}01 \text{ ng/m}^3$; respectively. The largest contribution PAHs to ΣBaPE in Jun and July were made by B(a)P ($1.26\text{E-}01 \text{ ng/m}^3$ and $1.15\text{E-}01 \text{ ng/m}^3$; accordingly). On the other hand, in June, both InPy and B(a)P showed the highest contribution of individual PAH to ΣBaPMEQ ($1.08\text{E-}01 \text{ ng/m}^3$ and $1.26\text{E-}01 \text{ ng/m}^3$). The results emphasize and confirm the importance of B(a)P as a surrogate compound for PAH mixture for ambient atmospheric particulate matter in Bangi.

Using a URBaP value of 1.1×10^{-6} per ng/m^3 , the estimated cancer risk for a lifetime of 70 years is 0.32 cancer cases per million people in June and 0.26 cancer cases per million people in July will be attributable to inhalation of $\text{PM}_{2.5}$ bound PAHs. Of the individual PAHs, DiB(a,h)An and B(a)P contributed the most to the estimated inhalation cancer risk in June with the reading $1.04\text{E-}07$ and $1.39\text{E-}07$; respectively. Meanwhile, in July, B(a)P ($1.26\text{E-}07$) contributed the most of the estimated inhalation cancer risk.

Alternatively, if URBaP value of 8.7×10^{-5} per ng/m^3 , the inhalation cancer is 25 cancer cases per million people in June and 20 cancer cases per million people in July

for an average lifetime of 70 years. For all sample studied in June and July, the largest contribution of individual PAHs to the estimated inhalation cancer risk was made by B(a)P. Thus, when using the value from epidemiology study, the value of inhalation cancer risk greatly increased but still below the health based guideline of 10^{-5} .

The ILTCR value for dermal contact associated with Σ PAH10-BaPe in June for adult is 2.1 cancer cases per million people, compared with 3.1 cancer cases per million people exposure for children. The dermal cancer risks due to Σ PAH10-BaPe exposure during July were 1.6 cancer cases per million people for adult and 2.4 cancer cases per million people for children respectively. Both B(b)Fl and B(a)P contributed the most to the estimated cancer risk due to dermal contact in both adult and children during in the month of June and July. However, All the calculated values for ILTCR due to dermal contact were within the USEPA acceptable level.

Determination of Benzo(A)Pyrene Diol Epoxide Adducts in Human Plasma Exposed to PAHs

In summary, the concentrations of BPDE-HSA adducts found are relatively small compared to the reported value from other studies. Thus, the exposure of airborne B(a)P during haze among is still low among pregnant women in Klang Valley. Although, the BPDE adducts level is lower, no threshold for dose response relationship appears to be exit for PAHs. Therefore, no absolutely safe levels could be established for these compounds.

In addition to that, human populations are commonly exposed to low levels of PAHs carcinogens. Some study, proved that even at low concentrations with long exposure time resulted in mutations cell. Thus, it is to highlight that even at low concentrations of carcinogens/mutagens are more relevant to human exposure.

9.2 RECOMMENDATIONS

The result in this study shows that motor vehicles contribute to the quantity of trace elements and PAHs in the atmosphere. Vehicles growth is adding to the country air quality problems. Therefore, the management and emissions of motor vehicles need to be considered to develop a better urban environment in the future. Establishment of modern emission reduction technology demands an adequate supply of low sulphur fuel, with the levels of 50 or 10 ppm. In addition to that, new vehicles standard emission should been finalized for both diesel and petrol vehicles. In addition to that, the establishment of lower particle size national ambient standard is needed since the fine particle observed in this study was the predominant particulate matter observed in ambient air.

As transboundry atmospheric pollutants caused by vegetation burning happened almost every year, thus the utilization of information technology to provide haze related information to relevant agencies as well as local citizen to prevent and control the spread of fire and enhanced public awareness on haze situation.

As part of this research investigation, a number of areas were identified for further investigation. These include:

- Further investigation includes the determination of trace elements and PAHs indoor in Klang Valley and compare between indoor and outdoor in study area.
- Undertaking road dust sampling to further refine the distributions and pathway of traffic generated from air to ground deposition.
- Validation of method development for blood detection using TXRF analysis including comparing several method of digestion of blood such as using microwave digestion.
- Detailed investigation of exposure of trace elements and PAHs in human blood and urine.

REFERENCES

- Abas, M.R.B., Noorsaadah, A.R., Nasr Yousef M.J. Omar, N.Y.M.J., Maah, M.J., Azizan A.S, Oros, D.R., Otto, A., Simoneit, B.R.T. 2004. Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. *Atmospheric Environment*. 38: 4223–4241.
- Abas, M.R.B., Simoneit, B.R.T., 1996. Composition of extractable organic matter of air particles from Malaysia: initial study. *Atmospheric Environment*. 30: 2779–2793.
- Abegaz, M. S., 2005. Investigation of input and distribution of polluting elements in Tinishu Akaki River, Ethiopia, based on the determination by ICP-MS. Laboratory of Analytical Chemistry Institute for Nuclear Science (UMI No. AAT 471762).
- Acosta, J.A., Cano, A.F., Arocena, J.M., Debela, F., Martínez- Martínez. S., 2009. Distribution of metals in soil particle size fractions and its implication to risk assessment of playground in Murcia City (Spain). *Geoderma*. 149:101–9.
- Adams P.J., Seinfeld J.H., Koch D.M., 1999. Global concentrations of tropospheric sulphate, nitrate, and ammonium aerosol simulated in a general circulation model. *Journal of Geophysical Research*. 104: 13791-13823.
- Adriaenssens, E., 2007. Focus on Spectroscopy: Analysis of Heavy Metals in Ambient Air. *International Labmate*. 15:1.
- Agency for Toxic Substances and Disease Registry (ATSDR), 2008. Toxicological Profile for Chromium.
- Agency for Toxic Substances and Disease Registry (ATSDR), 2010. Draft Toxicological Profile for Chromium. Retrieved June 2014, from <http://www.atsdr.cdc.gov/toxprofiles/tp7.pdf>.
- Ahern, H.E., Walsh, K.A., Hill, T.C.J., and Moffett, B.F., 2007. Fluorescent pseudomonads isolated from Hebriden cloud and rain water produce biosurfactants but do not cause ice nucleation. *Biogeosciences*. 4: 115-124.
- Aiken A.C., DeCarlo P.F., Kroll J.H., Worsnop D.R., Huffman J.A., Docherty K.S., Ulbrich I.M., Mohr C., Kimmel J.R., Sueper D., Sun Y., Zhang Q., Trimborn A., Northway M., Ziemann P.J., Canagaratna M.R., Onasch T.B., Alfarra M.R., Prevot A.S.H., Dommen J., Duplissy J., Metzger A., Baltensperger U., Jimenez J.L., 2008. O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. *Environmental Science & Technology*. 42: 4478-4485.
- Al-Jawadi, Z.A.M & Bashi, Z.I.D., 2013. Trace element on first and multiple pregnancy. *Biosciences Biotechnology Research Asia*. Vol 10(2):837-841.
- Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M. and Greenwood, J.C., 2001. Size Distributions of Trace Metals in Atmospheric Aerosols in the United Kingdom. *Atmospheric Environment*. 35: 4581–4591.
- Amann, M., Bertok, I., Cofala, J., Gyarfas, F., Heyes, C., Klimont, Z., Schöpp, W. and Winiwarter, W., 2005. Baseline Scenarios for the Clean Air for Europe (CAFE) Programme Final Report.

- Angerer, J.; Ewers, U.; Wilhelm, M., 2007. Human biomonitoring: State of the art. *Int. J. Hyg. Environ. Health*. 210: 201-228.
- Aranguiz, I., Barona, A., Gurtubai, L., 2002. Chemical analyses after consecutive extraction of inorganic components in suspended particulate matter in Bilbao (Spain). *Water Air and Soil Pollution*. 134: 41-55.
- Arditsoglou, A., Samara, C., 2005. Levels of total suspended particulate matter and major trace elements in Kosovo: A source identification and apportionment study. *Chemosphere*. 59: 669-678.
- Arey, J., Zielinska, B., Atkinson, R., Winer, A.M., 1987. Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high-NO_x episode in the Los Angeles basin. *Atmospheric Environment*. 21: 1437-1444.
- Arimoto, R., Kim, Y.J., Kim, Y.P., Quinn, P.K., Bates, T.S., Anderson, T.L., Gong, S., Uno, I., Chin, M., Huebert, B.J., Clarke, A.D., Shinozuka, Y., Weber, R.J., Anderson, J.R., Guazzotti, S.A., Sullivan, R.C., Sodeman, D.A., Prather, K.A., Sokolik, I.N., 2006. Characterization of Asian Dust during ACE-Asia. *Global and Planetary Change*. 52: 23-56
- Armstrong, B.G., Hutchinson, E., Unwin, J., Fletcher, T., 2004. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: a review and meta-analysis. *Environ Health Perspect.* 112(9):970-8.
- ATSDR, 1995. Toxicological Profile for Polycyclic Aromatic Hydrocarbons. Atlanta: Agency for Toxic Substances and Disease Registry. Available: <http://www.atsdr.cdc.gov/toxprofiles/tp69.html> [accessed February 8, 2009].
- ATSDR, 2002. Regulations and Guidelines Applicable. Agency for Toxic Substances and Disease Registry. Retrieved from <http://www.atsdr.cdc.gov/toxprofiles/tp11-c8.pdf>.
- ATSDR, 2002. Toxicological profile of copper. Division of Toxicology, Atlanta, GA.
- ATSDR, 2003. Toxicological profile information sheet. Division of Toxicology, Atlanta, GA. <http://www.atsdr.cdc.gov/toxiprofiles>.
- Autrup, H., Vestergaard, A.B., 1996. Transplacental transfer of environmental genotoxins—polycyclic aromatic hydrocarbon-albumin in nonsmoking women. *Environmental Health Perspectives*. 104 Suppl 3:625-7.
- Autrup, H., Vestergaard, A.B., Okkels, H., 1995. Transplacental transfer of environmental genotoxins: polycyclic aromatic hydrocarbon-albumin in non-smoking women, and the effect of maternal GSTm1 genotype. *Carcinogenesis*. 16(6):1305-9.
- Ayrault, S., Senhou, A., Moskura, M., Gaudry, A., 2010. Atmospheric trace element concentrations in total suspended particles near Paris, France. *Atmospheric Environment*. 44: 3700-3707.
- Azimi, S., Ludwig, A., Thevenot, D.R., Colin, J.L., 2003. Trace metal determination in total atmospheric deposition in rural and urban areas. *The Science of Total Environment*. 308: 247-254.

- Azimi, S., Rocher, V., Gamaud, S., Varrault, G. & Thevenot, D. R., 2005. Decrease of Atmospheric deposition of heavy metals in an urban area from 1994 to 2002 (Paris, France). *Chemosphere*. 61:645-651.
- Bach, P.B., Kelley, M.J., Tate, R.C., McCrory, D.C., 2003. Screening for lung cancer: a review of the current literature. *Chest*. 123:72–82.
- Baek S.O., Field R.A., Goldstone M.E., Kirk P.W., Lester J.N., Perry R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water, Air and Soil Pollution*.60: 279-300.
- Barceloux, DG., 1999. Chromium. *Clinical Toxicology*. 37(2), 173-194.
- Bauer, H., Weinke, G., Schueller, E., Berger, A., Kasper-Giebl, A., Puxbaum, H., Verneylen, R., Claeys, M., and Maenhaut, W., 2005. Contribution of bioaerosols to organic carbon in urban-fringe PM10 aerosols, European Aerosol Conference, Ghent.
- Begum, B.A., Kim, E., Jeong, C.H., Lee, D.W., Hopke, P.K., 2005. Evaluation of the potential source contribution function using the 2002 Quebec forest fire episode. *Atmos. Environ*. 39: 3719–3724.
- Benoff, S., A. Jacob and I.R. Hurley., 2000. Male infertility and environmental exposure to lead and cadmium. *Human Reproduction Update*. 6: 107-121.
- Bergdahl, I.A. , Schütz, A. , Gerhardsson, L. , Jensen, A. , Skerfving, S., 1997. Lead concentrations in human plasma, urine and whole blood . *Scand J Work Environ Health*. 23: 359 – 63 .
- Bilos, C., J.C. Colombo, C.N. Skorupka and M.J. Rodriguez Presa., 2001. Sources, distribution and variability of airborne trace metals in La Plata city area, Argentina. *Environ. Pollu*. 111: 149-158.
- Black RE., 2001. Micronutrients in pregnancy. *Br J Nutr*. 85: 93-197.
- Blanchard, D. C., A. H. Woodcock., 1980. The production, concentration and vertical distribution of sea-salt aerosol. *Ann. N.Y. Acad. Sci*. 338: 330-347.
- Bocskay, K., Tang, D., Orjuela, M., Liu, X., Warburton, D., Perera, F., et al., 2005. Chromosomal aberrations in cord blood are associated with prenatal exposure to carcinogenic polycyclic aromatic hydrocarbons. *Cancer Epidemiol Biomarkers Prev*. 14(2): 506-511.
- Boffetta, P., Jourenkova, N., Gustavsson, P., 1997. Cancer risk from occupational and environmental exposure to poly- cyclic aromatic hydrocarbons. *Cancer Causes Control*. 8(3): 444–472.
- Boman, B.C., Forsberg, A.B. and Järholm, B.G. , 2003. Adverse health effects from ambient air pollution in relation to residential wood combustion in modern society. *Scandinavian journal of work, environment and health*. 29(4): 251-260.
- Bostrom, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, 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 Suppl 3, 451-488.

- Bourotte, C., Forti, M.C., Taniguchi, S., Bicego, M.C., Lotufo, P.A., 2005. A winter time study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil. *Atmospheric Environment*. 39: 3799-3811.
- Brasseur, G.P., J.J. Orlando, G.S. Tyndall (editor), 1999. *Atmospheric Chemistry and Global Change*, Oxford University Press, New York, New York.
- Brauer, M., Amann, M., Burnett, R.T., Cohen, A., Dentener, F., Ezzati, M., et al., 2011. Exposure assessment for estimation of the global burden of disease attributable to outdoor air pollution. *Environ Sci Tech*. 46: 652-660.
- Brauer, M., and Jamal, H.H., 1998. Fires in Indonesia : crisis and reaction. *Environ. Sci. & Technol. News*. 32 (17): 404A-407A.
- Bryan, N.S., and Loscalzo, K., 2011. *Nitrite and Nitrate in Human Health and Disease*. Humana Press. New York.
- Brzoska, M.M. and J. Moniuszko-Jakoniuk., 2001. Interactions between Cadmium and Zinc in the organism. *Food and Chemical Toxicology*. 967-980.
- Busby, W., Stevens, E., Martin, C., Chow, F., Garner, R., 1989. Comparative lung tumorigenicity of parent and mononitro-polynuclear aromatic hydrocarbons in the BLU: Ha newborn mouse assay. *Toxicol. Appl. Pharmacol*. 99: 555-563.
- CAFE Working Group on Particulate Matter; Second position paper on particulate matter; 2004 December.
- Callén, M.S., López, 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. *Environ. Pollut*. <http://dx.doi.org/10.1016/j.envpol.2012.11.009> (in press)
- Cancio, J.A.L., Castellano, A.V., Martin, S.S., Rodriguez, J.F.S., 2004. Size distributions of PAHs in ambient air particles of two areas of Las Palmas de Gran Canaria. *Water Air and Soil Pollution*. 154: 127-138.
- Cantwell, M. G., King, J. W., Burgess, R. M., and Appleby, P. G., 2007. Reconstruction of contaminant trends in a salt wedge estuary with sediment cores dated using a multiple proxy approach. *Mar. Environ. Res*. 64: 225–246.
- Caricchia A.M., Chiavarini S., Pezza M., 1999. Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the City of Naples (Italy). *Atmospheric Environment*. 33: 3731-3738.
- Castellano, A.V., Cancio, J.L., Alema, P.S., Rodriguez, J.S., 2003. Polycyclic aromatic hydrocarbons in ambient air particles in the city of Las Palmas de Gran Canaria. *Environ Int*. 29:475–80.
- CCME (Canadian Council of Ministers of the Environment), 2010. Canadian soil quality guidelines for potentially carcinogenic and other PAHs: scientific criteria document. Winnipeg: CCME.
- Cecinato A., Marino F., Di Filippo P., Leopore L., Possanzini M., 1999. Distribution of n-Alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particulates. *Journal of Chromatography A*. 846: 255- 264.

- Chao, C.Y. and Wong, K.K. , 2002. Residential Indoor PM 10 and PM 2.5 in Hong Kong and the Elemental Composition. *Atmos. Environ.* 36: 265–277.
- Chen, J., and Thilly, W.G., 1996. Mutational spectra vary with exposure conditions: benzo(a)pyrene in human cells. *Mutat. Res.* 357: 209-217.
- Chen, J.-W., Wang, S.-L., Hsieh, D.P.H., Yang, H.-H., Lee, H.-L., 2012. Carcinogenic potencies of polycyclic aromatic hydrocarbons for back- door neighbors of restaurants with cooking emissions. *Sci. Total. Environ.* 417(418): 68–75.
- Chen, S.C. and Liao, C.M., 2006. Health Risk Assessment on Human Exposed to Environmental Polycyclic Aromatic Hydrocarbons Pollution Sources. *Sci. Total Environ.* 366: 112–123.
- Chen, T.B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K., Yu, K., Wu, X. and Tian, Q.Z., 2005. Assessment of Heavy Metal Pollution in Surface Soils of Urban Parks in Beijing, China. *Chemosphere.* 60: 542–551.
- Chen, Y.G., Sheng, G.Y. and Bi, X.H., 2005. Emission Factors for Carbonaceous Particles and Polycyclic Aromatic Hydrocarbons from Residential Coal Combustion in China. *Environ. Sci. Technol.* 39: 1861–1867.
- Chiang, K., Chio, C., Chiang, Y., Liao, C., 2009. Assessing hazardous risks of human exposure to temple airborne polycyclic aromatic hydrocarbons. *J. Hazard. Mater.* 166: 676–685.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., and Countess, R. J., 1996. Sources and Chemistry of PM10 aerosol in Santa Barbara Country, CA. *Atmospheric Environment.* 30(9): 1489-1499.
- Chow, J.C., Watson, J.G., Edgerton, S.A., Vega, E., 2002. Chemical composition of PM2.5 and PM10 in Mexico City during winter. *Sci. Total Environ.* 287, 177–201.
- Christensen, E. R. and Karls, J. F., 1996. Unmixing of lead, 137Cs, and PAH records in lake sediments using curve fitting with first- and second-order corrections. *Water. Res.* 30: 2543–2558.
- Chung, M.K., Regazzani, L., McClean, M., Herrick, R., Rappaport, S.M., 2013. A sandwich ELISA for measuring benzo(a)pyrene-albumin adducts in human. *Analytical Biochemistry.* 435: 140-149.
- Collins, J.F., Brown, J.P., Alexeeff, G.V., Salmon, A.G., 1998. Potency equivalency factors for some polycyclic aromatic hydro- carbons and polycyclic aromatic hydrocarbon derivatives. *Regul Toxicol Pharmacol.* 28(1):45–54.
- Conney, A. H. 1982. Induction of microsomal enzymes by foreign chemicals and carcinogenesis by polycyclic aromatic hydrocarbons: G. H. A. Clowes Memorial Lecture. *Cancer Res.* 42(12): 4875-4917.
- Cooper, R.G. 2008. Zinc toxicology following particulate inhalation. *Indian J Occup Environ Med.* 12(1): 10–13.
- Cousins, R.J., McMahon, R.J. 2000. Integrative aspects of zinc transporters. *J Nutr.* 130:1384S-1387S.

- Crépeaux, G., Bouillaud-Kremarik, P., Sikhayeva, N., et al., 2012. Late effects of a perinatal exposure to a 16 PAH mixture: Increase of anxiety-related behaviours and decrease of regional brain metabolism in adult male rats. *Toxicol Lett.* 211: 105-13.
- Crump, C., Crump, K., Hack, E., et al. 2003. Dose-response and risk assessment of airborne hexavalent chromium and lung cancer mortality. *Risk Analysis.* 23(6), 1147-1163.
- Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science.* 250: 1669–1678.
- DeMarini, D., Brooks, L., Warren, S., Kobayashi, T., Gilmour, M., Singh, P. 2004. Bioassay-directed fractionation and salmonella mutagenicity of automobile and forklift diesel exhaust particles. *Environ. Health Perspect.* 112: 814-819.
- Department of Environment (DOE), Malaysia, 1998. Environmental Quality Report 1998. Ministry of Science, Technology and Environment, Malaysia, Kuala Lumpur.
- Despres, V.R., Nowoisky, J.F., Klose, M., Conrad, R., Andreae, M.O and U. Poschl, U. 2007. Characterization of primary biogenic aerosol particles in urban, rural, and high-alpine air by DNA sequence and restriction fragment analysis of ribosomal RNA genes. *Biogeosciences.* 4: 1127–1141.
- Divi, R.L.; Beland, F.A.; Fu, P.P.; Von Tungeln, L.S.; Schoket, B.; Camara, J.E.; Ghei, M.; Rothman, N.; Sinha, R.; Poirier, M.C. Highly sensitive chemiluminescence immunoassay for benzo[a]pyrene-DNA adducts: Validation by comparison with other methods, and use in human biomonitoring. *Carcinogenesis* 2002, 23, 2043-2049.
- DOE – Department of Environment, Malaysia. 2009. Environmental Quality Report, 2008. Putrajaya : Department of Environment, Malaysia.
- DOE – Department of Environment, Malaysia. 2010. Environmental Quality Report, 2009. Putrajaya : Department of Environment, Malaysia.
- Dong, T.T.T., and Lee, B.K. 2009. Characteristics, toxicity, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea. *Chemosphere* 74: 1245–1253.
- Duan J., Bi, X., Tan, J., Sheng, G. and Fu, J. 2005. The Differences of the Size Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) Between Urban and Rural Sites of Guangzhou, China. *Atmos. Res.* 78: 190-203.
- Dumford, D., Dastoor, A., Figueras-Nieto, D. & Ryjkov A. 2010. Long range transport of mercury to the Arctic and across Canada. *Atmos. Chem. Phys.* 10:6063-6086.
- Durant, J., Busby, W., Lafleur, A., Penman, B., Crespi, C. 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat. Res.-Genet. Tox.* 371: 123-157.
- Duruibe, J.O., M.O.C. Ogwuegbu, and J.N. Ekwurugwu, 2007. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences.* 2(5): p. 112-118.
- Dutkiewicz VA, Qureshi S, Husain L, Schwab JJ, Demerjian KL. 2006. Elemental composition of PM 2.5 aerosols in Queens, New York. Evaluation of sources of fine-particle mass. *Atmos Environ.* 40:S347–59.

- Dutkiewicz, V.A., Das, M., Husain, L. 2000. The relationship between regional SO₂ emissions and downwind aerosol sulfate concentrations in the northeastern US. *Atmos Environ.* 34:1821–32.
- Dvonch, J.T., J.R. Graney, F.J. Marsik, G.J. Keeler, and R.K. Stevens. 1998. An investigation of source-receptor relationships for mercury in south Florida using even precipitation data. *The Science of the Total Environment.* 213:95-108.
- Easter, R.C., and Peters, L.K. 1994. Binary homogeneous nucleation: temperature and relative humidity fluctuations, non-linearity and aspects of new particles production in the atmosphere. *J. Geophys. Res. J. Appl. Meteorol.* 33:775-784.
- Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E.L. 2004. Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor- phase and PM 2.5 in Southern California urban and rural communities. *Aerosol Science and Technology.* 38: 447-455.
- Elster, J., Delmas, R.J., Petit, J.R., and Ehakova, K. 2007. Composition of microbial communities in aerosol, snow and ice samples from remote glaciated areas (Antarctica, Alps, Andes). *Biogeosciences.* 4: 1779-1813.
- Espinosa, A.J.F., Rodriguez, M.T., Rosa, F.J.B. and Sanchez, J.C.J. 2001. Size Distribution of Metals in Urban Aerosols in Seville (Spain). *Atmos. Environ.* 35: 2595–2601.
- Fadzil, M. F., Norhayati, M. T., Wan ,M. K. and Wan, M. Z. 2008. Concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) in the town of Kota Bharu, Kelantan Darul Naim. *Malaysian J. Anal. Sci.*, 12 (3): 609 – 618.
- Fang, G.C., Huang, Y.L. and Huang, J.H. 2010. Study of Atmospheric Metallic Elements Pollution in Asia during 2000-2007. *J. Hazard. Mater.* 180: 115–121.
- Fang, M. D., Chang, W. K., Lee, C. L., and Liu, J. T. 2009. The use of polycyclic aromatic hydrocarbons as a particulate tracer in the water column of Gaoping (Kaoping) Submarine Canyon, *J. Mar. Syst.* 76: 457–467.
- Fang, M., Zheng, M., Wang, F., To, K.L., Jaafar, A.B., Tong, S.L., 1999. The solvent-extractable organic compounds in the Indonesia biomass burning aerosols characterization studies. *Atmospheric Environment.* 33: 783–795.
- Fellenberg, G. 2000. The Chemistry of Pollution, John Wiley & Sons, England.
- Fernández Espinosa, A.J.F., Rodriguez, M.T., Rosa, F.J.B., Sanchez, J.C.J. 2001. Size distribution of metals in urban aerosols in Seville (Spain). *Atmospheric Environment* 35: 2595-2601.
- Ferreira-Baptista, L. and De Miguel, E. 2005. Geochemistry and Risk Assessment of Street Dust in Luanda, Angola: A Tropical Urban Environment. *Atmos. Environ.* 39: 4501– 4512.
- Fine, P. M., Shen, S., and Sioutas, C. 2004. Inferring the sources of fine and ultrafine particulate matter at downwind receptor sites in the Los Angeles basin using multiple continuous measurements. *Aerosol Science and Technology.* 38: 182-195.
- Fisher G.F. 2001. Source apportionment of polycyclic aromatic hydrocarbon wet and dry deposition at Massachusetts Bay. Ph.D. Thesis, Department of Chemistry, University of Massachusetts Lowell, USA.

- Fritz, J.S. 1999. Analytical Solid Phase Extraction, John Wiley and Sons Inc., New York.
- Gaffney J.S., Marley N.A., Cunningham M. M., Martello D.V., Anderson N.J. 2002. Using Natural ^{210}Pb and its Daughters (^{210}Bi and ^{210}Po) to Estimate Aerosol Residence Times. Proceedings of the NETL Conference "PM_{2.5} and Electric Power Generation: Recent Findings and Implications" Pittsburgh, PA, April 9-10, 2002. <http://www.netl.doe.gov/publications/proceedings/02/PM25/>.
- Gallo, V.; Khan, A.; Gonzales, C.; Phillips, D.H.; Schoket, B.; Gyorffy, E.; Anna, L.; Kovacs, K.; Moller, P.; Loft, S.; et al. 2008. Validation of biomarkers for the study of environmental carcinogens: A review. *Biomarkers*. 13: 505-534.
- Garcia-Suastegui, W.A.; Huerta-Chagoya, A.; Carrasco-Colin, K.L.; Pratt, M.M.; John, K.; Petrosyan, P.; Rubio, J.; Poirier, M.C.; Gonsebatt, M.E. 2011. Seasonal variations in the levels of PAH-DNA adducts in young adults living in Mexico City. *Mutagenesis*. 26: 385-391.
- Garg, B.D., Cadle, S.H., Mulawa, P.A., Groblicki, P.J., Laroo, C. and Parr, G.A. 2000. Brake Wear Particulate Matter Emissions. *Environ. Sci. Technol.* 34: 4463-4469.
- Gastano-Vinyals, G., D'Errico, A., Malaets, N., and Kogevinas, M. 2004. Biomarkers of exposure to polycyclic aromatic hydrocarbons from environmental air pollution. *Occupational and Environmental Medicine*. Vol 61(4): e12.
- Gelbon, H.V. 1980. Benzo(alpha)pyrene metabolism, activation and carcinogenesis: role and regulation of mixed-function oxidase and related enzymes. *Physiol.Rev.* 60: 1107-1166.
- Geller, M.D., Ntziachristos, L., Mamakos, A., Samaras, Z., Schmitz, D.A., Froines, R.R., Sioutas, C. 2006. Physicochemical and redox characteristics of particulate matter (PM) emitted from gasoline and diesel passenger cars. *Atmospheric Environment*. 40:6988-7004.
- Gidlow, D. A. 2004. In-Depth Review, Lead toxicity. *Occupational Medicine*. 54:76- 81.
- Gietl, J.K., Lawrence, R., Thorpe, A.J. and Harrison, R.M. 2010. Identification of Brake Wear Particles and Derivation of a Quantitative tracer for Brake Dust at a Major Road. *Atmos. Environ.* 44: 141-146.
- Gogou, A., Stratigakis, N., Kanakidou, M., Stephanou, E.G., 1996. Organic aerosols in eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry*. 25: 79-96.
- 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.
- Goodman, A.L., Underwood, G.M., Grassian, V.H., 2000. A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles. *Journal of Geophysical Research*. 105: 29053-29064.
- Goriaux, M., Jourdain, B., Temime, B., Besombes, J., Marchand, N., Albinet, A., Leoz-Garziandia, E., Wortham, H. 2006. Field comparison of particulate PAH measurements using a low-flow denuder device and conventional sampling systems. *Environ. Sci. Technol.* 40: 6398-6404.

- Grover, P.L. 1986. Pathways involved in the metabolisms and activation of polycyclic hydrocarbons. *Xenobiotica*. 16(10-11): 915-31.
- Guengerich, F.P. 2000. Metabolism of chemical carcinogens. *Carcinogenesis*. 21(3): 345-351.
- Gugamsetty, B., Wei, H., Liu, C.N., Awasthi, A., Hsu, S.C., Tsai, C.J., Roam, G.D., Wu, Y.C. and Chen, C.F. 2012. Source Characterization and Apportionment of PM 10, PM 2.5 and PM 0.1 by Using Positive Matrix Factorization. *Aerosol Air Qual. Res.* 12: 476–491.
- Guney, M., Zagury, G.J., Dogan, N. and Onay, T.T. 2010. Exposure Assessment and Risk Characterization from Trace Elements Following Soil Ingestion by Children Exposed to Playgrounds, Parks and Picnic Areas. *J. Hazard. Mater.* 182: 656–664.
- Guo, H., Lee, S.C., Ho, K.F, Wang, X.M., Zou, S.C. 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos Environ.* 37:5307–17.
- Guo, H., Wang, T., Simpson, I.J., Blake, D.R., Yu, X.M., Kwok, Y.H. and Li, Y.S. 2004. Source Contributions to Ambient VOCs and CO at a Rural Site in Eastern China. *Atmos. Environ.* 38: 4551-4500.
- Gupta, A.K., Karar, K., Srivastava, A. 2007. Chemical mass balance source apportionment of PM10 and TSP in residential and industrial sites of an urban region of Kolkata, India. *Journal of Hazardous Materials*. 142: 279-287.
- Gurney, M., Zagury, G.J., Dogan, N., and Onay, T.T. 2010. Exposure assessment and risk characterization from trace elements following soil ingestion by children exposed to playground, parks and picnic area. *J. Hazard. Mater.* 182: 656-664.
- Hadad, K., Mehdizadeh, S., Sohrabpour, M. 2003. Impact of different pollutant sources on Shiraz air pollution using SPM elemental analysis. *Environment International*. 29: 39-43.
- Halek, H., Nabi, G.H., Kavousi, A. 2008. Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, Iran, *Environ. Monit. Assess.* 143:303–311.
- Hall, J. L. 2002. Cellular Mechanisms for Heavy Metal Detoxification. *Journal of Experimental Botany*. Vol 53, No. 366, pp 1-11.
- Hall, J.E., Mizelle, H.L., Hilderbrandt, D.A., Brands, M.W. 1990. Abnormal pressure natriuresis. A cause or a consequence of hypertension?. *Hypertension*. 15:547-559.
- Hansen, L.D., and Eatough, D.J. 1991. Organic Chemistry of the atmosphere. Boca Raton. CRC Press.
- Hao, Y.C., Guo, Z.G., Yang, Z.S., Fang, M., Feng, J.L. 2007. Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China. *Atmospheric Environment*. 85: 27-37.
- Hardy, D.H., Myers, J. & Stokes, C. 2008. Heavy Metals in North Carolina Soils: Occurrence and Significance. Agronomic Division. N.C. Department of Agriculture and Consumer Services. Pages 1-2 <http://ncagr.gov/agronomi/pdf/files/hmetals.pdf>.
- Harris, C.C. 1989. Interindividual variations among humans in carcinogen metabolism, DNA adduct formation and DNA repair. *Carcinogenesis*. 10: 1563-1566.

- Harrison, R.M., Smith, D.J.T., Luhana, L. 1996. Source apportionment of atmospheric polycyclic aromatic hydro- carbons collected from an urban location in Birmingham. UK *Environmental Science and Technology*. 30: 825.
- Harrison, R.M., Smith, D.J.T., Pio, C.A., Castro, L.M. 1997. Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmospheric Environment* 31: 3309-3321.
- Harrison, R.M., Yin, J., Mark, D., Stedman, J., Appleby, R.S., Booker, J., Moorcroft, S. 2001. Studies of the coarse particle (2.5-10 μ m) component in UK urban atmospheres. *Atmospheric Environment*. 35: 3667-3679.
- Hashim, J.H., Hashim, Z., Omar, Z., Shamsudin, S.B. 2000. Blood lead levels of urban and rural Malaysian primary school children. *Asia Pac. J. Public Health*. 12(2): 65-70.
- Haywood, J. and Boucher, O. 2000. Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: a review. *Reviews of Geophysics*. 38(4): 513-543.
- Hecht, S.S. 1999. Tobacco smoke carcinogens and lung cancer. *J Natl Cancer Inst*. 91(14):1194-1210.
- Heintzenberg, J., Raes, F., and Schwartz, S. 2003. Chapter 4, Tropospheric Aerosols, The Changing Atmosphere: An Integration and Synthesis of a Decade of Tropospheric Chemistry Research (Global Change-The IGBP Series,), Guy Brasseur, Ronald G. Prinn, Alexander A. P. Pszenny, Springer.
- Henner, P., Schiavon, M., Morel, J.L., Lichtfouse, E. 1997. Polycyclic aromatic hydrocarbon (PAH) occurrence and remediations methods. *Analus Magazine*. 25(9-10): M56-59.
- Hennion, M.C., Pichon, V. 1994. Solid phase extraction of polar organic pollutants from water, *Environmental Science and Technology*. 28: 576A- 583A.
- Henry, R., C., C. W. Lewis, P. K. Hopke, and H. J. Williamson. 1984. Review of receptor model fundamentals. *Atmos. Environ*. 18: 1507-1515.
- Herngren, L., Goonetilleke, A., and Ayoko, G. A. 2005a. Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall. *Journal of Environmental Management*, 76(2): 149-158.
- Hien, PD., Binh, N.T., Truong,Y., Ngo, N.T., Sieu, L.N. 2001. Comparative receptor modeling study of TSP, PM₂, and PM₂₋₁₀ in Ho Chi Minh City. *Atmospheric Environment*. 35: 2669-2678.
- Hood, D.B., Ramesh, A., Chirwa, S., et al., 2011. Developmental toxicity of polycyclic aromatic hydrocarbons. *Reproductive and Developmental Toxicology*. 44: 593-606.
- Hopke, P. 1991. Receptor Modeling for Air Quality Management. Elsevier Scientific Publisher, New York, 1-10.
- Hoppel, W., Frick, G. M., Larson, R.E., 1986. Effect of nonprecipitation clouds on the aerosol size distribution in the marine boundary layer. *Geophysical Research Letters*, 13(2): 125-128.

- Howard, D.J., Ota, R.B., Briggs, L.A., Hampton, M., Pritsos, C.A. 1998. Environmental tobacco smoke in the workplace induces oxidative stress in employees, including 8-hydroxy-2'-deoxyguanosine. *Cancer Epidemiol Biomarkers Prev.* 7: 141-146, http://www.epa.gov/oswer/riskassessment/ragse/pdf/part_e_final_revision_10-03-07.pdf.
- Hu, H. 2002. Human health and heavy metals exposure. In: *Life support: The environment and human health* (Ed.: M. McCally). MIT Press.
- Hu, T.F., Cao, J.J., Shen, Z.X., Wang, G.H., Lee, S.C. and Ho, K.F. 2012. Size Differentiation of Individual Atmospheric Aerosol during Winter in Xi'an, China. *Aerosol Air Qual. Res.* 12: 951–960.
- Hu, Y., Bai, Z., Zhang, L., Wang, X., Zhang, L., Yu, Q. and Zhu, T. 2007. Health Risk Assessment for Traffic Policemen Exposed to Polycyclic Aromatic Hydrocarbons (PAHs) in Tianjin, China. *Sci. Total Environ.* 382: 240– 250.
- Hwang, H. M., Wade, T. L. & Sericano, J. L. 2003. Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico and United States. *At. Env.* 37: 2259-2267.
- IARC (International Agency for Research on Cancer). 2010. Some non-Heterocyclic polycyclic aromatic hydrocarbons and some related Exposures. IARC Monogr. Eval. Carcinog. Risk Hum. 92 (IARC, Lyon).
- IARC (International Agency for Research on Cancer). 2012. Agents Classified by the IARC Monographs. Available: In: List of Classifications by Alphabetical Order, vol. 1e105 <http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf>.
- IPCC. Climate Change. 2007. The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Ishibe, N., Hankinson, S.E., Colditz, G.A., Spiegelman, D., Willett, W.C., Speizer, F.E, et al., 1998. Cigarette smoking, cytochrome P450 1A1 polymorphisms, and breast cancer risk in the Nurses' Health Study. *Cancer Res.* 58(4):667–671.
- Jacob, D. J., 1999. Introduction to Atmospheric Chemistry. Chapter 3: Simple Methods. Princeton University Press, Princeton New Jersey. Page 24.
- Jacob, J., Seidel, A. 2002. Biomonitoring of polycyclic aromatic hydrocarbons in human urine. *Journal of Chromatography B - Analytical Technologies in the Biomedical and Life Sciences* 778: 31-47.
- Jacobson-Kram, D.; Albertini, R.J.; Branda, R.F.; Falta, M.T.; Iype, P.T.; Kolodner, K.; Liou, S.H.; McDiarmid, M.A.; Morris, M.; Nicklas, J.A.; et al. 1993. Measurement of chromosomal aberrations, sister chromatid exchange hprt mutations and DNA adducts in peripheral lymphocytes of human populations at increased risk for cancer. *Environ. Health Perspect.* 101: 121-125.
- Jaenicke, R. 2005. Abundance of cellular material and proteins in the atmosphere, *Science*, 308, p. 73.
- Jamal, H.H., and Zailina, H. 1994. Jerebu dan impak kesihatan: satu penilaian (Haze and its health impacts : an assessment). *Buletin Kesihatan Masyarakat*, 1(2): 1-11.

- Jamal, H.H., Zailina, H., Juliana, J., Syarif, H.L. and Ridzwan, H. 1998. Respiratory functions of elementary schoolchildren exposed to the 1997. Kuala Lumpur haze. Abstract. *Epidemiology*, 9(4) July Suppl. S103.
- Juliana, J. 1998. Persekitaran Dan Serangan Asma Di kalangan Kanak-kanak Di Kuala Lumpur dan Terengganu (The Environment and Asthmatic Attacks among Children in Kuala Lumpur dan Terengganu). Master of Science (Environmental Health) Thesis, Universiti Putra Malaysia.
- K. Max Zhang, Eladio M. Knipping, Anthony S. Wexler, Prakash V. Bhave, Gail S. Tonnesen. 2005. Size distribution of sea-salt emissions as a function of relative humidity. *Atmospheric Environment*. 39: 3373–3379.
- Kafferlein, H.U., Marczynski, B., Mensing, T., Bruning, T. 2010. Albumin and hemoglobin adducts of benzo(a)pyrene in human-analytical methods, exposure assessment, and recommendations for future directions. *Critic. Rev. Toxicol.* 40:126-150.
- Kameda, T. 2011. Atmospheric chemistry of polycyclic aromatic hydrocarbons and related compounds. *J Health Sc.* 57(6): 504–11.
- Kanellopoulou, E. A. 2001. Determination of heavy metals in wet deposition of Athens. *Global Nest: The International Journal*. 3(1):45-50.
- Karanasiou, A.A., Sitaras, I.E., Siskos, P.A. and Eleftheriadis, K. 2007. Size Distribution and Sources of Trace Metals and n-alkanes in the Athens Urban Aerosol during Summer. *Atmos. Environ.* 41: 2368 – 2381.
- Kavouras, I. G., Koutrakis, P., Tsapakis, E., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyala, P. 2001. Sources apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods, *Environ Sci Technol* (UK). 35: 2288-2294.
- Khalili, N.R., Scheff, P.A., Holsen, T.M. 1995. PAH source finger prints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment* 29, 533-542.
- Khan, M.F., Hirano, K., Masunaga, S. 2010. Quantifying the sources of hazardous elements of suspended particulate matter aerosol collected in Yokohama, Japan. *Atmospheric Environment*. 44: 2646-2657.
- Kim, J.H., Stansbury, K.H., Walker, N.J., Trush, M.A., Strickland, P.T., and Sutter, T.R. 1998. Metabolism of benzo(a)pyrene and benzo(a)pyrene-7,8-diol by human cytochrome P450 1B1. *Carcinogenesis*. Vol 19(10): 1847-1853.
- Kim, K.H. 2004. Relationships between spatial and temporal variabilities in airborne metal distributions in Won Ju City, Korea. *Environment International*. 29: 901-906.
- Kimbrough, D.E., Cohen, Y., Winer, A.M, et al. 1999. A critical assessment of chromium in the environment. *Critical Reviews in Environmental Science and Technology*. 29(1), 1-46.
- Klockenkaemper, R., Knoth, J., Prange, A., and H. Schwenke. 1992. Total reflection X-ray fluorescence spectroscopy. *Anal. Chem.* Vol.64, No. 23: 1115A.

- Klopov, V.P. 1998. Persistent organic compounds in women residing in the Russian arctic. *International Journal of Circumpolar Health*. 57 Suppl 1:555-60.
- Knipping, E.M., Dabdub, D. 2003. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environmental Science and Technology* 37: 275–284
- Kong, S., Lu, B., Ji, Y., Zhao, X., Bai, Z., Xu, Y., Liu, Y. and Jiang, H. 2012. Risk Assessment of Heavy Metals in Road and Soil Dusts within PM_{2.5}, PM₁₀ and PM₁₀ Fractions in Dongying City, Shandong Province, China. *J. Environ. Monit.* 14: 791–803.
- Kowalczyk, G.S. and Gordon, G.E. and Rheingrover, S.W. 1982. Identification of Atmospheric Particulate Sources in Washington, DC, Using Chemical Element Balances. *Environ. Sci. Technol.* 16: 79–90.
- Krishna, G.G & Kapoor, S.V. 1991. Potassium depletion exacerbates essential hypertension. *Annals of Internal Medicine*. 115(2):77-83
- Krishna, G.G., Miller, E., Kapoor, S. 1989. Increased blood pressure during potassium depletion in normotensive men. *N Engl J Med*. 320: 1177-82.
- Krueger, B. J., Grassian, V.H., Laskin, A., and Cowin, J.P. 2003. The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, *Geophys. Res. Lett.* . 30(3): 1148.
- Kulkarni, P., Venkataraman, C., 2000. Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. *Atmospheric Environment*. 34: 2785–2790.
- Ladipo, O.A. 2000. Nutrition in pregnancy: mineral and vitamin supplements. *Am J Clin Nutr.* 72(Suppl):280S-290S.
- Landrigan, P., Aykanat, B., Ertas, N., et al. 2004. Children's health and the environment: public health issues and challenges for risk assessment. *Environ Health Perspect.* 112(2): 257-265.
- Latif, M.T., Brimblecombe, P., Ramli, N.A., Sentian, J., Sukhapan, J., Sulaiman, N. 2005. Surfactants in south east Asian aerosols. *Environ. Chem.* 2, 198–204.
- Lavine, B.K. 2000. Clustering and Classification of Analytical Data, in Encyclopedia of Analytical Chemistry. John Wiley & Sons, Ltd. p. 9689-9710.
- Lee BM, Yin BY, Herbert R, Hemminki K, Perera FP, Santella RM. 1991. Immunologic measurement of polycyclic aromatic hydrocarbon-albumin adducts in foundry workers and roofers. *Scand J Work Environ Health*. 17:190–4.
- Lee, B.K. and Hieu, N.T. 2011. Seasonal Variation and Sources of Heavy Metals in Atmospheric Aerosols in a Residential Area of Ulsan, Korea. *Aerosol Air Qual. Res.* 11: 679–688.
- Lee, W.J., Wang, Y.F., Lin, T.C., Chen, Y.Y., Lin, W.C., Ku, C.C., Cheng, J.T. 1995. PAH characteristics in the ambient air of traffic-source. *Science of the Total Environment*. 159: 185-200.
- Leister, D.L. and Baker, J.E. 1994. Atmospheric deposition of organic contaminants to the Chesapeake Bay, *Atmospheric Environment*. 28: 1499- 1520.

Levine, J.S. (Ed.), 1991. Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications. MIT Press, Cambridge, MA.

Li, P.H., Han, B., Huo, J., Lu, B., Ding, X., Chen, L., Kong, S.F., Bai, Z.P. and Wang, B. 2012. Characterization, Meteorological Influences and Source Identification of Carbonaceous Aerosols during the Autumn-winter Period in Tianjin, China. *Aerosol Air Qual. Res.* 12: 283–294.

Lieber, D.C. 2008. Protein damage by reactive electrophiles: target and consequences. *Chem.Res.Toxicol.* 21: 117-128.

Lin, Y.S, Kupper L.L., Rappaport, S.M. 2005. Air samples versus biomarkers for epidemiology. *Occup Environ Med.* 62:750–760.

Lin, C-J. and Pehkonen, S.O. 1999. The chemistry of atmospheric mercury: a review. *Atmospheric Environment.* 33: 2067-2079.

Ljung, K., Selinus, O., Otabbong, E. 2005. Metals in soils of children's urban environments in the small northern European city of Uppsala. *Sci Total Environ.* 366:749–59.

Lobert, J.M., Scharffe, D.H., Hao, W.M., Crutzen, P.J., 1990. Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature.* 346: 552–554.

Loli, P., Topinka, J., Georgiadis, P., et al., .2004. Benzo[a]pyrene- enhanced mutagenesis by asbestos in the lung of λ -lacI transgenic rats. *Mutat Res-Fund Mol M*, 553, 79-90.

Majewska, U. , Bana, D, Braziewicz, J., Kubala-Kuku, A., Pajek, M., . Sychowska, I., Wudarczyk-Moćko,J., Antczak, G., Borkowska, B and Gozdz, S. 2014. X-Ray Fluorescence Techniques in Medical Applications: Reference Values of Elements in Human Serum Urine and Hair. *Acta Physica Polonica A.* Vol 124: 864-868.

Malhotra, V.K 1998. Biochemistry for Students. Tenth Edition. Jaypee Brothers Medical Publishers (P) Ltd, New Delhi, India.

Man, Y.B., Sun, X.L., Zhao, Y.G., Lopez, B.N., Chung, S.S., Wu, S.S., Cheung, K.C., and Wang, M.H. 2010. Health risk assessment of abandoned agricultural soils based on heavy metal content in Hong Kong the world most populated city. *Environ Int.* 36: 570-576.

Manahan, S.E. 2009. Environmental Chemistry, ninth ed. CRC Press, New York.

Manalis, N., G. Grivas, V. Protonotarios, A. Moutsatsou, S. Samara and A. Chaloulakou. 2005. Toxic metal content of particulate matter (PM₁₀), within the Greater Area of Athens. *Chemosphere*, 60: 557-566.

Marczazan, G.M., Vaccaro, S., Valli, G. and Vecchi, R. 2001. Characterisation of PM₁₀ and PM 2.5 Particulate Matter in the Ambient Air of Milan (Italy). *Atmos. Environ.* 35: 4639–4650.

Marcè, R.M and Borrull, F. 2000. Solid Phase extraction of polycyclic aromatic compounds, *Journal of Chromatography A.* 885: 273-290.

Marchand, N., Besombes, J.-L., Chevron, N., Masclet, P., Aymoz, G., Jaffrezo, J.L. 2004. Polycyclic aromatic hydrocarbons (PAHs) in the atmospheres of two French alpine valleys: sources and temporal patterns. *Atmos. Chem. Phys.* 4: 1167-1181.

- Martinez, T., Lartigue, J., Avila-Perez, P., Zarazua, G., Navarrate, M., Tajeda, S. 2004. Determination of trace elements in blood samples by TXRF analysis. *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 259, No 3: 511-514.
- Martinis, B.S., Okamoto, R., Kado, N.Y., Gundel, L.A., Carvalho, L.R.F. 2002. Polycyclic aromatic hydrocarbon in bioassay-fractionated extract of PM 10 collected in Sao Paolo, Brazil. *Atmos Environ* (UK). 36: 307-314.
- Masclat P, Mouvier G, Nikolaou K. 1986. Relative decay index and sources of polycyclic aromatic hydrocarbons. *Atmos Environ*. 20: 439–46.
- Mastral A.M. and Callen M.S. 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation, *Environmental Science and Technology*, 34: 3051-3057.
- Matter, U., Siegmann, H. C., and Burtcher, H. 1999. Dynamic field measurements of submicron particles from diesel engines, *Environ. Sci. Technol*. 33: 1946-1952.
- Mayer, J. 2006. Transboundary perspectives on managing Indonesia's fires. *The Journal of Environment & Development*, 15(2): 202–233.
- Melissa C. Evans, Scott W. Campbell, Venkat Bhethanabotla Noreen D. Poor. 2004. Effect of sea salt and calcium carbonate interactions with nitric acid on the direct dry deposition of nitrogen to Tampa Bay, Florida. *Atmospheric Environment* 38: 4847–4858.
- Menchini, E., Monfredini, F., Merli, F. 1999. The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome 1993–1998. *Atmos Environ*. 33:3739–50.
- Mertz W. 1981. The essential trace elements. *Science*. 213: 1332-1338.
- Mirante, F., Alves, C., Pio, C., Pindado, O., Perez, R., Revuelta, M.A., Artiñano, B. 2013. Organic composition of size segregated atmospheric particulate matter, during summer and winter sampling campaigns at representative sites in Madrid, Spain. *Atmospheric Research*. Volume 132-133: 345-361.
- Mohieldein, A.H., Dokem, A.A., Osman, Y.H.M., Idris, H.M.A. 2007. Serum calcium level as a marker of pregnancy induced hypertension. *Sudan JMS*. Vol 2, No 4.
- Moller, M., Alfheim, I., Larsen, S., Mikalsen, A. 1980. Bioassays of extract of ambient particulate matter, *Environ Sci Technol* (UK). 16: 221-225.
- Moreno Grau, S., Perez Tornell, A., Bayo, J., Moreno, J., Angosto, J.M., Moreno Clavel, J. 2000. Particulate matter and heavy metals in the atmospheric aerosol from Cartagena, Spain. *Atmospheric Environment*. 34: 5161-5167.
- Mott, J.A., Mannino, D.M., Alverson, C.J., Kiyu, A., Hashim., J., Lee, T., Falter, K., Redd, S.C. 2005. Cardiorespiratory hospitalizations associated with smoke exposure during the 1997 Southeast Asian forest fire. *Journal of Hygiene and Environmental Health*. Vol 208, Iss. 1-2: 75-85.
- Muezzinoglu, A. & Cizmecioglu, S. C. 2006. Deposition of heavy metals in Mediterranean Climate area. *Atmospheric Research*. 81:1-16.

- Murray, R.K., Granner, D.K., Mayes, P.A., Rodwell, V.W. 2000. Harper's Biochemistry, 25th Edition, McGraw-Hill, Health Profession Division, USA.
- Naeher, L., Brauer, M., Lipsett, M., Zelikoff, J., Simpson, C., Koenig, J. and Smith, K., 2007. Woodsmoke Health Effects: A Review. *Inhalation Toxicology*. 19(1): 67- 106.
- Nasir, M.H., Choo, W.Y., Rafia, A., Md., M.R., Theng, L.C., Noor, M.M.H. 2000. Estimation of Health Damage Cost For 1997-Haze Episode in Malaysia Using the Ostro Model. Proceedings Malaysian Science and Technology Congress. Confederation of Scientific and Technological Association in Malaysia (COST-AM), Kuala Lumpur, in Press.
- Nathan, S.B., and Joseph, L. 2011. Nitrate and nitrite in human health and disease. Springer, New York.
- NEA. 2013. National Environment Agency of Singapore. <http://www.haze.gov.sg> (Accessed on Jun 2014).
- Nebert, D.W., and Dalton, T.P. 2006. The role of cytochrome P450 enzymes in endogenous signaling pathways and environmental carcinogenesis. *Nat. Rev. Cancer*. 6: 947-960.
- Nel A., Xia T., Mädler L., Li N. 2006. Toxic Potential of Materials at the Nanolevel. *Science*. 311: 622-627.
- Nicholson, K.W., and Branson, J.R. 1990. Factors affecting resuspension by road traffic. *Sci Total Environ*. 93: 349-358.
- Nielsen, T. 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmospheric Environment*. 30: 3481–3490.
- Nielsen, T., Jørgensen, H.E., Larsen, J.C.H., Poulsen, M. 1996. City air pollution of polycyclic aromatic hydrocarbons and other mutagens: occurrence sources and health effects. *Sci Total Environ*. 189/190:41 – 9.
- Niragu, J.O., Pacyna, J.M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*. 333:134–9.
- Nisbet, C., LaGoy, P. 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol*. 16: 290–300.
- Norris, S.J., Brooks I. M, Moat, B. I., Yelland, M. J., Leeuw, G. de., Pascal, R.W., Brooks, B. 2013. Near-surface measurements of sea spray aerosol production over whitecaps in the open ocean. *Ocean Sci.*, 9:133–145.
- Noura, Al-Jameil., Hajera, T, Huda, Al-Mayouf., Haya, I.A, Naif, D.A., Sereen, M.H., Farah, A.K. 2014. Analysis of serum trace elements-copper, manganese and zinc in preeclamptic pregnant women by inductively coupled plasma optical emission spectrometry: a prospective case controlled study in Riyadh, Saudi Arabia. *Int J Clin Exp Pathol*. 7(5):1900-1910.
- Ny, T.M. and Lee, K.B. 2011. Size Distribution of Airborne Particulate Matter and Associated Metallic Elements in an Urban Area of an Industrial City in Korea. *Aerosol and Air Quality Research*, 11: 643–653.
- O'Dell, B.L., and Sunde, R.A. 1997. Handbook of Nutritionally Essential Mineral Elements. Marcel Decker Inc. New York. 2:6.

Oanh, N.T.K., Reutergardh, L.B., Dung, N.T., Yu, M.H., Yao, W.X., Co, H.X. 2000. Polycyclic aromatic hydrocarbons in the airborne particulate matter at a location 40km north of Bangkok, Thailand. *Atmospheric Environment*. 34: 4557–4563.

Oda, J., Maeda, I., Mori, T., Yashuara, A., Saito, Y. 1998. The relative proportions of polycyclic aromatic hydrocarbons and oxygenated derivatives in accumulated organic particulates as affected by air pollution sources. *Environmental Technology*. 19: 961–976.

OEHHA. 1993. Benzo[a]pyrene as a Toxic Air Contaminant. Part B. Health Effects of Benzo[a]pyrene. Berkeley, CA:California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section.
OEHHA. 2003. The Air Toxics Hot Spots Program Guidance Manual for Preparation of Health Risk Assessments. Oakland, CA:California Environmental Protection Agency, Office of Environmental Health Hazard Assessment.

OEHHA. 2005. Air Toxics Hot Spots Program Risk Assessment Guidelines. Oakland, CA:California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section.

Ohura, T., T. Amagai, M. Fusaya and H. Matsushita. 2004. Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations. *Environ. Sci. Tech.* 38: 77-83.

Okona-Mensah, K.B., Battershill, J., Boobis, A., Fielder, R., 2005. An approach to investigating the importance of high potency polycyclic aromatic hydrocarbons (PAHs) in the induction of lung cancer by air pollution. *Food Chem. Toxicol.* 43: 1103–1116.

Olmez, I., Gullu, G., Aras, N.K. and Keskin, S.S. 2004. Seasonal Patterns of Atmospheric Trace Element Concentrations in Upstate New York, USA. *J. Radioanal. Nucl. Chem.* 259: 157–162.

Omar, N.Y.M.J., Tan Chin Mon, Noorsaadah A. Rahman, M. Radzi Bin Abas. 2006. Distributions and health risks of polycyclic aromatic hydrocarbons (PAHs) in atmospheric aerosols of Kuala Lumpur, Malaysia. *Science of the Total Environment* 369: 76–81.

Omar, N.Y.M.J., Abas, M.R.B., Kamal, A.K., Norhayati, M.T. 2002. Concentrations of PAHs in atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmospheric Environment* 36: 247–254.

Onder, S., Dursun, S., Gezgin, S.& Demirbas, A. 2007. Determination of heavy metal pollution in grass of city centre green areas(Konya,Turkey). *Polish Journal of Environmental Studies*. 16 (1): 145-154.

Ostro, B., Feng, W.Y., Broadwin, R., Green, S., Lipsett, M. 2007. The effects of components of fine particulate air pollution on mortality in California: Results from CALFINE. *Environmental Health Perspectives*. 115: 13-19.

Ozcan, M. 2003. Mineral Contents of some Plants used as condiments in Turkey. *Food Chemistry*. 84: 437-440.

Pacyna, J.M. 1998. Source inventories for atmospheric trace metals. In Atmospheric Particles. Harrison, R.M., Van Grieken, R.E. (Eds). IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, 5. Chichester, UK: John Wiley & Sons Ltd. pp 387-423.

Pacyna, Jozef. 2002. Heavy Metals in the Artie: Artie Monitoring and Assessment Plan. Amap Report. 98:8.

Paiva, A.de,A., Rondo, P.H.C., Pagliusi, R.A., Latorre, M.do.R.D.O., Cardoso, M.A.A., Gondim, S.S.R. 2007. Relationship between the iron status of pregnant women and their newborns. *Rev Saude Publica*. 41(3): 321-7.

Palanissamy, A. 2013. Haze free air in Singapore and Malaysia-the spirit of the law in South East Asia. *International Journal of Education and Research*. Vol 1 No 8.

Panther BC, Hooper MA, Tapper N. 1999. A comparison of air particulate matter and associated polycyclic hydrocarbons in some tropical and temperate urbane environments. *Atmos Environ*. 33: 4087 – 99.

Parekh, P.P., Ghauri, B., Siddiqi, Z.R., Husain, L. 1987. The use of chemical and statistical methods to identify sources of selected elements in ambient air aerosols in Karachi, Pakistan. *Atmospheric Environment*. 21: 1267-1274.

Park, J.S., Wade, T.L., Sweet, S. 2001. Atmospheric distribution of polycyclic aromatic hydrocarbons and deposition to Galveston Bay, Texas, USA. *Atmos Environ*. 35:3241–9.

Park, S.S., Kim, Y.J., Kang, C.H. 2002. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. *Atmospheric Environment*. 36: 2917-2924.

Pathak, A.K, Singh, M.M., Kumara, V., Arya, S., and Trivedi, A.K. 2012. Assessment of physico- chemical properties and microbial community during composting of municipal solid waste (Viz. KIitchen waste) at Jhansi City, U.P. (India). *Recent Research in Science and Technology*. 4(4):10-14.

Petry, T., Schmid, P., Schlatter, C. 1996. The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). *Chemosphere* 32, 639-648.

Pirrone, M., Costa, P., Pacyna, J., and Ferrara, R. 2001. Mercury emission to the atmosphere from natural and antropogenic sources in the Mediterranean region. *Atmos Environ*. 35: 2997-3006.

Pirrone,N., Keeler, G.J., and Nriagu, J.O. 1996. Regional differences in worldwide emissions of mercury to the atmosphere. *Atmos. Environ*. 30: 2981-2987.

Poirier, M.C. and Weston, A. 1996. Human DNA adduct measurements state of the art. *Environ. Health. Perspect*.104(Suppl 5): 883-893

Poirier, M.C.; Santella, R.M.; Weston, A. 2000. Carcinogen macromolecular adducts and their measurement. *Carcinogenesis*, 21, 353-359.

Poirier, M.C.; Weston, A.; Schoket, B.; Shamkhani, H.; Pan, C.F.; McDiarmid, M.A.; Scott, B.G.; Deeter, D.P.; Heller, J.M.; Jacobson-Kram, D.; et al. 1998. Biomonitoring of United States Army soldiers serving in Kuwait in 1991. *Cancer Epidemiol. Biomarkers Prev.* , 7, 545-551.

Pope, C.A. and Dockery, D.W. 2006. Health effects of fine particulate air pollution: Lines that connect. *Journal of the Air & Waste Management Association*. 56(6): 709-742.

- Pope, C.A., III, Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J. 2004. Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease. *Circulation*. 109: 71-77.
- Pöschl, U. 2005. Atmospheric aerosols: composition, transformation, climate and health effects. *Angew. Chem. Int. Ed.* 44: 7520–7540.
- Pósfai, M., Molnár, A. 2000. Aerosol particles in the troposphere: a mineralogical introduction. In *Environmental Mineralogy*. Edited by David J. Vaughan and Roy A. Wogelius, Budapest: Eotvos University Press. pp 434.
- Prange, A., Boddeker, H., Michaelis, W. 1989. Multi-element determination of trace elements in whole blood and blood serum by TXRF. *Fresenius Z Anal Chem.* 335:914-918.
- Pryor, S.C., Sorensen, L.L., 2000. Nitric acid-sea salt reactions: implications for nitrogen deposition to water surfaces. *Journal of Applied Meteorology*. 39: 725–731.
- Pufulete, M., Battershill, J., Boobis, A., Fielder, R., 2004. Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbons: a UK perspective. *Regul. Toxicol. Pharmacol.* 40: 54–66.
- Pyle, D.M and Mather, T.A. 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos Environ.* 37: 5115-5124.
- Qadir, M.A., Zaidi, J.H. 2006. Characteristics of the aerosol particulates in the atmosphere in an urban environment at Faisalabad, Pakistan. *Journal of Radioanalytical and Nuclear Chemistry* 267, 545-550.
- Qishlaqi, A. & Moore, F. 2007. Statistical Analysis of Accumulation and Sources of Heavy Metals Occurrence in Agricultural Soils of Khoshk River Banks, Shiraz, Iran. *American-Eurasian Journal of Agriculture & Environmental Science*. 2 (5): 565-573.
- Qiu, C., Cheng, S., Xia, Y., et al.,. 2011. Effects of subchronic benzo(a)pyrene exposure on neurotransmitter receptor gene expression in the rats hippocampus related with spatial learning and memory change. *Toxicology*. 289: 83-90.
- Quiterio, S.L., da Silva, C.R.S., Arbilla, G., Escalreira, V. 2004a. Metals in airborne particulate matter in the industrial district of Santa Cruz, Rio de Janeiro, in an annual period. *Atmospheric Environment*. 38: 321-331.
- Ragosta M, Caggiano R, D’Emilio M, Macchiato M. 2002. Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of Southern Italy. *Atmospheric Environment*. 36(19): 3071–3087.
- Ragunathan, N., Krock, K.A., Klawun, C., Sasaki, T.A., Wilkins, C.L. 1999. Review, Gas chromatography with spectroscopic detectors, *Journal of Chromatography A*, 856: 349-397.
- Ramanathan, V., Li, F., Ramana, M.V., Praveen, P.S., Kim, D., Corrigan, C.E., Nguyen, H., Stine, H.A., Schauer, J.J., Carmichael, G.R., Adhikary, B., Yoon, S.C. 2007. Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing. *Journal of Geophysical Research: Atmosphere*. Vol 112(D22): 27.

- Ramesh, A., Walker, S.A., Hood, D.B., Guillen, M.D., Schneider, K., Weyand, E.H. 2004. Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. *International Journal of Toxicology* 23: 301-333.
- Ravindra, K., Sokhi, R., Van Grieken, R. 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos. Environ.* 42: 2895-2921.
- Rehwagen, M., Müller, A., Massolo, L., Herbarth, O., Ronco, A., 2005. Polycyclic aromatic hydrocarbons associated with particles in ambient air from urban and industrial areas. *Sci. Total. Environ.* 15, 199–210.
- Re-Poppi, N., Santiago-Silva, M. 2005. Polycyclic aromatic hydrocarbons and other selected organic compounds in ambient air of Campo Grande City, Brazil. *Atmospheric Environment*. 39: 2839-2850.
- RIVM. 1999a. "Environmental Risk Limits in The Netherlands", Dutch National Institute of Public Health and the Environment (RIVM), report No. 601640 001.
- RIVM. 1999b. "Setting Integrated Environmental Quality Standards: Environmental Quality Standards for Soil, Water & Air", Dutch National Institute of Public Health and the Environment (RIVM).
- Rizzio, E., Bergamaschi, L., Valcuvia, M.G., Profumo, A., Gallorini, M. 2001b. Trace elements determination in lichens and in the airborne particulate matter for the evaluation of the atmospheric pollution in a region of northern Italy. *Environment International*. 26: 543-549.
- Rizzio, E., Giaveri, G., Arginelli, D., Gini, L., Profumo, A., Gallorini, M. 1999. Trace elements total content and particle sizes distribution in the air particulate matter of a rural residential area in north Italy investigated by instrumental neutron activation analysis. *Science of the Total Environment*. 226: 47-56.
- Rizzo, E., Bergamaschi, G., Profuma, A., Gallorini, M. 2001a. The use of neutron activation analysis for particles size fractionation and chemical characterization of trace elements in urban air particulate matter. *Journal of Radioanalytical and Nuclear Chemistry*. 248: 21-28
- Roelle, P.A., Aneja, V.P., Gay, B., Geron, C. Pierce, T. 2001. Biogenic nitric oxide emissions from cropland soils. *Atmospheric Environment*. 35: 115-124.
- Rogge, W, F., Hildemann, L., Mazurek, M, A., Cass, G, R., Simonet, B, R, T. 1993. Sources of fine organic aerosol: 3.road dust tire debris ad organometallic brake lining dust, roads as sources and sink, *Environ Sci Technol* (UK). 27: 636-651.
- Rondó, P.H.C., Abbott, R., Rodrigues, L.C., Tomkins, A.M. 1995. Vitamin A, folate, and iron concentrations in cord and maternal blood of intra-uterine growth retarded and appropriate birth weight babies. *Eur J Clin Nutr*. 49(6):391-9.
- Ruchirawat, M., Mahidol, C., Tangiarukij, C., Pui-ock, S., Jensen, O., Kampeerawipakorn, O., Tuntaviron, K., Arampongphan, A., Autrup, H. 2002. Exposure to genotoxins present in ambient air in Bangkok, Thailand-particle associated polycyclic aromatic hydrocarbons and biomarkers. *Sci. Total. Environ.* 287: 121-132.

- Saarnio, K., Sillanpää, M., Hillamo, R., Sandell, E., Pennanen, A.S., Salonen, R.O., 2008. Polycyclic aromatic hydrocarbons in size-segregated particulate matter from six urban sites in Europe. *Atmos. Environ.* 42: 9087–9097.
- Salam, A., Bauer, H., Kassim, K., Ullah, S.M., Puxbaum, H. 2003. Aerosol chemical characteristics of a mega city in Southeast Asia (Dhaka, Bangladesh). *Atmospheric Environment*. 37: 2517-2528.
- Samara, C. and Voutsas, D. 2005. Size Distribution of Airborne Particulate Matter and Associated Heavy Metals in the Roadside Environment. *Chemosphere* 59: 1197– 1206.
- Samura, A., Al-Agha, O., Tuncel, S.G. 2003. Study of trace and heavy metals in rural and urban aerosols of Uludağ and Bursa (Turkey). *Water, Air and Soil Pollution. Focus* 3: 111-129.
- Sanderson, E.G., Farant, J.P. 2004. Indoor and outdoor polycyclic aromatic hydrocarbons in residences surrounding a Soderberg aluminum smelter in Canada. *Environmental Science & Technology*. 38: 5350-5356.
- Sani, S., 1987. Urbanization and the Atmospheric Environment in the Low Tropics. Karya Press, Kuala Lumpur.
- Santos-Burgoa, C., C. Rios, L.A. Nercadi, R. Arecuga-Serrano, F. Cano- Vall and R.A. Eden-Wynter. 2001. Exposure to manganese; health effects on the general population, a pilot study in central Mexico. *Environ. Res. Sect. A*, 85: 90-104.
- Sastry, N. 2002. Forest fires, air pollution, and mortality in Southeast Asia. *Demography*. 39(1): 1-23.
- Sayer, J. M., Chadha, A., Agarwal, S. K., Yeh, H. J. C., Yagi, H., and Jerina, D. M. 1991. Covalent nucleoside adducts of benzo[a]pyrene 7,8-diol 9,10-epoxides: structural reinvestigation and characterization of a novel adenosine adduct on the ribose moiety. *The Journal of Organic Chemistry*. 56(1): 20-29.
- Schauer, C., Niessner, R., Poschl, U. 2003. Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts. *Environ. Sci. Technol.* 37: 2861-2868.
- Schlesinger, R.B., Kunzli, N., Hidy, G.M., Gotschi, T. and Jerrett, M., 2006. The health relevance of ambient particulate matter characteristics: Coherence of toxicological and epidemiological inferences. *Inhalation Toxicology*. 18(2): 95-125.
- Schuelze, J., Hartung, A., Kieb, H., Kraft, J., Lies, K.H. 1984. Identification of oxygenated polycyclic aromatic hydrocarbons in diesel particulate matter by capillary gas chromatography and capillary gas chromatography/mass spectrometry. *Chromatographia*. 19: 391–397.
- Scott, B.G.; Deeter, D.P.; Heller, J.M.; Jacobson-Kram, D.; et al. Biomonitoring of United States Army soldiers serving in Kuwait in 1991. *Cancer Epidemiol. Biomarkers Prev.* 1998, 7, 545-551.
- Seiler, W., Crutzen, P.J., 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Climatic Change*. 2: 207–247.

- Seinfeld, J. H. and Pandis, S. N. 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. New York, John Wiley & Sons, Inc.
- Seinfeld, J.H. and Pandis, S.N. 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley & Sons, Inc., New York. 1998.
- Seinfeld, J.H., Pankow, J.F., 2003. Organic atmospheric particulate material. *Annual Review of Physical Chemistry*. 54: 121–140.
- Selinus, O. 2004. Medical Geology: an emerging speciality. *Terrae*. 1(1): p. 8-15.
- Shah, M.H., Shaheen, N. 2008. Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan. *Water Air and Soil Pollution* 190: 13-25.
- Shah, M.H., Shaheen, N. and Jaffar, M. 2006a. Characterization, Source Identification and Apportionment of Selected Metals in TSP in an Urban Atmosphere. *Environ. Monit. Assess.* 114: 573–587.
- Shah, M.H., Shaheen, Z., Nazir, R. 2012. Assessment of the trace elements level in urban atmospheric particulate matter and source apportionment in Islamabad, Pakistan. *Atmospheric Pollution Research*. 3:39-45
- Shamsiah Abdul Rahman, Mohd Suhaimi Hamzah, Abdul Khalik Wood, Md Suhaimi Elias, Nazaratul Ashifa Adullah Salim, Ezwiza Sanuri. 2011. Sources apportionment of fine and coarse aerosol in Klang Valley, Kuala Lumpur using positive matrix factorization. *Atmospheric Pollution Research*. 2:197-206.
- Shantakumar, S., Gammon, M.D., Eng, S.M., Sagiv, S.K., Gaudet, M.M., Teitelbaum, S.L., et al.,. 2005. Residential environmental exposures and other characteristics associated with detectable PAH-DNA adducts in peripheral mononuclear cells in a population-Based sample of adult females. *J Expo Anal Environ Epidemiol*. 15(6): 482–490.
- Sharma, H., Jain, V.K., Khan, Z.H. 2008. Atmospheric polycyclic aromatic hydrocarbons (PAHs) in the urban air of Delhi during 2003. *Environ Monit Assess*, 147:43–55
- Shi, G., Chen, Z., Bi, C., Wang, L., Teng, J., Li, Y. and Xu, S. 2011. A Comparative Study of Health Risk of Potentially Toxic Metals in Urban and Suburban Road Dust in the Most Populated City of China. *Atmos. Environ.* 45: 764–771.
- Shi, J., Peng, Y., Li, W., Qiu, W., Bai, Z., Kong, S., Jin, T. 2010. Characterization and source identification of PM10-bound polycyclic aromatic hydrocarbons in urban air of Tianjin, China, *Aerosol Air Qual. Res.* 10: 507–518.
- Shinggu, D. Y., Ogugbuaja, V. O., Barminas, J. T. & Toma, I. 2007. Analysis of street dust for heavy metal pollutants in Mubi, Adamawa State, Nigeria. *International Journal of Physical Sciences*. 2(11) :290-293.
- Shridhar, V., Khillare, P.S., Agarwal, T., Ray, S. 2010. Metallic species in ambient particulate matter at rural and urban location of Delhi. *Journal of Hazardous Materials*. 175: 600-607.
- Simoneit, B.R.T., 1984. Organic matter of the troposphere FIII. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. *Atmospheric Environment*. 18: 51–67.

- Simoneit, B.R.T., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y. 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment*. 25A: 2111–2129.
- Singh, H.J., Mohammad, N.H., Nila, A. 1999. Serum calcium and parathormone during normal pregnancy in Malay women. *J Matern Fetal Med*. 8(3): 95-100
- Smith, D, J.T., and Harrison, S, M. 1996. Concentrations, trends and vehicles sources profile of PAHs in the UK atmosphere, *Atmos Environ* (UK). 30: 2513-2525.
- Smith, D.J.T. and Harrison, R.M. 1998. Polycyclic Aromatic Hydrocarbons in Atmospheric Particles. In “Atmospheric Particles”, R.M. Harrison and R. Van Grieken Eds., John Wiley & Sons.
- Soetan, K.O., Olaiya, C.O., Oyewala, O.E. 2010. The important of trace elements for humans, domestic animals and plants: A review. *African Journal of Food Science*. Vol 4(5): 200-222.
- Sohrabpour, M., Mirzaee, H., Rostami, S., Athari, M. 1999. Elemental concentrations of the suspended particulate matter in the of Tehran. *Environmental International*. 25: 75-81.
- Song, Y ., Zhang, Y .H., Xie, S.D., Zeng, L.M., Zheng, M., Salmon, L.G., Shao, M. and Slanina, S. 2006. Source Apportionment of PM 2.5 in Beijing by Positive Matrix Factorization. *Atmos. Environ*. 40: 1526–1537.
- Srimuruganandam, B., and Shiva Nagendra, S.M. 2012. Sources of PM 10 and PM 2.5 mass using chemical mass balance model at urban side. *Sci. Total. Environ*. 1(433): 819
- Srivastava, A., Gupta, S. and Jain, V.K. 2008. Source Apportionment of Total Suspended Particulate Matter in Coarse and Fine Size Ranges over Delhi. *Aerosol Air Qual. Res*. 8: 188–200.
- Steets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.H., and Yarber, K.F. 2003. An inventory of gaseous and primary aerosol emission in Asia in the year 2000. *J,Geophys.Res*. 108: 8809.
- Sternbeck, J., Sjodin, A. and Andreasson, K. 2002. Metal Emissions from Road Traffic and the Influence of Resuspension Results from Two Tunnel Studies. *Atmos. Environ*. 36: 4735–4744.
- Su, Y., Lei, Y.D., Wania, E., Shoeib, M., Harner, T. 2006. Regressing gas/particle partitioning data for polycyclic aromatic hydrocarbons. *Environmental Science and Technology*. 40: 3558–3564.
- Suzuki, K and Yoshinaga, J. 2007. Inhalation and dietary exposure to polycyclic aromatic hydrocarbon and urinary 1-hydroxypyrene in non smoking university students. *Int Arch Occup Environ Health*. 81: 115-121.
- Tang D, Phillips DH, Stampfer M, Mooney LA, Hsu Y, Cho S, Tsai WY, Ma J, Cole KJ, She MN, Perera FP. 2001. Association between carcinogen-DNA adducts in white blood cells and lung cancer risk in the physicians health study. *Cancer Research*. 61:6708–6712.
- Tas, S., Buchet, J.P., Lauwerys, R. 1994. Determinants of benzo(a)pyrene diol epoxide adducts to albumin in workers exposed to polycyclic aromatic hydrocarbon. *Int Arch Occup Environ Health*. 66: 343-348.

Tobiszewski, M., and Namies'nik, J. 2012. PAH diagnostic ratios for the identification of pollution emission sources, *Environ. Pollut.* 162: 110–119.

Tong STY, Lam KC. Home sweet home. 2000. A case study of household dust contamination in Hong Kong. *Sci Total Environ.* 256:115–23.

Tong, H., Sweetman, J., Karasek, F. 1984. Quantitative analysis of polycyclic aromatic compounds in diesel exhaust particulate extracts by combined chromatographic techniques. *Journal of Chromatography.* 312: 183–202.

Topinka J., Rossner P.Jr, Milcova A., Schmuczerova J., Svecova V., Sram R.J. 2011. DNA adducts and oxidative DNA damage induced by organic extracts from PM2.5 in an a cellular assay. *Toxicology Letters.* 202: 186-192.

Tornqvist M, Fred C, Haglund J, Helleberg H, Paulsson B, Rydberg P. 2002. Protein adducts: quantitative and qualitative aspects of their formation, analysis and applications. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences.* 778:279–308.

Tsapakis, M., Stephanou, E. 2003. Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. *Atmos. Environ.* 37: 4935-4944.

U.S. Environmental Protection Agency, 1989. Risk Assessment Guidance for Superfund, vol. I: Human Health Evaluation Manual. EPA/540/1-89/002. Office of Soil Waste and Emergency Response. US Environmental Protection Agency. Washington, D.C. <http://www.epa.gov/superfund/programs/risk/ragsa/index.htm>.

U.S. Environmental Protection Agency, 1996. Soil Screening Guidance: Technical Background Document. EPA/540/R-95/128. Office of Soil Waste and Emergency Response. U.S. Environmental Protection Agency. Washington, D.C. <http://www.epa.gov/superfund/resources/soil/toc.htm#p1>.

U.S. Environmental Protection Agency, 2001. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites. OSWER 9355.4-24. Office of Soil Waste and Emergency Response. U.S. Environmental Protection Agency. Washington, D.C. <http://www.epa.gov/superfund/resources/soil/ssgmarch01.pdf>.

U.S. Environmental Protection Agency, 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment). OSWER 9285.7-02EP. Office of Soil Waste and Emergency Response. U.S. Environmental Protection Agency. Washington, D.C.

U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation. 1989. Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual (Part A). EPA_540-R-070-002. OSWER 9285.7- 82.

U.S. Environmental Protection Agency. 1991. Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions. Washington, D.C. OSWER Directive 9355.0-30. [As cited in USEPA, 2009a].

U.S. Environmental Protection Agency. 2009. Human Health Risk Assessment Work Plan for the Upper Columbia River Site Remedial Investigation and Feasibility Study. Prepared by Syracuse Research Corporation for U.S. EPA Region 10, Seattle, WA.

USEPA (United States Environmental Protection Agency). 2005. Guidelines for Carcinogen Risk Assessment EPA/630/P-03/001B. Risk Assessment Forum. National Center for Environmental Assessment, Washington DC.

USEPA. 1994. Determination of Trace Elements in Water and Wasters by Inductively Coupled Plasma-Mass Spectrometry-Method 200.8. U.S. Environmental Protection Agency, OHIO 45268.

USEPA. 1999. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, U.S. Environmental Protection Agency Cincinnati, OH 45268.

USEPA. 2004. Air quality criteria for particulate matter. Vol 1, 2, and 3. Research Triangle Park NC: National Center for Environmental Assessment-RTP Office.

USEPA. 2004. Human Health Evaluation Manual Part E (Supplemental Guidance for Dermal Risk Assessment). Available at: http://www.epa.gov/oswer/riskassessment/ragse/pdf/part_e_final_revision_10-03-07.pdf.

USEPA. 2009. Human Health Evaluation Manual Part F (Supplemental Guidance for Inhalation Risk Assessment). http://www.epa.gov/oswer/riskassessment/ragsf/pdf/partf_200901_final.pdf.

Vahakangas, K., and Pelkonen, O. 1989. Host variations in carcinogenic metabolism and DNA repair. In Lynch, H.T. and Hiramaya, R. (eds) Genetic epidemiology of cancer. CRC Press. Boca Raton. Page 6-40.

Valavanidis, A., Fiotakis, K., Vlahogianni, T., Bakeas, E.B., Triantafillaki, S., Paraskevopoulou, V., Dassenakis, M. 2006. Characterization of atmospheric particulates, particle-bound transition metals and polycyclic aromatic hydrocarbons of urban air in the centre of Athens (Greece). *Chemosphere*. 65: 760-768.

Valigura, R.A. 2001. An introduction to the first assessment of nitrogen loads to US estuaries with an atmospheric perspective. pp. 1-10. In R.A. Valigura, R.B. Alexander, M.S. Castro, T.P. Meyers, H.W. Paerl, P.E. Stacey and R.E. Turner (eds.) Nitrogen loading in coastal water bodies: an atmospheric perspective. AGU. Washington, D.C.

Vasconcellos, P.C., Zacarias, D., Pires, M.A.F., Pool, C.S., Carvalho, L.R.F. 2003. Measurements of polycyclic aromatic hydrocarbons in airborne particles from the metropolitan area of São Paulo city, Brazil. *Atmos Environ*. 37:3009-18.

Vassilakos, C., Veros, D., Michopoulos, J., Maggos, T. and O' Connor, C.M. 2007. Estimation of Selected Heavy Metals and Arsenic in PM₁₀ Aerosols in the Ambient Air of the Greater Athens Area, Greece. *J. Hazard. Mater*. 140: 389-398.

Veerabhadran Ramanathan, Muvva V., Ramana., Roberts. G, Dohyeong Kim, Craig Corrigan, Chul Chung & David Winker. 2007. Warming trends in Asia amplified by brown cloud solar absorption. *Nature*. 448: 575-578.

Versieck, J & Cornelis, R. 1980. Normal levels of trace elements in human blood plasma or serum. *Anal Chim. Acta*. 116-217.

- Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W. and Hitzenberger, R. 2008. Source Apportionment of Particulate Matter in Europe: A Review of Methods and Results. *J. Aerosol Sci.* 39: 827–849.
- Vignati, E., Facchini, M.C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., Dowd, C.D.O. 2010. Global scale emission and distribution of sea-spray aerosol: Sea-salt and organic enrichment. *Atmospheric Environment*. 44: 670-677.
- Vir, S.C., Love, A.G.G., Thompson, W. 1981. Serum and hair concentrations of copper during pregnancy. *Am J Clin Nutr.* 34:2382-2388.
- Voutsas, D., Samara, C. 2002. Labile and bioaccessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas, *Atmospheric Environment* 36: 3583-3590.
- Vu, V.T., Lee, B.K., Kim, J.T., Lee, C.H., Kim, I.H. 2011. Assessment of carcinogenic risk due to inhalation of polycyclic aromatic hydrocarbons in PM10 from an industrial city: a Korean case-study. *J. Haz. Mat.* 189: 349-356.
- Wang, C.X., Zhu, W., Peng, A., Guichreit, R. 2001. Comparative studies on the concentration of rare earth elements and heavy metals in the atmospheric particulate matter in Beijing, China, and in Delft, the Netherlands. *Environment International*. 26: 309-313.
- Wang, H.K., Huang, C.H., Chen, K.S. and Peng, Y.P. 2010. Seasonal Variation and Source Apportionment of Atmospheric Carbonyl Compounds in Urban Kaohsiung, Taiwan. *Aerosol Air Qual. Res.* 10: 559–570.
- Wang, X., X. Bi, G. Sheng and J. Fu. 2006. Hospital indoor PM10/PM2.5 and associated trace elements in Huangzhou, China. *Sci. Total Environ.* 366: 124-135.
- Watson, J.G. 2002. Visibility: science and regulation. *Journal of the Air and Waste Management Association*. Vol 52(6): 628-713.
- Watson, J.G. and Chow, J.C. 2000. Reconciling Urban Fugitive Dust Emissions Inventory and Ambient Source Contribution Estimates: Summary of Current Knowledge and Needed Research. DRI Document No. 6110.4F.
- Watson, J.G., Chow, J.C., Fujita, E.M. 2001. Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment*. 35: 1567-1584.
- Wesely, M.L. & Hicks, B.B. 2000. A review of the current status of knowledge on dry deposition. *Atmospheric Environment*. 34:2261-2282.
- Wester, P.W., Muller, J..JA., Slob, W., et al.,. 2012. Carcinogenic activity of benzo[a]pyrene in a 2 year oral study in Wistar rats. *Food Chem Toxicol.* 50: 927-35.
- Whitall, D., Hendrickson, B., Paerl, H., 2003. Importance of atmospherically deposited nitrogen to the annual nitrogen budget of the Neuse River estuary, North Carolina. *Environmental International*. 29: 303–399.

WHO (World Health Organization), 2000. Air Quality Guidelines for Europe. European Series No 91, World Health Organization. WHO Regional Publications, Geneva.

WHO, 2004. Health aspects of air pollution: results from the WHO project “Systematic review of health aspects of air pollution in Europe”, World Health Organization, Regional Office for Europe, Bonn, Germany, Copenhagen, Denmark.

WHO, 2005. WHO air quality guidelines global update. 2005. World Health Organization, Regional Office for Europe, Bonn, Germany., Copenhagen, Denmark.

WHO, 2006. WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Geneva, Switzerland.

WHO. 2000. Guidelines for Air Quality. World Health Organization. Geneva. Retrieved from <http://www.who.int/environmentalinformation/Air/Guidelines/aqguide7.pdf>.

Wickramasinghe, A.P., Karunaratne, D.G.G.P., Sivakanesan, R. 2012. PM 10 bound polycyclic aromatic hydrocarbons: biological indicators, lung cancer risk of realistic receptors and ‘source-exposure-effect relation- ship’ under different source scenarios. *Chemosphere*. 87: 1381–1387.

Widory,D., Liu, X., and Dong, S.. 2010. Isotop of lead and strontium in aerosols (TSP & PM 2.5) in Beijing. *Atmospheric Environment*. 44(30): 3679-3687.

Wilson, R. and J. Spengler. 1996. Particles in Our Air: Concentrations and Health Effects. Harvard University Press, Boston.

World Health Organization, 1998. Report of the Bioregional Workshop on Health Impacts of Haze Related Air Pollution. WHO, Manila, Philippines.

World Health Organization. 2002. World Health Report. Reducing Risk, Promoting Healthy Life. WHO, Geneva, Switzerland.

Xie, S.D., Liu, Z., Chen, T. and Hua, L. 2008. Spatiotemporal Variations of Ambient PM 10 Source Contributions in Beijing in 2004 Using Positive Matrix Factorization. *Atmos. Chem. Phys.* 8: 2701–2716.

Xue,W, and Warshawsky,D. 2005. Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbon and DNA damage: a review. *Toxicol Appl Pharmacol*. 206:(1), 73-93.

Yu, J., Griffin, R.J., Cocker, D.R., Flangan, R.C., Seinfeld, J.H., Blanchard, P. 1999. Observation of gaseous and particulate products of monoterpene oxidation in forest atmosphere. *Geophysical Research Letters*. 26: 1145-1148.

Yunker, M. B. and Macdonald, R. W. 2003. Petroleum biomarker sources in suspended particulate matter and sediments from the Fraser River Basin and Strait of Georgia, Canada, Org. *Geochem*. 34: 1525–1541.

Yunker, M. B., Macdonald, R. W., Snowdon, L. R., and Fowler, B. R. 2011. Alkane and PAH biomarkers as tracers of terrigenous organic carbon in Arctic Ocean sediments, Org. *Geochem*. 42: 1109– 1146.

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre, S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, Org. *Geochem*. 33: 489–515.

- Zailina, H., Juliana, J., Azman, Z.A. and Azizi, O. 1996. Perhubungan partikel terampai (PM10) dengan pesakit asma (The relationship between suspended particles (PM10) with asthmatic patients). *PERTANIKA J. of Sci. and Technol.*, 4(2): 275-82.
- Zailina, H., Juliana, J., Norzila, M.Z., Azizi, H.O. and Jamal, H.H. 1997. The relationship between Kuala Lumpur haze and asthmatic attacks in children. *Malaysian J. Child Health*, 9 (2): 151-159.
- Zappoli, A., Andracchio, S., Fuzzi, S., Facchini, M.C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E., Hansson, H.-C., Rosman, K., Zebühr, Y. 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos. Environ.* 33: 2733–2743.
- Zeiger, E. 2001. Mutagens that are not carcinogens: faulty theory or faulty tests? *Mutat. Res-Genet. Toxicol.* 492: 29-38.
- Zereini, F., Alt, F., Messerschmidt, J., Wiseman, C., Feldmann, I., Von Bohlen, A., Muller, J., Liebl, K., Puttmann, W. 2005. Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am Main, Germany. *Environmental Science and Technology*. 39: 2983-2989.
- Zhang, S., Hou, S., Ma, X., Qin, D., and Chen, T. 2007. Culturable bacteria in Himalayan glacial ice in response to atmospheric circulation. *Biogeosciences*. 4: 1-9.
- Zheng, M., Cheng, Y., Zeng, L.M and Zhang, Y.H. 2011. Developing Chemical Signatures of Particulate Air Pollution in the Pearl River Delta Region, China,” *Journal of Environmental Sciences*. Vol. 23, No. 7: 1143-1149.
- Zheng, N., Liu, J., Wang, Q. and Liang, Z. 2010a. Heavy Metals Exposure of Children from Stairway and Sidewalk Dust in the Smelting District, Northeast of China. *Atmos. Environ.* 44: 3239–3245.
- Zheng, N., Liu, J., Wang, Q. and Liang, Z. 2010b. Health Risk Assessment of Heavy Metal Exposure to Street Dust in the Zinc Smelting District, Northeast of China. *Sci. Total Environ.* 408: 726–733.
- Zheng, N., Liu, J., Wang, Q. and Liang, Z. 2010b. Heavy metals exposure of children from stairway and sidewalk dust in the Smelting District, Northeast of China. *Atmospheric Environment*. 44: 3239–3245.
- Zoller, W. H., E. S. Gladney, and R. A. Duce. 1974. Atmospheric concentrations and sources of trace metals at the south pole. *Science*. 183:198-200.