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Development of Analytical Methods for Particulate-bound Polycyclic Aromatic Hydrocarbons (PAHs) in Thailand

By

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This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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Abstract

This study developed analytical methods to quantify particulate-bound polycyclic aromatic hydrocarbons (pPAHs). The methods were used to characterise PAHs in house dust and particulate matter (PM_{10}) samples, respectively, in two case studies. Dust samples were collected from rural households in Malawi to represent indoor particles from biomass fuel combustion. PM_{10} samples were collected from three sites in the Bangkok Metropolitan Administration (BMA), Thailand to represent air pollutants in roadside, industrial and urban background environments. PAHs were quantified using a gas chromatograph-mass spectrometer (GC-MS). Comprehensive two-dimensional gas chromatograph coupled with time-of-flight mass spectrometer (GCxGC TOFMS) was used for the screening of unknown air pollutants in PM_{10}.

Low molecular weight 2-ring and 3-ring PAHs were more abundant in dust samples collected in Malawi, while high molecular weight 4-ring to 6-ring PAHs were more abundant in PM_{10} samples collected in Thailand. Spatial and temporal variations in PM_{10} and pPAH concentrations were examined between and within the three sampling sites in Thailand. Annual average benzo[a]pyrene (BaP) concentrations were 0.47 ± 0.39 ng m^{-3}, 0.35 ± 0.27 ng m^{-3} and 0.24 ± 0.19 ng m^{-3} at the roadside, industrial and urban background sites, respectively.

Cancer risks associated with pPAHs were estimated using BaP and BaP toxic equivalency (BaP-TEQ) concentrations. The highest incremental lifetime cancer risk was found in the residential adult group at 4.2×10^{-7} at the industrial site. Although the highest PM_{10} and total PAHs concentrations were found at the roadside site, the highest carcinogenic potential of total PAH (in terms of BaP toxic equivalency concentration) was found at the industrial site. Thus, the cancer risk estimation relies more on the composition of pPAHs than its concentration. Estimated lifetime lung cancer risks associated with pPAHs in all three sites were in the 'acceptable' range of less than 1×10^{-6} defined by the United States Environmental Protection Agency.

Dedication

To my parents, my sister and my dearest niece – Annabelle Pamin Bettenhausen.
I would not be who I am today without your love and support.

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Firstly, I would like to express deep gratitude to my supervisors, Professor Robert Kalin and Dr Iain Beverland, for their guidance, continuous support, motivation and especially for putting pressure and keep pushing me to accomplish my goal. It has been a great pleasure to work with them, and the experience gained during this time has widened my vision. I am particularly grateful for the assistance enthusiastically given by Mara Knapp who always does her best to keep the lab running under any circumstances. Without Mara's great help, it will be impossible to complete all experiments on time. A big thank you goes to Tatyana Peshkur, former SETN chemist, for providing invaluable training on ASE technique that enabled me to perfect my experiment. Thanks also to friends and colleagues at the University of Strathclyde (Muk, Puk, Kai, Nog, P'Tai, Nong Tai, Prai, Ple, Pupae, Elli, Sadia, Laura, Fabrizio and Chris–particularly to Ryan) for making life in Glasgow more enjoyable. I am extremely thankful to Tanya, my personal physiotherapist, and David who patiently read my thesis. There are many good friends who are not mentioned here, but I wish they know that they are an important part of my success.

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Lastly, I would like to thank the most important people in my life, my family, for supporting me on everything I do.

Amornphat (Ann) Tadsanaprasittipol

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List of Abbreviations

µg	microgramme (1 µg = 1 x 10^{-6} g)
µm	micrometre
1D-GC	one-dimensional GC
ACE	acenaphthene
ACY	acenaphthylene
ADAF	age-dependent adjustment factors
amu	atomic mass unit
ANT	anthracene
ASE	accelerated solvent extraction
AT	averaging time
BaA	benzo[a]anthracene
BaP	benzo[a]pyrene
BaP	benzo[a]pyrene
BaP-TEQ	BaP toxic equivalent
BbF	benzo[b]fluoranthene
BkF	benzo[k]fluoranthene
BMA	Bangkok Metropolitan Administration
BP	benzo[g,h,i]perylene
BW	body weight
CA	contaminant concentration in air
CHR	chrysene
CSF	cancer slope factor
DBA	dibenz[a,h]anthracene

df	film thickness
D-PAHs	deuterated PAHs
EC	exposure concentration
ED	exposure duration
EF	exposure frequency
EGAT	Electricity Generating Authority of Thailand – Nonthaburi
ET	exposure time
FLT	fluoranthene
FLU	fluorene
g	gramme
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GC-QMS	GC-MS with quadrupole mass analyser
GCxGC	comprehensive two-dimensional gas chromatography
h	hour
i.d.	internal diameter
IARC	International Agency for Research on Cancer
ILCR	incremental lifetime cancer risk
IP	indeno[1,2,3-cd]pyrene
IR	inhalation rate
IUR	inhalation unit risk
LADD	lifetime average daily dose
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantification

LT	lifetime
m/z	mass-to-charge ratio
min	minute
mL	millilitre
mm	millimetre
ms	millisecond (1 ms = 1 x 10^{-3} s)
N	naphthalene
N/A	not available
ng	nanogramme (1 ng = 1 x 10^{-9} g)
NHAD	National Housing Authority Dindaeng
NIST	National Institute of Standards and Technology
nm	nanometre
OEHHA	Office of Environmental Health Hazard Assessment
PAHs	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCD	Pollution Control Department
PFE	pressurised fluid extraction
pg	picogramme (1 pg = 1 x 10^{-12} g)
PHE	phenanthrene
PLE	pressurised liquid extraction
PM	particulate matter
PM_{10}	particulate matter with aerodynamic diameters less than 10 µm
pPAHs	particulate-bound polycyclic aromatic hydrocarbons
PRD	Public Relations Department
PYR	pyrene

s	second
SIM	selected ion monitoring
SPE	solid-phase extraction
SRM	standard reference material
TEF	toxic equivalency factor
TOFMS	time-of-flight mass spectrometer
UR	adult unit risk
US EPA	United States Environmental Protection Agency
vs.	versus
WHO	World Health Organisation
y	year

Chapter 1

Introduction

1.1 Background

Air pollution associated with particulate matter (PM) is a common public health issue worldwide. Particulate matter is generally classified into two size ranges: fine particles measuring less than 2.5 μm ($PM_{2.5}$) and coarse particles sized between 2.5 and 10 μm (PM_{10}). Both acute and long-term exposures to PM can lead to a broad range of adverse health outcomes including respiratory and cardiovascular diseases, lung cancer and shortened life expectancy (WHO, 2005). WHO has recommended air quality guidelines for health protection exposure to outdoor PM_{10} for acute exposure as 24-hour mean at 50 μg m^{-3} and annual mean for long-term exposure at 20 μg m^{-3}. Apart from its toxicity, PM is also known to contain various harmful substances depending on emission sources including polycyclic aromatic hydrocarbons (PAHs), particularly benzo[a]pyrene (BaP) that is related to the development of lung cancer (Buening *et al.,* 1978). Concerning the lung cancer risk from PAHs exposure, BaP is often used as a benchmark for carcinogenic PAHs and the European Commission specified the annual mean of 1 ng m^{-3} (EC, 2004).

PAHs exist in all phases of environment from air, water, soil as well as sediment. Anthropogenic PAHs are emitted from incomplete combustion of organic materials and are in semi-volatile compounds those mostly incorporated into the particulate phase. Low molecular weight PAHs with 2 or 3 fused benzene rings predominantly exist in the gas phase and are less harmful to health. Chronic exposure to PAHs is known to cause lung cancer owing to the carcinogenicity and mutagenicity of some high molecular weight PAHs including benzo[a]pyrene, dibenz[a,h]anthracene, benz[a]anthracene, benzo[b]floranthene, benzo[k]floranthene, chrysene and indeno[1,2,3-cd]pyrene (IARC, 2010). This research focuses on the characterisation

of polycyclic aromatic hydrocarbons (PAHs) in airborne particles and their potential carcinogenic effects from long-term inhalation exposure.

In order to estimate cancer risk of particulate-bound PAHs, the quantification of particulate-bound PAHs was carried out using the combination of pressurised fluid extraction and gas chromatography mass spectrometry technique. PAHs were extracted from particulate samples under high pressure and temperature, and then the quantification of 16 US EPA priority listed PAHs was performed by a gas chromatograph-mass spectrometer (GC-MS) that separated the PAHs mixture and selectively identified target compounds according to their masses. Analytical methods were verified in a follow-up study of PAHs in residential soot and dust in rural areas of Malawi (Chidziwisano, 2012). Dust samples collected from rural households were used in the method development and instrument familiarisation. Methods were tested and laboratory skills were developed prior to the analysis of particulate matter samples.

The main study of this research is to evaluate the air quality related to particulate bound PAHs and health risk in the Bangkok Metropolitan Administration (BMA). A long-term sampling of particles to encompass the seasonal variation of PAHs is vital to the determination of PAHs concentrations for cancer risk assessment. PM_{10} samples collected at three ambient air monitoring stations in the BMA were analysed for one year. Annual mean PAHs concentrations were determined and lung cancer risks were estimated in three study areas classified as industrial, roadside and urban background sites. The results of PM_{10}-bound PAHs were compared and contrasted with previous studies in Thailand and other cities where airborne particle issue raised the awareness on public health.

1.2 Scope of Thesis

This research focuses on polycyclic aromatic hydrocarbons (PAHs) in particulate matter and their potential adverse health effects. PAHs are emitted from incomplete combustion of organic materials such as fossil fuels, coal, and fire woods. Samples used in this study include dust samples collected from rural households in the south

of Malawi (Chikwawa districts) and ambient particulate matter (PM_{10}) samples collected from urban areas in central Thailand (Nonthaburi province and Bangkok).

Malawi dust samples represent the residential source of PAHs emitted from solid fuels burning in households that poses significant health impacts in developing countries. Dust samples were used during the method development in order to verify analytical methods while validating data from the previous study. Household dust samples were used during optimisation of extraction and analytical methods in order to develop highly efficient analytical methods for particulate-bound PAHs measurement. Pressurised fluid extraction (PFE) technique was selected for the extraction of PAHs from particulate. US EPA priority 16 PAHs were analysed using a gas chromatograph-mass spectrometer with the quadrupole mass analyser (GC-QMS). The extraction method was further optimised for the extraction with quartz fibre filter used for ambient PM_{10} sampling. After the identification of targeted PAHs by comparing spectrum obtained from the analysis of a mixed standard solution with mass spectrum in the database, an analytical method for the quantification was developed. The GC-MS quantification of 16 PAHs was performed under selected ion monitoring (SIM) mode to enable a higher sensitivity and lower detection limits suitable for a trace analysis. This exploratory research investigated indoor particulate phase PAHs from household combustion sources that effect smaller populations, but which may still however, pose significant health risk due to limitation of available appropriate healthcare.

PM_{10} samples from the BMA represent three types of environmental surroundings in urban areas, e.g., motor vehicle emissions, industrial emissions and urban background near residential sources. The main focus of this research is to identify and quantify particulate-bound PAHs in order to evaluate their toxicity that posed a health risk to a large population in the urban area of central Thailand. PAHs analysis was carried out in PM_{10} archived samples to obtain long-term data for risk assessment. Ambient PM_{10} were monitored and regulated according to the Thailand National Ambient Air Quality Standard at 120 $\mu g\ m^{-3}$ for a 24-hour mean (PCD, 2004). PM_{10} mass concentrations were analysed and samples were preserved by the Pollution Control Department (PCD) Laboratory. Samples were preserved at -20°C

until transferred to the Department of Civil and Environmental Engineering for PAHs analysis.

Analytical methods developed in this study shall be applied in the air quality monitoring in other regions of Thailand. A better understanding on the state of PM_{10}-bound PAHs in ambient air is a fundamental part of the public health protection and policy development.

1.3 Research Aim and Objectives

The aim of this research was to characterise particulate-bound polycyclic aromatic hydrocarbon (pPAHs) in the general area of the Bangkok Metropolitan Administration (BMA) and to evaluate their potential adverse health effects. Concentrations of pPAHs in particulate matter (PM_{10}) were determined during a one year sampling period in order to construct a long-term database for health risk assessment. Profiles of pPAHs in BMA were investigated to evaluate the potential health risk to people exposed to polluted urban air. The chronic exposure to carcinogenic PAHs in PM_{10} may lead to the development of lung cancer. Furthermore, the characterisation of PM_{10} and pPAHs could give rise to the source identification which is essential in the development of emission control measures.

The research objectives were:

(i) To develop efficient analytical methods for the analysis of 16 US EPA priority PAHs in particulate samples using a pressurised fluid extraction system and a quadrupole GC-MS

(ii) To characterise and evaluate the air quality situation associated with particulate-bound PAHs at three ambient air sampling sites representing roadside, industrial and urban background environments in the Bangkok Metropolitan Administration (Thailand)

(iii) To investigate spatial and seasonal variations of PM_{10} and PM_{10}-bound PAHs in urban areas of central Thailand

(iv) To estimate the human health risk associated with the long-term exposure to pPAHs in the Bangkok Metropolitan Administration

(v) To develop a high sensitivity and high resolution method for the screening of non-targeted air pollutants and unknown compounds in airborne particulate samples (PM_{10})

1.4 Thesis Outline

This thesis explains the development of analytical methods for the determination of polycyclic aromatic hydrocarbons in particulate samples. The methods were applied for the characterisation of long-term particulate-bound PAHs concentrations which were used for the estimation of lung cancer risk.

Chapter 2 presents an introduction and background of problems caused by particulate matter and the significance of the study on particulate phase PAHs.

Chapter 3 examines analytical techniques for the extraction, identification and quantification of PAHs in particulate samples.

Chapter 4 describes a follow-up study of indoor PAHs exposure in rural area of Malawi. The results of a preliminary study on analytical method development using dust samples were compared with the results of a previous study on the soot samples. Dust samples collected from rural households in Malawi were utilised in methods verification.

Chapter 5 describes the main study of ambient particulate-bound PAHs in the Bangkok Metropolitan Administration area of Thailand. Concentrations of PM_{10}-bound PAHs were quantified from the long-term PM_{10} samples collected in urban background, roadside and industrial ambient air sampling sites. The characterisation of PAHs and source identification are illustrated in this chapter.

Chapter 6 illustrates the time series analysis and seasonal variation of ambient pPAHs measured at three sampling sites. The results show variations of PM_{10} and PAHs related to climate conditions.

Chapter 7 assesses health risks of long-term exposure to pPAHs in terms of the incremental lifetime cancer risk to the population by age group.

Chapter 8 presents the application of comprehensive two-dimensional gas chromatography (GCxGC) for the screening of potential air pollutants in PM_{10} samples from three sampling sites.

Chapter 9 summarises the key findings of this thesis and recommendations for future work.

Chapter 2

Literature Review

2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of semi-volatile organic compounds composed of at least two conjugated benzene rings. They are ubiquitous contaminants in the environment and are emitted from both natural and anthropogenic sources such as forest fire, volcanic eruption, industries, incinerations, fuel combustion activities, and etc. Anthropogenic PAHs are mainly emitted from incomplete combustion of organic materials including combustion of fossil fuels, burning of biomasses and vehicle emissions. PAHs are a public health concern due to their detrimental effects on human health including acute, carcinogenic and mutagenic effects. Strong evidence of the carcinogenic effect of exposure to atmospheric PAHs is shown by inhalation studies of benzo[a]pyrene (BaP) in Syrian golden hamsters that resulted in the development of tumours in the pharynx and larynx of exposed hamsters (Thyssen *et al.,* 1981). A recent study also showed that the DNA damage in Chinese hamster lung fibroblasts was associated with higher molecular weight PAHs (Teixeira *et al.,* 2012).

The control of PAHs emissions cannot be effectively implemented due to the wide range, scale and variety of source types. Temporal emissions of PAHs can be intermittent, continuous or seasonal, while spatial distributions range from small local household activities to large scale industries. As a result, PAHs are distributed into all phases of the environment and exposure is unavoidable. The most concerning health effects of PAHs have been the carcinogenicities of several semi-volatile PAHs appearing in the particulate phase. Toxicity of BaP has been intensively investigated in both animals and humans. The carcinogenicity of BaP is high and associated with lung cancer development. The need to understand health risks induced by PAHs

exposure, particularly lung cancer that is associated with BaP, makes the development of accurate and reliable methods for PAHs measurement essential.

The sampling of atmospheric PAHs existing in gas and particulate phases requires a combination of a trapping adsorbent that can absorb gaseous PAHs and a filter to collect particles. After sampling, which is mostly carried out for 24 hours, samples should be carefully preserved under suitable conditions to maintain their integrity. As mentioned in EPA analytical method, post-collection volatilisation may occur and cause non-volatile PAHs dispersion (US EPA, 1999). Another challenge is the determination of PAHs contained in particulate samples as they are often found in a complex mixture. The conventional sample pre-treatment is the Soxhlet extraction using up to 1000 mL of organic solvents refluxing for almost 24 hours. Several clean-up steps and the concentration of extracted sample are required prior to the analysis. The official protocol for PAHs analysis is a highly time and resource consuming method, thus studies have been conducted for alternative analytical methods to reduce the time and improve the separation and identification of PAHs in complex mixture samples.

PAHs occur as a complex mixture in a semi-volatile range causing difficulties in purification and characterisation. The analysis of PAHs in many environmental matrices involves several steps from the extraction of PAHs from the sample matrix, clean-up of the extract, separation, identification and quantification of PAHs. It is crucial that PAHs are efficiently recovered so as to capture as much as is contained in a sample. Loss and contamination of samples should be prevented during the subsequent clean-up and concentration. Sample pre-treatment should be carried out efficiently prior to chemical analysis. The accurate extraction of PAHs from environmental samples is the first step in obtaining reliable data. Several techniques were tested in order to replace the Soxhlet extraction method such as microwave-assisted extraction, supercritical fluid extraction, accelerated solvent extraction and 'quick easy cheap effective rugged and safe' (QuEchERS) extraction (Saim *et al.,* 1997; Karthikeyan, Balasubramanian and See, 2006; Albinet, Tomaz and Lestremau, 2013). Among several techniques investigated, pressurised fluid extraction (PFE) resulted in a high extraction efficiency of analytes from particulate matrices

including polychlorinated biphenyls (PCBs) in solid environmental samples (Björklund *et al.,* 1999). In addition to the high extraction efficiency, PFE can be completed in a shorter time and require a smaller amount of solvent compared with the Soxhlet method.

To analyse a mixture containing various PAHs, the gas chromatographic technique is often employed for the separation of compounds that can be volatilised into the gas phase. Gas chromatography-mass spectrometry (GC-MS) has been widely used in PAHs analysis and already superseded the high performance liquid chromatography (HPLC) in the US EPA method TO-13A (US EPA, 1999). The equipment is suitable for separation and detection of thermally labile organic compounds in the volatile to semi-volatile range. A mixture of PAHs in a sample extract is subjected to chromatographic separation and detection by a mass spectrometer. Identification of compounds can be performed by comparing collected sample mass spectrum with a reference library of spectrum compiled in a database of pure compounds. The advantage of the GC-MS over the HPLC technique is the positive identification of analytes according to their masses. The positive identification feature of a mass spectrometer increases the confidence in identification and measurement of compounds within the sample. GC with a universal detector such as FID can be used for the quantification of PAHs. However, the identification of PAHs using the mass spectrometer is recommended for confirmation and repetition may be required occasionally when the instrument conditions are modified (US EPA, 1999). The use of GC-MS for the analysis of airborne PAHs has gained enormous popularity during the past decade (Liu *et al.,* 2007). Measurement of atmospheric PAHs in gas and particulate phases matter has been carried out by GC-MS (Borrás and Tortajada-Genaro, 2007; Delgado-Saborit *et al.,* 2010; Delgado-Saborit *et al.,* 2013).

Recently, the advance in PAHs analysis was demonstrated in the fast-screening of PAHs using PFE with in-cell clean-up for sample pre-treatment and a comprehensive two-dimensional gas chromatography (GCxGC) for a rapid screening of numerous pollutants (Ong *et al.,* 2003). Extraction efficiencies of 24 PAHs in soil including 16 US EPA priority PAHs were comparable between accelerated solvent extraction (ASE) methods with and without the in-cell clean-up agent as shown in Figure 2.1.

Concentrations of alkyl PAHs derivatives including 2-methylnaphhalene (2), 1-methylnaphhalene (3), 2,6-dimethylnaphthalene (5), 2,3,5-trimethylnaphthalene (8), 1-mehylphenanthrene (12), N (1) and 3-ring PAHs (ACY:6, ACE:7, FLU:9, ANT:11) were relatively low in soil samples suggesting the distribution of more volatile PAHs in the gas phase. Concentrations PHE (10) and PAHs ranges from 4-ring to 6-ring (13-24) were high. The extract from accelerated solvent extraction without using a SiO_2 clean-up agent was purified by a short column chromatography. The advantage of in-cell clean-up in ASE is not only shortened sample preparation time but also a reduced clean-up step. As such it also prevents the loss of PAHs and the risk of contamination of the sample that may occur during clean-up. A major drawback of the GCxGC is the amount of information it produces which requires a high capacity data processing system to analyse. The data processing and interpretation may take longer than the sample analysis time. As a consequence, despite its high sensitivity and separation ability, the GCxGC is not ideal for routine quantitative work.

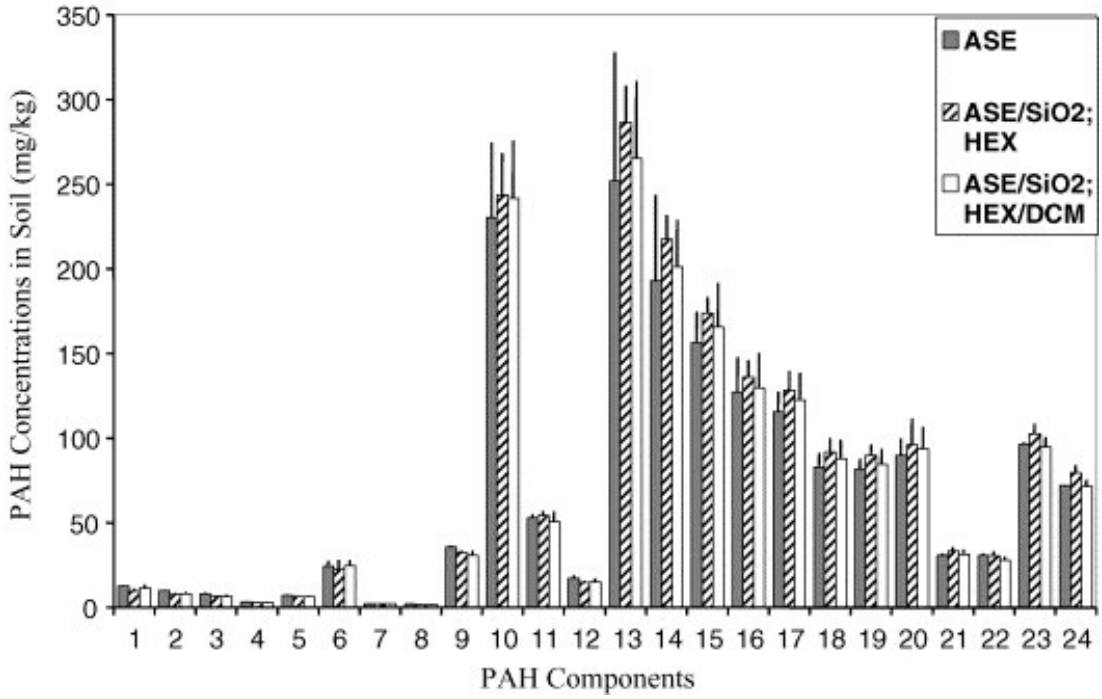

Figure 2.1 Comparison of 24 soil PAHs concentrations using three pressurised fluid extraction with and without in-cell clean-up agent (SiO_2) (Reprinted from Ong *et al.* (2003). Copyright (2003) with permission from Elsevier). PAHs analysed in soil sample using three ASE methods ranged from 2-ring naphthalene (1) to 6-ring benzo[g,h,i]perylene (24).

Owing to their mutagenic and carcinogenic activities, 16 PAHs were included in the US EPA priority pollutants and were monitored over time. The European Commission used benzo[a]pyrene as the marker for carcinogenic PAHs in ambient air and set the target value of 1 ng m^{-3} (EC, 2004). Chemical structures of the US EPA 16 priority PAHs are shown in Figure 2.2. Characterisation of particulate-bound PAHs, source identification and cancer risk assessment were conducted in many countries (Nassar, 2011; Singh, Gadi, and Mandal, 2011; Park, Kim, and Kang, 2002). Most studies focused on 16 prioritised PAHs as they encompass several known carcinogenic and mutagenic PAHs. Particulate-bound PAHs pose a health risk concern as they are distributed in the respirable particle size range that can easily enter into the human respiratory system. A long-term exposure to PAHs particularly via this inhalation route may lead to the development of lung cancer (IARC, 2010).

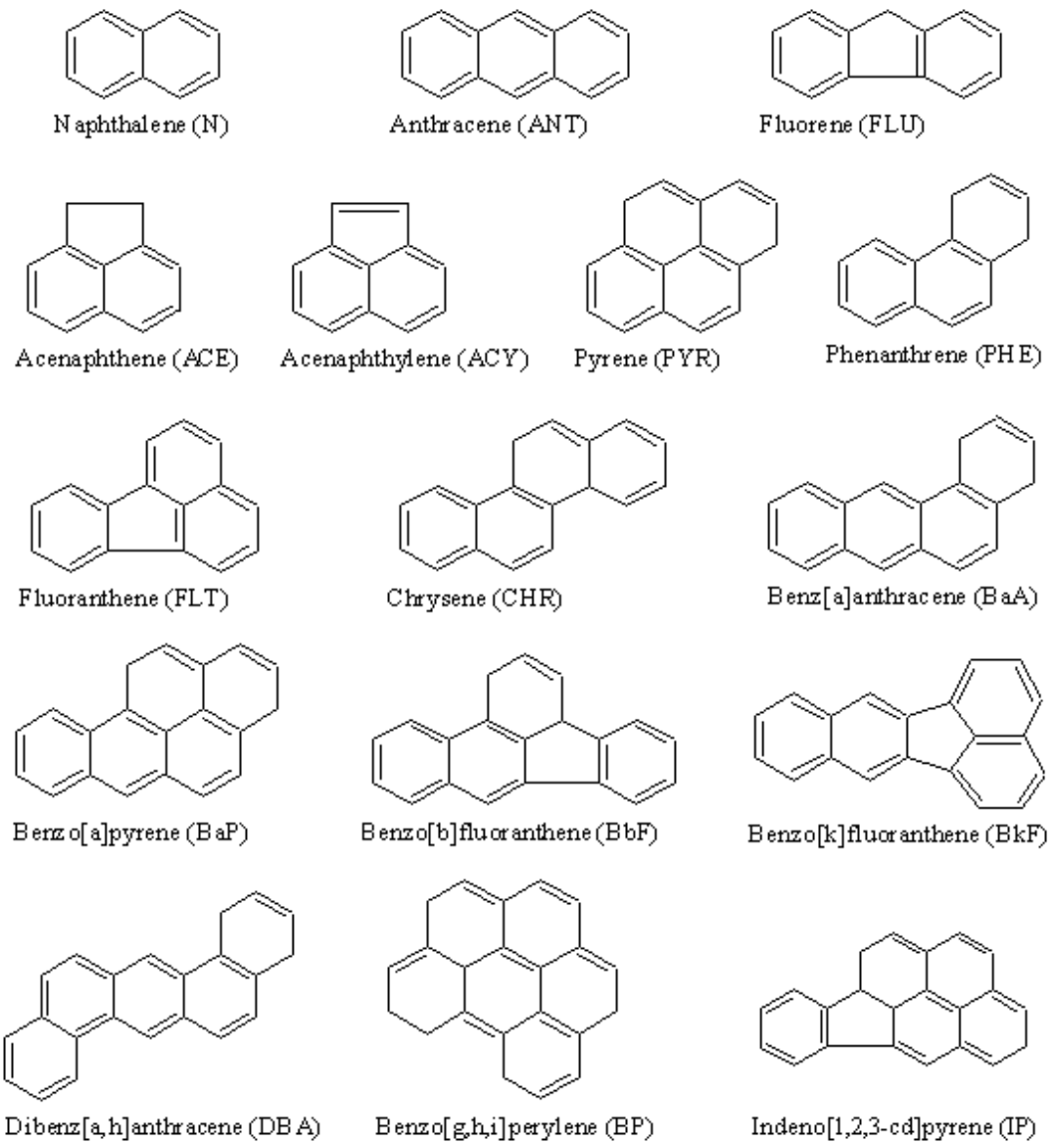

Figure 2.2 Chemical structures of 16 PAHs in the US EPA priority pollutants list.

Another major emission source of PAHs is the burning of biomass fuels during forest fires where atmospheric PAHs are emitted together with other pollutants such as carbon monoxide, volatile organic compounds and organic acids. Forest fires not only have impacts on the environment but also cause adverse health effects and casualties. Open burning of agricultural residues also causes air pollution, particularly the high concentrations of particulate matter under dry weather conditions. In the northern and southern parts of Thailand, seasonal smoke haze from agricultural residues burning and forest fires have caused problems for public

health, transportation and tourism. Burning of agricultural residues has long been a general practice in agricultural land clearing particularly in paddy fields, corn and sugar cane plantations due to its minimal cost and being less labour intensive than other processes.

Seasonal variations of PAHs have been found related to local activities. A study on seasonal variation of PM_{10} and PM_{10}-bound PAHs in Chiang Mai and Lamphun provinces in the north of Thailand indicated that PM_{10} concentrations were elevated during the dry season (December-March). The elevation was mainly associated with vegetative burning (Pengchai *et al.,* 2009). In Australia, the exposure to air pollutants during seasonal bushfire had resulted in the increase in emergency department attendances as well as hospital admissions of patients with respiratory conditions. A time-series ecological study revealed a strong association between daily PM_{10} levels and emergency department attendances of patients with smoke related respiratory symptoms (Tham *et al.,* 2009). Agricultural residue burning and forest fire can be significant sources of ambient particulate matter and PAHs that poses health risks to people in rural areas. Thus, the proper fire management such as prescribed burning might be introduced in order to reduce the severity of forest and bush fires as well as the emission of toxic pollutants including PAHs.

Outdoor air pollution has been a major problem in megacities as it poses a health risk to a large population. An increase in population and urbanisation has led to several environmental issues especially deterioration of air quality in urban areas. Bangkok, the capital city of Thailand, having an area of 1562 km^2 and a population of approximately 8 million people is considered a megacity in Southeast Asia. The city has faced a prolonged air pollution problem owing to severe and prolonged traffic congestions. The study on temporal variation of particulate-bound PAHs (pPAHs) in urban areas of Bangkok, Thailand and Tokyo, Japan showed that PAHs concentrations in the general area of Tokyo were higher than those found in the general area of Bangkok. However, higher levels of PAHs were detected in Bangkok roadside areas than in Tokyo during the sampling periods which were conducted in summer time in both countries (Boonyatumanond *et al.,* 2007). High PM_{10} levels found at roadside air quality monitoring stations indicated this difference could be

due to higher emissions from the transportation sector in Bangkok. The source apportionment of PAHs in street dust in Bangkok showed a high correlation between aerosols and heavy-duty diesel vehicles (Chetwittayachan, Shimazaki, and Yamamoto, 2002). Similar to other studies, PAHs that dominated the particulate phase of roadside air samples in Bangkok were found to be 4-ring to 6-ring PAHs while 3-ring to 4-ring including methylphenanthrenes dominated the gas phase (Boonyatumanond *et al.,* 2007). While higher levels of PM_{10} in the northern part of Thailand are normally found in the winter, seasonal variations of PM_{10} and PM_{10}-bound PAHs in the central part of Thailand have not been investigated. This study aimed to characterise PM_{10}-bound PAHs in urban areas of central Thailand and their variations in order to better understand the emission trend as well as to evaluate the health risk of exposure to pPAHs.

The concern of indoor air pollution on health effects associated with PAHs has been raised in several countries due to the use of biomass fuels. Biomass burning was found to be a significant source of both indoor and outdoor particulate matter. Indoor particulate matter is identified as a cause of health impairment in various regions where biomass fuels and firewood are used for cooking or heating. The intensive use of wood-fired heating during winter was a significant source of particulate matter in rural residential areas near Stuttgart, Germany (Bari *et al.,* 2011). Studies on chemical characterisation of air pollution from the burning of different biomass fuels have showed that cooking stoves and fire places were major sources of indoor PAHs levels which varied significantly among different types of biomass fuels, stove types and burning conditions (Lisouza, Owuor and Lalah, 2011; Zou, Zhang, and Atkiston, 2003). The characterisation of PAHs from soot samples in Western Kenya households implied that changing the fuel type from dry cow dung to shrubs and crop residues may reduce the level of exposure to PAHs from home cooking and space warming (Lisouza, Owuor and Lalah, 2011). Biomass fuels such as firewood, crop residues and shrubs are widely used for cooking and heating in many countries. They are significant sources of indoor PAHs. The composition of particulate-bound PAHs emitted depends on both fuel types and burning conditions. Since burning

conditions have an influence on PAHs emission levels, the optimisation of burning conditions may result in a reduction of indoor PAHs concentrations.

It is known that carcinogenic PAHs are widespread in the environment arising from a wide range of anthropogenic activities. Studies on PAHs have been carried out in all aspects including the speciation and quantification, sources identification as well as health risk assessment. This research focused on the development of analytical methods for the analysis of PM_{10}-bound PAHs in the ambient air. PM_{10} samples measured and archived by the Pollution Control Department laboratory for regulatory purposes were analysed for 16 US EPA priority PAHs. Samples were systematically collected and contained long-term data of ambient particulate-bound PAHs in the Bangkok Metropolitan Administration. The analysis of PM_{10}-bound PAHs can give rise to a better understanding of the current pPAHs situation, and their associated health risks. Such background information is essential for policy makers to understand the pollutant situation and to formulate necessary policy and mitigation measures for public health protection.

2.2 Atmospheric PAHs in Thailand

Particulate matter is one of the most concerning air pollution issues in Thailand. High PM_{10} concentrations were found in urban areas mostly near roadside, industrial areas and in countryside areas mostly in the north of Thailand (PCD, 2013). Roadside PM_{10} data in 2013 showed that PM_{10} concentrations in three urban areas of Bangkok breached the 24-hour averaged national ambient air quality standard of 120 $\mu g\ m^{-3}$ up to 15% of measurement days per year and exceeded the annual standard at all three sites selected in this study. PM_{10} is the most severe air quality problem in central and northern areas of Thailand. Exposure to high PM concentrations may lead to adverse health effects caused by its physical properties as well as chemical properties. PAHs are highly associated with particulate matter, therefore, PM_{10}-bound PAHs concentrations should be investigated for public health protection purposes.

Studies in Bangkok showed a high proportion of smaller particles in PM_{10} implying that they originated from high temperature combustion sources. A size-segregation

study using a 5-fraction size segregated sampler collecting particle sizes <0.95, 0.95-1.5, 1.5-3, 3-7.2 and >7.2 µm in parallel with a PM_{10} sampler at the Chulalongkorn University site in the downtown area of Bangkok showed that loading of pPAH more than 97% were associated with the particle size of <0.95 µm (Thongsanit *et al.,* 2003). The result showed that the very fine particle size <0.95 µm contributed to approximately 48% of PM_{10} weight and $PM_{1.5}$ comprised around 60% of total PM_{10} weight. PAHs measured from total suspended particles at 4 sampling sites approximately 40 km north of Bangkok showed that traffic was the main emission source and concentrations of PAHs were lower along sites further away from the main road (Kim Oang *et al.,* 2000). Benzo[g,h,i]perylene and coronene found at the roadside site were indicators of diesel vehicles. Naphthalene was not found in any sample and 3-ring PAHs concentrations were extremely low as they were mainly associated with gas phase and daily temperatures were relatively high (27.5 – 29°C) during the sampling period. It can be inferred that major sources of PM in urban areas are traffic emissions.

Recently, the study area of pPAHs has shifted to the northern region of Thailand i.e. Chiang Mai, Lamphun, as they experience concurrent haze episodes in the dry season mostly from the open burning of agricultural residues and forest fires (Chantara *et al.,* 2010; Pongpiachan *et al.,* 2015). An analytical method was developed for the determination of pPAH in the Chiang Mai case study (Chantara and Sangchan, 2009). The method involved a MiniVol Air Sample for PM_{10} collection, ultrasonic extraction and GC-MS analysis giving relatively low limits of detection for 16 US EPA priority PAHs in the range of 0.16 – 0.45 ng m^{-3}. Seasonal variation of PM_{10} in Chiang Mai observed from June 2005 – June 2006 showed highest PM_{10} concentrations during the dry season (December – March) and lowest in the rainy season (June – September) and the trend of PAHs concentrations appeared similarly (Chantara *et al.,* 2010). The study indicated that major components of PAHs in PM_{10} in all seasons were 4-ring to 6-ring PAHs that accounted for more than 90% of total 16 PAHs weight. Carcinogenic PAHs including BaA, CHR, BbF, BkF, BaP, DBA and IP were significant constituents of

PM_{10} found in Chiang Mai and Lamphun provinces. The exposure to high PM_{10} may lead to significant health effects from carcinogenic PAHs.

A previous study on atmospheric PAHs measurements carried out in central and northern parts of Thailand focused on areas with high particulate matter levels. Studies conducted in the Bangkok Metropolitan Administration showed that vehicle emissions were one of the emission sources of high molecular weight PAHs including BaP. Traffic related PAHs that were dominant in roadside PM in Bangkok from existing literatures were IP, BP, BbF, benzo[e]pyrene and coronene (Kim Oang *et al.,* 2000; Thongsanit *et al.,* 2003; Boonyatumanond *et al.,* 2007). BaP was found at lower concentration levels and might occur from several sources. More importantly, vehicle emissions mainly contribute to fine particle ($PM_{2.5}$) that is likely to contain higher proportions of mutagenic and carcinogenic PAHs than coarse particles ($PM_{2.5-10}$). People exposed to roadside particulate matter are likely to confront a higher risk from exposure to high toxicity PAHs.

2.3 Sources of Atmospheric PAHs

Atmospheric PAHs appear in gaseous and particulate phases and are emitted from both natural and anthropogenic sources. Anthropogenic emissions range from small scale such as cooking in a household to large scale fuel combustion in industrial or energy sectors. Transportation and vehicular emissions are common sources of PAHs in urban areas. Biomass fuels are significant sources of indoor particles and PAHs particularly in rural households where open fire places or three stone stoves are used for cooking (Lisouza *et al.,* 2011). PAHs emitted during high temperature combustion are from pyrogenic sources such as vehicle engines, wood burning and coal burning. PAHs emitted from petroleum products are of petrogenic sources such as coal tar, crude oil and creosote.

Different activities can result in different PAHs emission profiles or markers associated with specific source types. An example of a single PAH biomarker is 1-methyl-7-isopropylphenanthrene (retene) from wood burning or wildfires (Alves *et al.,* 2011). However, PAHs are mostly emitted as a complex mixture and the detection of ratios contained within combination PAHs are more useful for source identification

than a single marker. Diagnostic ratios of PAHs are usually taken into account in identification of emission sources (Ravindra *et al.,* 2008; Tobiszewski and Namieśnik, 2012). Ratios between some PAHs usually with similar ring numbers were compiled from various emission sources and used to identify potential sources (Alves, 2008). As a result, PAHs released from petroleum products or petrogenic sources and PAHs formed via pyrolysis or pyrogenic sources can be distinguished by determining diagnostic ratios.

Atmospheric PAHs emitted into the atmosphere from various sources are a hindrance to the identification of emission sources which is the fundamental step for air pollution management. Approaches for the source apportionment of PAHs involve the use of ratios between PAHs or diagnostic ratios, comparison of sample PAHs profiles with known emission source profiles and various statistical analysis tools. All approaches take into account several PAHs concentrations in a sample owing to the simultaneous formation of various PAHs from a source. The use of individual PAH in the source identification can be easily misleading and factors influencing degradation of PAHs can play a vital role when attempting the source apportionment.

Typical PAHs diagnostic ratios are mostly determined from a homologous series, PAHs with the same molecular formula, to avoid differentiation from physical properties. Although using PAHs that are very similar in their properties, emission from similar sources may vary under unstable burning conditions. Diagnostic ratios are usually given in ranges and diagnostic ratios of similar source types or combustion processes may differ between literatures. Some diagnostic ratios used for the source identification of PAHs are listed in Table 2.1.

Table 2.1 Diagnostic ratios between PAHs.

Ratio	Value	Source interpretation	Reference
FLT/(FLT+PYR)			
	<0.4	Petroleum	Yunker *et al.* (2002)
	0.4 – 0.5	Petroleum combustion	
	>0.5	Grass/wood/coal combustion	

Ratio	Value	Source interpretation	Reference
	<0.5	Petrol emissions	Ravindra *et al.* (2008)
	>0.5	Diesel emissions	
BaA/(BaA+CHR)			
	<0.2	Petrogenic	Yunker *et al.* (2002)
	>0.35	Combustion	
IP/(IP+BP)			
	0.2 – 0.5	Liquid fossil fuel combustion	Ma *et al.* (2010)
	<0.2	Petroleum	Yunker *et al.* (2002)
	0.2 – 0.5	Petroleum combustion	
	>0.5	Grass/wood/coal combustion	
	0.6 – 0.64	Rice straw burning	Jenkins *et al.* (1996)

Even though PAHs diagnostic ratios are one of the most useful tools for source apportionment, any interpretation based on a single ratio is not enough for accurate source identification. Diagnostic ratios should be applied cautiously and may be combined with other techniques where appropriate to better characterise a complex PAHs mixture. A successful case in using a combination of PAHs diagnostic ratios to identify sources of PAHs in the Fraser River basin (British Columbia, Canada) is shown in Figure 2.3. A cross plot between diagnostic ratios relies on several PAHs concentration ratios to identify potential sources. The combination of diagnostic ratios or the binary ratio approach can strengthen the source interpretation.

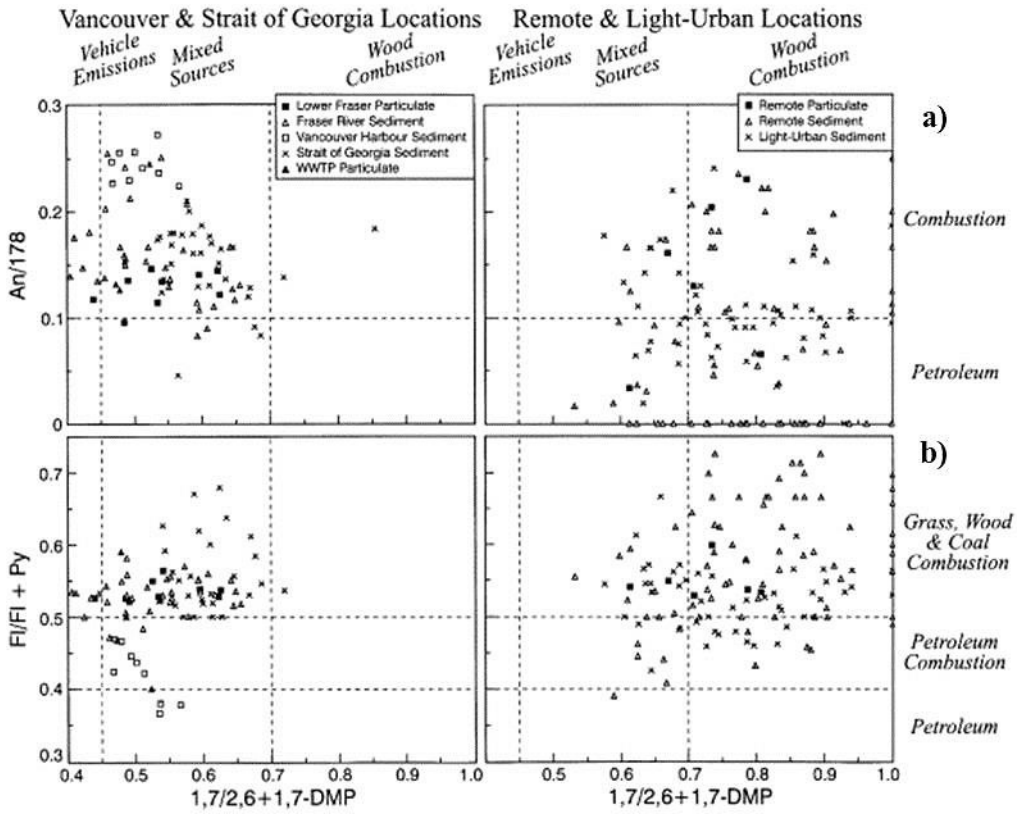

Figure 2.3 Cross plot of PAHs diagnostic ratios of a) ANT/(ANT+PYR) and b) FLT/(FLY+PYR) versus 1,7-dimethylphenanthrene(DMP)/(1,7-DMP+2,6-DMP) as indicators for PAHs sources of suspended particulate and sediment samples (Reprinted from Yunker *et al.* (2002). Copyright (2002) with permission from Elsevier).

Combinations of PAHs diagnostic ratios were used in the source identification of PM_{10} in Chiang Mai, Thailand (Chantara *et al.*, 2010). The use of diagnostic ratios for source identification of PM_{10}-bound PAHs in Chiang Mai showed that diesel engines were predominant sources of PAHs from traffic emissions with ratios of IP/(IP+BP) between 0.50 – 0.60 in all samples collected during June 2005 – June 2006. Wiriya *et al.* (2013) used binary ratio between FLT/(FLT+PYR) and IP/(IP+BP) and identified that fuel combustion and biomass burning were potential sources of PM_{10}-bound PAHs in Chiang Mai measured during dry seasons of 2010 and 2011.

Potential sources of roadside particulate-bound PAHs were analysed and PAHs profiles were compared with PAHs in Bangkok street dust and air samples

(Boonyatumanond *et al.*, 2007). Gas and particulate samples were analysed for 18 PAHs containing 3-ring to 7-ring and their profiles were illustrated in Figure 2.4. Soot samples from vehicles collected from the inside wall of gasoline vehicle exhaust pipes showed high percentage of high molecular weight PAHs whereas phenanthrene, pyrene and methylphenanthrene isomers were dominant in diesel vehicle soot. The roadside air contained high proportions of 3-ring PHE and its methylated isomers. Fluoranthene and pyrene were 4-ring PAHs that were highly partitioned in the gas phase (PUF) while other high molecular weight 4-ring to 7-ring PAHs were associated with the particle phase (filter).

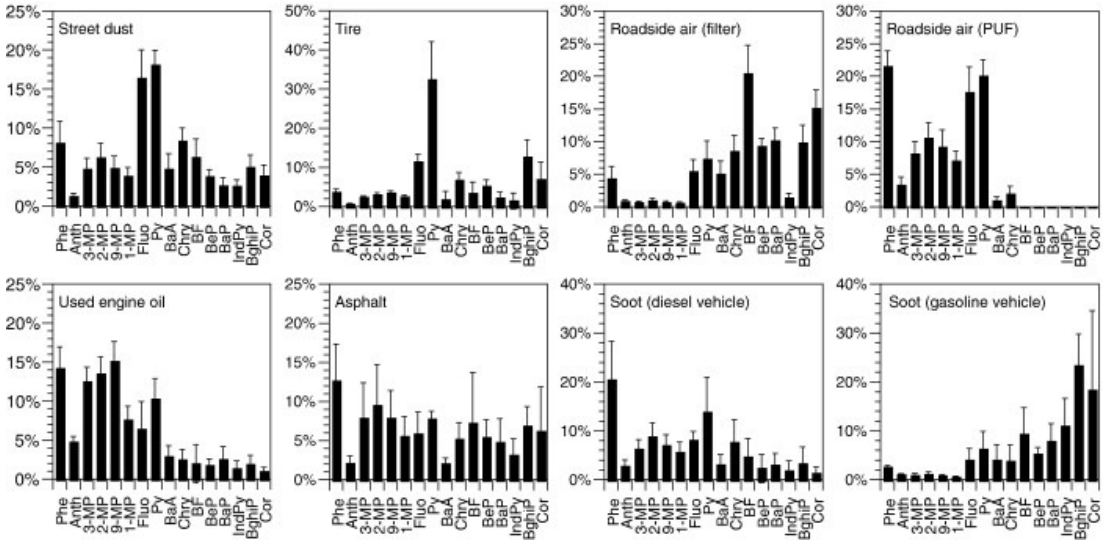

Figure 2.4 Profiles of PAHs in street dust, gaseous and particulate air samples in Bangkok compared with potential source profiles of tire, used engine oil, asphalt, diesel and gasoline soot samples. Concentrations of individual PAH species were normalised to total PAHs in each sample (Reprinted from Boonyatumanond *et al.* (2007). Copyright (2007) with permission from Elsevier).

One limitation of PAHs source identification using diagnostic ratios or emission factors is the degradation of PAHs which causes the alteration of ratios and changes in PAH profiles. Factors known to influence atmospheric PAHs degradation are sunlight and oxidants. A simulation study on PAHs photo-decomposition showed that the combination of sunlight and ozone gave rise to the fastest rate of degradation. BaP half-life was reduced from 5.30 hours under simulated sunlight to 0.58 hour in the presence of 0.2 ppm ozone (Ravindra *et al.,* 2008). Photochemical

reactions resulted in the removal of atmospheric PAHs, thus the half-life of PAHs were significantly shortened when exposed to sunlight and atmospheric oxidants as shown in Table 2.2. The photochemical degradation of pPAH was indicated by diurnal variations of diagnostic ratios between ANT/(ANT+PHE) and BaP/(BaP+BeP) measured in rural areas of Europe (Alves *et al.,* 2006). Ratios were higher during daytime and lower during night-time suggesting significant decreases of more reactive PAHs during the daytime. It is clearly demonstrated that concentrations of atmospheric PAHs are influenced by several factors. The use of PAHs ratios for the source apportionment should be carefully examined to identify potential sources but not to strictly eliminate the possibility of other sources not included in the ratio ranges.

Table 2.2 Half-life of PAHs under simulated atmospheric conditions (Ravindra *et al.,* 2008)

PAHs	MW	Half-life (hours)	
		Sunlight	Sunlight and ozone (0.2 ppm)
ANT	178	0.20	0.15
PYR	202	4.20	2.75
BaA	228	4.20	1.35
BaP	252	5.30	0.58
BeP	252	21.10	5.38
BbF	252	8.70	4.20
BkF	252	14.10	3.90
DBA	278	9.60	4.80

The source identification of atmospheric PAHs is vital for the development of countermeasures. Particulate matter arises from local and regional sources causing problems in different scales. Exposure to pPAHs in urban areas is mostly associated with traffic emissions while burning of agricultural residues are common sources in rural areas. Therefore, appropriate control strategies should be customised to take

account of these variations, in order to efficiently reduce atmospheric PAHs emissions.

2.4 Health Effects of Ambient PAHs Exposure

Carcinogenic and mutagenic effects of PAHs exposure related to lung cancer were found in workers of various industries including coal gasification, coke production, paving and roofing with coal-tar pitch, carbon electrode manufacture, chimney sweeps and other exposures to soot (IARC, 2010). Animal studies data showed strong evidence of carcinogenic activities for various high molecular weight PAHs, i.e. benzo[a]fluoranthene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[c]fluorene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, dibenz[a,j]anthracene, indeno[1,2,3-cd]pyrene, etc. Some alkylated PAHs were found to exhibit positive results in carcinogenicity tests in animals including 2-methylfluoranthene, 3-methylfluranthene and 5-methylchrysene. Lung cancer incidences were strongly associated with some occupational exposures and thus carcinogenicity was classified accordingly. Occupational exposures identified as carcinogenic to humans, Group 1 of IARC classification, were exposures during coal-tar distillation, paving and roofing with coal-tar pitch and aluminium production. Benzo[a]pyrene as individual PAH species is carcinogenic to humans based on available evidence of both cohort epidemiological studies and animal studies (Armstrong *et al.,* 2004).

Previous cohort studies in the USA identified significant increase in lung cancer risk rate with the increase in PM_{10} and $PM_{2.5}$ concentrations (Vineis *et al.,* 2004). Epidemiological evidence of the positive relationship between the exposure to air pollutants and lung cancer has been determined from carcinogenic potencies of multiple components. As such it is not possible to disintegrate carcinogenicity of a single pollutant. Cancer risk evaluation should incorporate all possible potential constituents. Therefore, toxic equivalency factors for PAHs were proposed for carcinogenic PAHs and some PAHs not classified as carcinogenic to humans (Nisbet and LaGoy, 1992; Petry, Schmid, and Schlatter, 1996, Jung *et al.,* 2010). The health risk assessment associated with the occupational and environmental exposure to

atmospheric PAHs is generally represented as a lifetime lung cancer risk – in other words, the number of lung cancer cases developed through a life-time exposure in a million people. The WHO recommended acceptable excess lifetime cancer risk level is 1/1,000,000 or one case in a million people (WHO, 2000).

Previous studies in Bangkok showed that exposure to high PM_{10} resulted in a significant increase in daily mortality. Short-term exposure to ambient PM in the BMA caused approximately 4,000 – 5,500 premature deaths per year (Schwela *et al.,* 2006). Previous studies demonstrated that long-term PM exposure resulted in higher cardiovascular incident and mortality rate (Anderson *et al.,* 2011). Relationships between lung cancer and outdoor particulate matter exposure were confirmed in both PM_{10} and $PM_{2.5}$ (Hamra *et al.,* 2014). High concentrations of respirable particles can cause acute health effects while chronic exposure to carcinogens and mutagens in particulate may result in higher risk of cancer development. In-depth study on PM_{10} and PAHs exposure showed that high concentrations of particulate and PAHs increased levels of biomarkers (Ruchirawat *et al.,* 2002). Exposure to atmospheric PAHs can cause adverse health effects and lung cancer is the most concerning owing to evidence found between BaP exposure and lung cancer in humans (IARC, 2010).

Seasonal high PM_{10} concentrations were found in the north of Thailand during the dry season (December 2005 – March 2006) with the maximum concentration range of 140 – 182 $\mu g\, m^{-3}$ at 4 air sampling stations in Chiang Mai and Lamphun provinces (Pengchai *et al.,* 2009). Carcinogenic risk estimated from total toxicity equivalent concentrations of BaP resulted in a lung cancer burden of 2 cases per year. A study on the carcinogenic risk of the exposure to PAHs associated with fine particles ($PM_{2.5}$) was conducted in the north of Thailand (Pongpiachan *et al.,* 2015). The cancer risk from the exposure to $PM_{2.5}$-bound PAHs was investigated during the biomass burning period. Diagnostic ratios revealed that vehicular emissions were predominant sources of $PM_{2.5}$-bound PAHs and there was no significant difference between PAHs before and after haze episodes. The result implied that biomass burning was not a significant source of $PM_{2.5}$. However, open burning of biomass and forest fires in the study area have been major sources of elevated ambient

particulate concentrations during the dry season causing deterioration of air quality and chronic exposure to respirable particles together with other toxic air pollutants.

The study in Chiang Mai area showed that cancer risk estimation from inhalation unit risk of 8.7 x 10^{-2} per (µg m^{-3}) at the BaP toxicity equivalent concentration of 0.61 ng m^{-3} resulted in a lifetime cancer risk of 5.31 x 10^{-5} or 90 cases per 1.7 million population (Wiriya *et al.,* 2013). Another study on health risk assessment in Chiang Mai found the lifetime exposure to $PM_{2.5}$-bound PAHs ranged between 4.8 x 10^{-6} and 6.0 x 10^{-6} when using WHO recommended IUR (Pongpiachan *et al.,* 2015). While Wiriya *et al.* (2013) proposed that PM_{10}-bound PAHs were from open burning sources, the latter study identified vehicular emissions as major sources of $PM_{2.5}$-bound PAHs and PAHs concentrations were not influenced by seasonal haze. These results implied that people were exposed to pPAHs from vehicular emitted fine particles with additional PM_{10}-bound PAHs during the dry season haze episode.

2.5 International Guidelines

Air quality guidelines have been established for public health protection internationally. According to WHO guidelines for particulate matter, PM_{10} concentration should be maintained below 50 and 25 µg m^{-3} for 24-hour and annual mean concentrations, respectively (WHO, 2005). A review of global ambient air quality standards (AAQS) for PM_{10} indicated that 69 out of 96 countries established the 24-hour AAQS, however, only 34 countries AAQS values were within the 50 µg m^{-3} WHO air quality guideline (Vahlsing and Smith, 2012). The existing AAQSs pertain to approximately 84% of world population (2008) which would result in better public health protection if the AAQSs were complied with.

For carcinogenic PAHs which are highly associated with particulate matter, WHO estimated the inhalation unit risk (IUR) of BaP according to epidemiological studies in coke oven workers at 8.7×10^{-5} per ng m^{-3} (WHO, 2000). The high IUR value resulted in the low corresponding exposure concentration of BaP. Calculated from the given IUR value, BaP concentration at 1.2, 0.12 and 0.012 ng m^{-3} are required to contract excess lifetime lung cancer risks of 1/10,000, 1/100,000 and 1/1,000,000, respectively.

While the EU adopted the WHO guideline for 24-hour PM_{10} concentration, the annual limit value is set at 40 μg m^{-3} (EU, 2008). PAHs target value is set at 1 ng m^{-3} of BaP in PM_{10} implying the significance of health risk concern on carcinogenic PAHs exposure (EC, 2004).

Despite these international measures, atmospheric PAHs are not regulated in Thailand and there were no available environmental monitoring records. Previous research on airborne PAHs was mostly conducted in high particulate environments so as to clearly demonstrate health effects. The need to establish an air quality standard or guidelines depends on the severity and frequency of situations adversely affecting human health. National ambient air quality standards for PM_{10} and $PM_{2.5}$ are shown in Table 2.3. This study focused on the long-term measurement of PM_{10}-bound PAHs in urban areas of central Thailand. The evaluation of the pPAHs situation and its associated health risks may lead to the development of policy or control measures required for public health protection.

Table 2.3 Air quality guidelines and ambient air quality standards for particulate matter and PAHs concentrations.

Country	PM_{10} (μg m^{-3})		$PM_{2.5}$ (μg m^{-3})		PAHs (as BaP) (ng m^{-3})	Reference
	24-hr	annual	24-hr	annual	annual	
Australia	50		25	8		Department of the Environment (2016)
European Union	50	40		25	1	EC (2015)
Malaysia	150	50				ADB (2006)
Singapore	50	20	37.5	12		National Environment Agency (2016)
Thailand	120	50	50	25		PCD (2004)
UK	50	40			0.25	DEFRA (2012)

Country	PM_{10} ($\mu g\ m^{-3}$)		$PM_{2.5}$ ($\mu g\ m^{-3}$)		PAHs (as BaP) ($ng\ m^{-3}$)	Reference
	24-hr	annual	24-hr	annual	annual	
UK (except Scotland)				25		DEFRA (2012)
Scotland	50	18		12		DEFRA (2012)
USA	150		35	12[a]		US EPA (2016)
Global (WHO recommended guidelines)	50	20	25	10		WHO (2005)

[a] Primary standards provide public health protection including protecting the health of sensitive populations

Chapter 3

Methodology

3.1 Background

Analytical methods for measuring organic pollutants in particulate samples have been developed to identify and quantify risk of exposure to mutagens and carcinogens as inhalation exposure is unavoidable. Difficulties in sampling, sample preservation, trace analysis and complex mixtures contained in samples are challenges for method development. Airborne PAHs is a mixture of various organic compounds emitted during incomplete combustion of organic fuels. The measurement methodologies require high separation and sensitivity. Official analytical methods were previously Soxhlet extraction and subsequently high performance liquid chromatography analysis which has been replaced by the gas chromatography-mass spectrometry (US EPA, 1999). The regulatory requirement to monitor ambient concentrations of benzo[a]pyrene and toxic PAHs has led to the development of alternative methods to the conventional Soxhlet extraction due to it being time consuming and the large volume of solvents used. This study aimed to develop high efficiency analytical methods for the measurement of PAHs in ambient particulate matter.

The use of the gas chromatography-mass spectrometry technique has superseded high performance liquid chromatography with its selectivity, specificity and sensitivity. The advantage of mass spectrometry is that it positively identifies analytes corresponding to their mass profiles called mass spectra. Mass spectra of pure substances are produced and compiled in a database to compare with unknown compounds in a sample. Purification or separation of a complex mixture sample is the most important step to correctly identifying an unknown compound as the reference mass spectrum is produced from a pure reference compound (NIST, 2016).

Therefore, the optimisation of sample preparation and chromatographic separation focus on extracting analytes from sample matrices, removing interferences and separating mixture components as much as possible while minimising time and effort required in PAHs analysis.

The development of an extraction technique focused on reducing extraction time, minimising solvent volume, and shortening sample preparation procedure while maintaining sample integrity. Various techniques were tested as alternative to conventional Soxhlet extraction such as ultrasonic extraction, microwave-assisted extraction, supercritical fluid extraction and pressurised fluid extraction (Saim *et al.*, 1997; Liu *et al.*, 2007; Masala *et al.*, 2012). Several techniques achieved satisfactory extraction efficiency; therefore choices of appropriate techniques are available depending on available resources.

Gas chromatography-mass spectrometry is one of the most versatile tools for the analysis of organic compounds in the past few decades (Pandey, Kim and Brown, 2011). GC-MS combined gas chromatography for separation of complex samples and mass spectrometry for identification of unknown substances. It is widely used in various fields of study e.g. drug development, natural products, pesticide analysis, forensic science and environmental analysis. PAHs in environmental samples are mostly associated with particle owing to their high boiling points. The higher molecular weight compounds possess more possible structural isomers thus causing difficulties in chemical analysis. Challenges in PAHs analysis are to separate mixtures of several compounds and then identify and quantify them accurately.

3.1.1 Gas Chromatography (GC)

Gas chromatography is one of the most widely used techniques for separation of complex mixture samples containing thermally labile components that can be volatilised under high temperature and transported through a chromatographic column by an inert carrier gas. The sample is injected into the column at a high temperature inlet where it is volatilised and transported through a long capillary column. The inside wall of the capillary column is coated with solid and liquid stationary phases that play important roles in separation of the components while

traversing along the column. The gaseous solution of samples is transported by an inert carrier gas. Analytes or solutes are separated along the column. The order of elution generally depends upon boiling points and polarities of compounds. While passing through a column coated with the stationary phase, sample molecules with different properties interact with the stationary phase differently resulting in chromatographic separation. Major components of a typical gas chromatograph are shown in Figure 3.1.

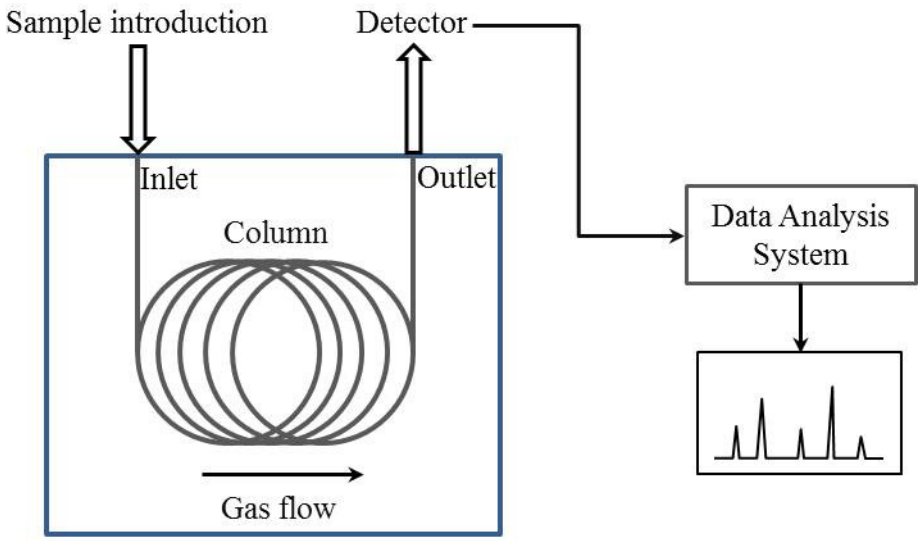

Figure 3.1 Block diagram showing major components of a gas chromatograph.

The elution time or retention time (t_R) of a solute depends on the solute-column interaction. While the carrier gas is flowing through the column, sample components may react by adsorption or absorption to the stationary phase causing separation of components that dissolved in the mobile phase. Solutes that interact more with the stationary phase are retained and exit the column later than ones with less interaction. Separation efficiency of a chromatographic column is demonstrated by the van Deemter equation (see equation 3.1) showing the relationship between the height equivalent to a theoretical plate (HETP) and the linear velocity of a carrier gas of packed columns (Jones, 1961; Sparkman, Penton and Kitson, 2011). The A term, Eddy diffusion, can be omitted in capillary columns with no packing. The simplified version of the van Deemter equation is known as Golay equation (see equation 3.2).

$$HETP = A + B/u + Cu \qquad \text{Equation 3.1}$$

Where:

A = multiple paths effect

B = longitudinal diffusion term

C = resistance to a mass transfer controlled by diffusion in the liquid phase

u = average linear velocity of the carrier gas

Optimum linear velocity (u_{opt}) is obtained by differentiating the van Deemter equation with respect to the velocity at u equals zero (Mjøs and Waktola, 2015).

$$HETP = B/u + (C_s + C_m) \cdot u \qquad \text{Equation 3.2}$$

$$u_{opt} = \sqrt{\frac{B}{C}} \qquad \text{Equation 3.3}$$

Where:

C_s = resistance to a mass transfer in the stationary phase

C_m = resistance to a mass transfer in the mobile phase

Figure 3.2 illustrates that the relationship between the plate height and optimum linear velocity depends on the type of carrier gas in the van Deemter plot. The smaller plate height reflects higher numbers of theoretical plate which should result in a better separation. Theoretically the best carrier gas shown in the van Deemter plot is hydrogen which allows a higher flow rate while maintaining low HETP. However, it is not as widely used as helium owing to hydrogen's safety issues. GC instrumentation consists of several heating elements and gas line connections. The flammability of hydrogen gas is the major drawback when risks from GC operating conditions are considered.

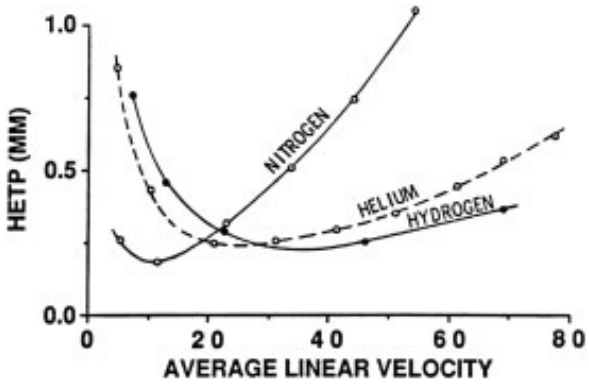

Figure 3.2 Plot of the height equivalent to a theoretical plate and the average linear velocity (cm sec^{-1}) for a thin-film column using different carrier gases (Reprinted from Poole (2012). Copyright (2012) with permission from Elsevier).

3.1.2 Mass Spectrometry (MS)

Mass spectrometry is an analytical technique to measure charged species of organic or inorganic molecules. Sample molecules are ionised in the gas phase by a suitable ionisation method generating ions that are separated according to their mass-to-charge ratios (m/z) and detected qualitatively by their m/z or quantitatively by their abundance (Yadav, 2005; Gross, 2010). Major components of a mass spectrometer are composed of sample inlet, ion source, mass analyser and detector. A mass spectrometer requires a vacuum system which provides a suitable environment, mean free path, for mass separation and analysis. The high vacuum, below 10^{-5} mbar, is required to prevent bimolecular interaction of molecular ions formed within the ion source (Herbert and Johnstone, 2003).

The most important step of mass spectrometry analysis is the formation of ions. Samples entering into MS as neutral molecules need to be transformed to charged species/ions to be recognised by the detector. Ion formation is performed in the ion source part of a mass spectrometer. The process of ion formation can be done by hitting a neutral species with a high energy electron to transfer energy that exceeds the ionisation energy of the neutral species. This electron ionisation (EI) method predominantly results in the loss of an electron and produces a positive radical ion as shown in the equation 3.4 (Gross, 2010). Charged species produced in the ion source are directed to the mass analyser where a signal is detected and then multiplied.

Molecular ions, charged species produced by electron ionisation, can be detected by the mass analyser and can undergo further fragmentation giving a mass spectrum that is used to characterise an unknown species. A schematic diagram of a quadrupole mass spectrometer is shown in Figure 3.3.

$$M + e^- \rightarrow M^{+\bullet} + 2e^- \qquad \text{Equation 3.4}$$

For GC-MS, a gas chromatograph acts as the sample inlet which also performs separation of a sample that contains variety of analytes. After chromatographic separation, molecules of analytes enter into the ion source and are ionised by high energy electrons. Sample ions are selectively accelerated via a quadrupole mass analyser into the detector respective to their m/z creating a signal at the detector. A graphical illustration of the GC-MS result is called a chromatogram or total ion chromatogram in which the intensity is shown as the total sum of ion masses (abundance) reaching the detector at the same time (retention time). The detector can be operated in scan mode where all ions within a specified range are monitored throughout the MS acquisition time or in selected ion monitoring (SIM) mode where only specified ions are monitored in a specific period of time during the acquisition. Methods for qualitative and quantitative analyses of target PAHs for a routine monitoring of particulate samples were developed using a quadrupole GC-MS in scan and SIM mode.

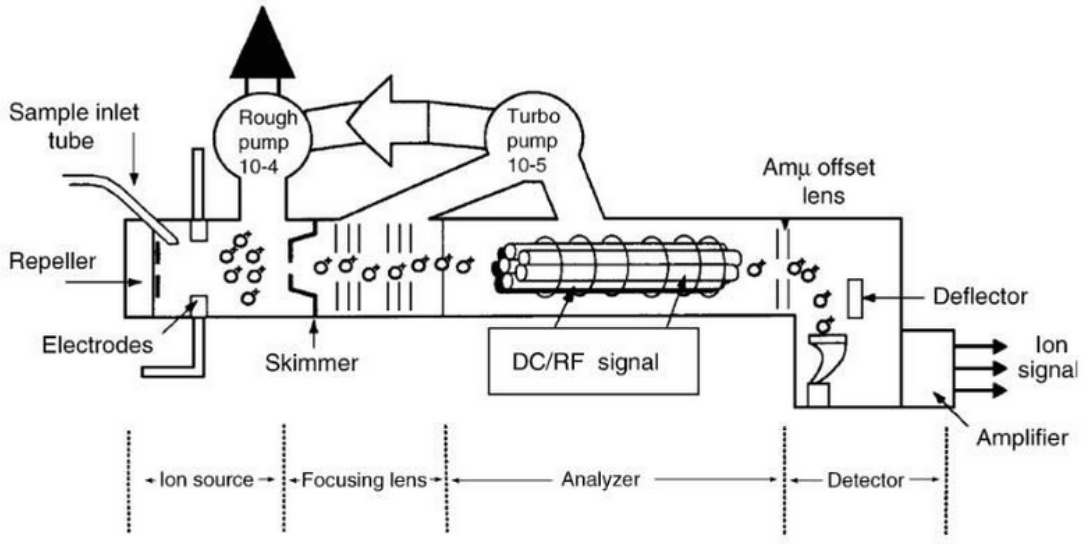

Figure 3.3 Schematic diagram of a quadrupole mass analyser (Reprinted from McMaster (2007). Copyright (2007) with permission from John Wiley and Sons).

3.1.3 Comprehensive Two-Dimensional Gas Chromatography – Time-of-Flight Mass Spectrometry (GCxGC TOFMS)

Method for the non-targeted screening of PAHs, alkyl-PAH derivatives and other potential toxic air pollutants in PM_{10} samples from Thailand is developed using a GCxGC TOFMS. A comprehensive method aimed to extend the analytical range and to explore a variety of air contaminants is carried out using an Agilent 7890A gas chromatograph coupled with a Leco Pegasus 4D time-of-flight mass spectrometer (TOFMS). GCxGC TOFMS has been utilised in various complex mixtures analysis owing to the GCxGC dimensionality that introduces more than one separation mechanisms enables the group type analysis or structured chromatograms (Murray, 2012). This can be achieved by maximising the orthogonality of the GCxGC by selecting columns with different separation mechanisms such as volatility, polarity or molecular shape. The technique has another advantage of signal enhancement from the modulator which refocuses the sample peak before injects it into the second column. Coeluted components from the first column were separated in the second dimension as illustrated in Figure 3.4.

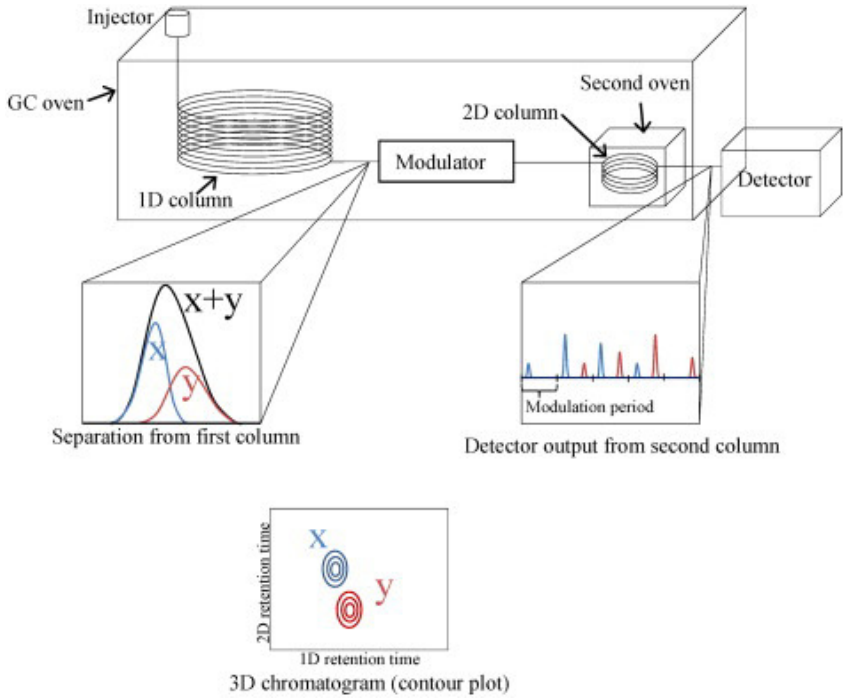

Figure 3.4 Schematic diagram of a comprehensive two-dimensional gas Chromatography (Reprinted from Murray (2012). Copyright (2012) with permission from Elsevier).

Recently, GCxGC has gained popularity in environmental analysis as it can be applied for both non-targeted and targeted analysis at trace level. Four GCxGC column combinations were tested for the separation of complex PAH mixtures including 97 alkyl-, nitro-, oxy-, thio-, chloro-, bromo- and high molecular weight PAHs (Manzano, Hoe and Simonich, 2012). The results showed that the normal phase column combination (Rtx-5MS x Rxi-17) could not give good separation in the second dimension as their separation mechanisms were not true orthogonal. The best separation was achieved using the liquid crystal (LC-50) and nanostationary phase (NPS-35) columns which could separate 89 PAHs without partial or complete coelution. GCxGC FID and GCxGC MS gave comparable results in the analysis of targeted PAHs and oxy-PAHs in urban aerosols of Helsinki, Finland (Kallio *et al.,* 2003). A mass selective detector is required for non-targeted analysis which is another advantage of GCxGC TOFMS.

3.2 Materials and Methods

3.2.1 Samples

Two types of samples used for particulate-bound PAHs analysis in this study were dust samples from Malawi rural households and particulate samples (PM_{10}) from the central area of Thailand. House dust and PM_{10} samples generated during combustion of different fuel types and processes should exhibit significantly different PAHs compositions. Dust samples represented PAHs emitted from the low temperature combustion of biomass fuels while ambient PM_{10} samples represented roadside, industrial and urban background particles. Dust samples were analysed at the beginning of this study in order to refine extraction and analytical methods for PM_{10} samples.

3.2.1.1 Dust samples from Malawi

Dust samples were collected from rural areas of Malawi namely Balaka and Chikwawa districts from 38 households by floor sweeping. The previous study investigated the effect of stove types on the emission of indoor air pollution by analysing PAHs in soot and dust samples (Chidziwisano, 2012). Households participated in the sampling campaign were equipped with improved cook stoves which aimed to reduce indoor air pollution emitted from the burning of biomass fuels used for home cooking. Both sampling sites represented rural area of South Malawi where biomass fuels were commonly used on a daily basis. Soot samples were collected by scraping the inside walls of rooms where cooking was performed. Dust samples collected from floor sweeping were kept in tightly capped glass vials then transferred to the Department of Civil and Environmental Engineering (University of Strathclyde) where they were stored at -80°C until extraction and analysis. The quantification of PAHs in soot and dust samples in the previous study was performed by a quadrupole GC-MS (Chidziwisano, 2012). Dust samples remained well preserved under -80°C and were used for the verification of extraction and analysis methods. The sampling locations are shown in Figure 3.5.

Figure 3.5 Map of Malawi showing sampling sites in Balaka and Chikwawa.

3.2.1.2 PM_{10} samples from Thailand

Particles with aerodynamic diameter of less than 10 µm (PM_{10}) were collected at three air quality monitoring sites operated by the Pollution Control Department (PCD) Thailand. PCD is the government agency responsible for the monitoring of Thailand's environmental status. Automated air quality monitoring stations have been operated in major cities all over Thailand for continuous monitoring of criteria air pollutants including carbon monoxide, nitrogen dioxide, ozone, sulphur dioxide and particulate matter. High PM_{10} level is one of the major concerned air quality issues in urban areas of Thailand. The background concentration of urban PM_{10} in Bangkok is approximately two times higher than recommended guidelines and thus poses health risks to the public. Previous studies in Thailand pointed out high

carcinogenic PAHs in high particulate matter areas; however, pPAHs the general environment has not been investigated. This research focuses on the PM_{10}-bound PAHs in the urban environment that may pose significant health risk to a large population.

Ambient 24-hour integrated PM_{10} samples are collected every 6 days using high-volume air samplers. Sampling sites were located at the National Housing Authority Dindaeng, the Electricity Generating Authority of Thailand – Nonthaburi, and the Public Relations Department. Three monitoring sites are shown in Figure 3.6. Sampling sites were characterised according to the surrounding environment and major emission sources. Sampling site categories are summarised in Table 3.1.

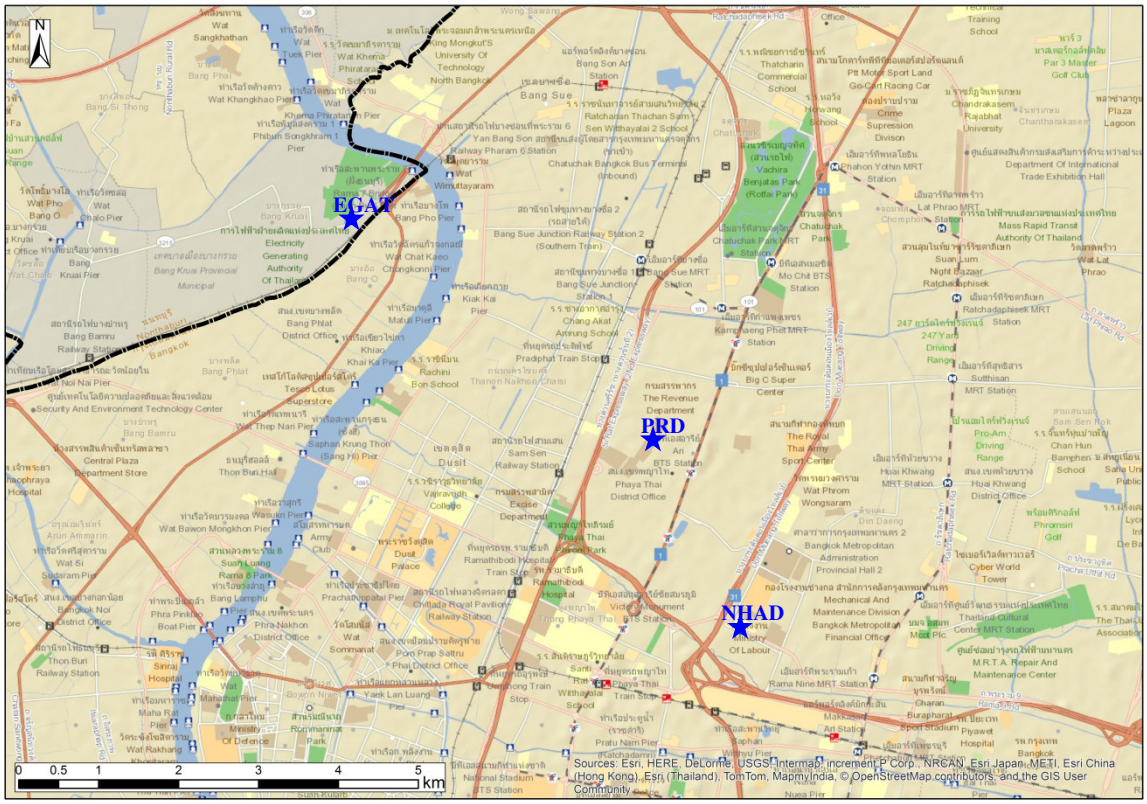

Figure 3.6 PM_{10} sampling sites in the Bangkok Metropolitan Administration: 1) National Housing Authority Dindaeng (NHAD), 2) Electricity Generating Authority of Thailand – Nonthaburi (EGAT) and 3) Public Relations Department (PRD).

All samples were weighed and PM_{10} mass concentrations were calculated by the PCD analyst. Prior to this study, PM_{10} samples were archived at the PCD laboratory under room temperatures which may reach 30°C in summer. In order to prevent the volatilisation of PAHs, samples used in this study were kept refrigerated. After weighing, filters were wrapped with aluminium foil and preserved at -20°C until their transportation to the Department of Civil and Environmental Engineering laboratory (University of Strathclyde) where they were kept at -80°C until extraction and analysis.

Table 3.1 Sampling site characteristics.

No.	Sampling sites (Abbreviations)	Emission sources	Classification
1	National Housing Authority Dindaeng (NHAD)	Express ways Main streets	Roadside
2	Electricity Generating Authority of Thailand – Nonthaburi (EGAT)	North Bangkok Power Plant (Block 1)	Industrial
3	Public Relations Department (PRD)	Small road	Urban background

3.2.2 Standards and reagents

All solvents used for sample preparation (hexane, toluene and methanol) were HPLC grade purchased from Fisher Scientific (Fisher Scientific UK Ltd., Loughborough, UK). Deuterated PAHs (D-PAHs) standards including 98 atom %D purity of naphtalene-d_8, fluorene-d_{10}, anthracene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} were purchased from Sigma-Aldrich (Sigma-Aldrich Company Ltd., Dorset, UK). The standard solution mixture of acenapthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} at 2000 µg mL^{-1} and TCL Polynuclear Aromatic Hydrocarbon Mix containing 16 PAHs at 2000 µg mL^{-1} were obtained from Supelco Analytical (Sigma-Aldrich Company Ltd., Dorset, UK).

Drying agents for accelerated solvent extraction, anhydrous sodium sulphate, was purchased from Fisher Scientific (Sigma-Aldrich Company Ltd., Dorset, UK). Reagents used for in-cell clean-up were silica gel pore size 60Å, 63-200 µm from Fluka Analytical and pelletised diatomaceous earth from Sigma-Aldrich (Sigma-Aldrich Company Ltd., Dorset, UK). Anhydrous sodium sulphate and pelletised diatomaceous earth were baked at 480°C for 8 hours prior to use. Silica gel 60 was deactivated with 10% deionised water after baking under the same conditions. Reagents for ASE extraction were freshly prepared every week and kept in a desiccator to prevent contamination and moisture absorption.

3.2.3 Sample preparation

3.2.3.1 Sample extraction

Pressurised fluid extraction (PFE) or pressurised liquid extraction (PLE) technique has been successfully developed for the extraction of organic contaminants from solid samples such as dust, particulate matter, soil and sediment. Extraction efficiencies of persistent organic compounds including PCB congeners and chlorinated pesticides in environmental samples by PFE were comparable with Soxhlet extraction (Schantz, Nichols, and Wise, 1997). The technique applied a high pressure to the heated extraction cell filled with the sample and optional clean-up agents while passing extraction solvent(s) through the cell to elute organic components. The extraction pressure played an important role in the extraction when temperature was held constant. Higher efficiency was achieved when pressure was increased higher than 1500 psi. Another advantage of PFE is the solvent selection where single solvent or mixed solvents at different ratios can be used to elute samples from each extraction cell in cycles. Sample extracts can be combined into a collection vial or collected separately. This feature enables an automated fractionation of a sample in a shorter time period compared with a chromatographic column separation.

Pressurised liquid extraction of urban dust and diesel dust standard reference material samples (SRM1649, SRM1649a, SRM1650, SRM 2975) using different solvents gave high recoveries in the range of 90-110% (Björklund, Nilsson, and Bøwadt, 2000).

PFE has been developed as an alternative for the conventional Soxhlet extraction which is time consuming and requires a large volume of solvents. The comparison between PFE and the Soxhlet extraction showed that the former technique resulted in a higher extraction efficiency for higher molecular weight PAHs in diesel particulate matter (SRM1650 and SRM2975) (Schantz, Nichols, and Wise, 1997). ASE is a powerful tool for the extraction of organic compounds and proved to be equivalent to the Soxhlet or Soxtec extraction for PAHs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), however, extracts may require further purification depending upon sample matrices (Popp *et al.,* 1997; Richter *et al.,* 1997). Solid-phase extraction (SPE), liquid-liquid extraction (LLE) or column chromatography can be used to clean-up sample extracts prior to the analysis.

Recently ASE extraction has been further developed with online or in-cell clean-up to obtain extracts ready for analysis without subsequent clean-up (Xue *et al.,* 2012). The application of PFE with in-cell clean-up compared with post extraction clean-up showed no significant difference in 24 PAH concentrations in soil samples (Ong *et al.,* 2003). It can efficiently extract analytes strongly bound with solid matrices (Björklund, Nilsson, and Bøwadt, 2000). The mechanism of PFE for the extraction of analytes in solid sample matrices is illustrated in Figure 3.7.

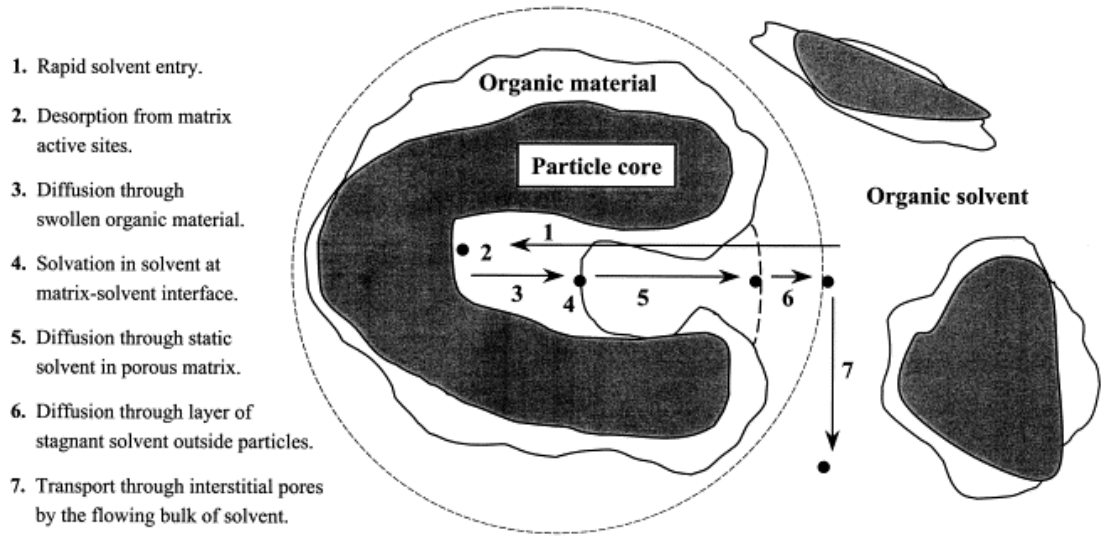

Figure 3.7 A model of pressurised fluid extraction mechanism for analytes adsorbed on particles (Reprinted from Björklund, Nilsson, and Bøwadt (2000). Copyright (2000) with permission from Elsevier).

Accelerated solvent extraction system model ASE350 (Dionex, Camberley, UK) was used for the extraction of PAHs in dust and particulate matter samples. Stainless steel extraction cells of 5, 10, 34 and 100 mL were selected as appropriate for different sample sizes. Recoveries of ASE methods were tested by spiking isotope labelled PAH standards, deuterated PAHs (D-PAHs), onto samples prior to the extraction.

To reduce steps in sample preparation and prevent loss of target compounds occurring during the extraction process, silica gel and anhydrous sodium sulphate were packed together with samples as in-cell clean-up agents. The role of clean-up agents is to remove interferences and moisture that may cause difficulties in sample preparation especially the clean-up step. Contents of sample packed in an ASE cell were illustrated in Figure 3.8.

- A 5 g aliquot of dust was packed into a 34 mL ASE cell with Silica gel (approximately 3 g) and anhydrous sodium sulphate (approximately 3 g), the remaining cell volume was filled with diatomaceous earth.
- A quartz fibre filter containing PM_{10} was cut into small pieces and packed into a 100 mL ASE cell with Silica gel (approximately 3 g) and anhydrous

sodium sulphate (approximately 3 g), the remaining cell volume was filled with diatomaceous earth.

- A blank cell (method blank) filled with packing and clean-up agents was extracted and analysed with each batch of up to 10 samples (10% of samples) for the purpose of quality control.

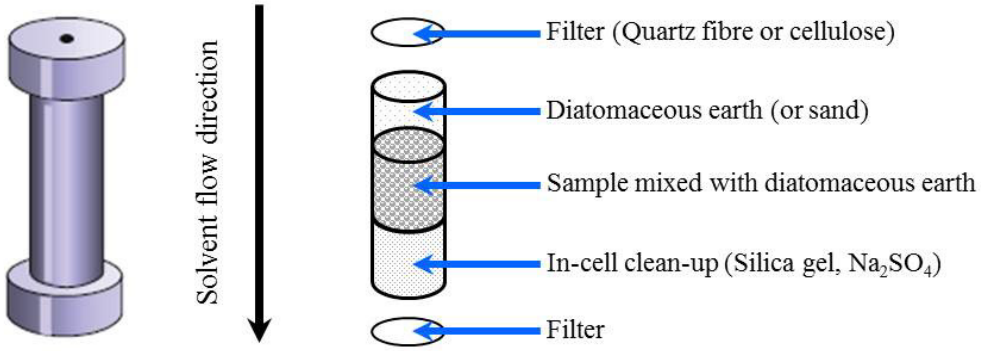

Figure 3.8 Schematic diagram of an ASE sample cell (adapted from Thermo Fisher Scientific, 2013).

All packing agents including silica gel, anhydrous sodium sulphate, and pelletised diatomaceous earth were baked at 450°C for 8 hours prior to use. Silica gel was deactivated with 10%w/w deionised water. An ASE extraction cell was prepared by lining with a filter at the bottom before filling with approximately 3 g of silica gel and 3 g of anhydrous sodium sulphate. The sample was filled into the cell together with diatomaceous earth. The remaining cell volume was filled up with diatomaceous earth or sand. The void volume in a sample cell will increase the amount of solvent used and thus filling up with inert material is recommended. Another filter was placed at the top of the sample cell and the cap was tightly closed by hand. Cell caps must be hand tightened without using any additional tools. Over tightening of the screw cap may cause damage to the cell or failure in the extraction.

ASE methods were tested for extraction efficiency using surrogate PAHs solution containing naphthalene-d_8, anthracene-d_{10} and chrysene-d_{12} spiked onto each sample prior to the extraction. Deuterated PAHs were used to assure the extraction of low molecular weight 2-ring and 3-ring PAHs and high molecular weight 4-ring PAHs.

Extraction recovery percentages were determined to evaluate ASE conditions. Dionex ASE350 equipped with stainless steel extraction cells was operated at the extraction temperature of 110°C with the pressure at least 1500 psi. Each cell was extracted in 3 cycles at 6 minutes static time. An aliquot of approximately 5 g dust sample was placed into a 34 mL extraction cell with clean-up agents and diatomaceous earth. The extraction solvent used was hexane: toluene at 4:1 ratio for dust sample. Solvent flush volume was set at 60% of cell volume. Extracts from 3 cycles were collected into a glass collection vial. The sample extract was dried with anhydrous sodium sulphate then filtered into a glass vessel for evaporation.

The extraction of PM_{10} filter sample was performed in a similar manner. A 100 mL extraction cell was used for a PM_{10} filter sample. Extraction solvent ratio was 1:4 of hexane to toluene. The flush volume of solvent was set at 30% of cell volume. Extracts from 3 cycles were combined together and then the extract was evaporated to approximately 1 mL.

For the analytical method development of PM_{10} filter sample, 22 filters acquired during March – July 2013 were used for the homogeneity test. Filters were subdivided into two and four pieces using a pizza cutter, wrapped with aluminium foil and stored at -20°C before being transferred to the Civil and Environmental Engineering Department laboratory for further chemical analysis. In order to determine the homogeneity of PM_{10} sample, each filter section was extracted and analysed as an individual sample. PAHs concentrations were tested for the difference in their sample means by pair t-test and ANOVA for two and four segments, respectively. Total PAH concentrations were combined when reporting ambient concentrations. Filter weighing and sample preparation performed at the Pollution Control Department laboratory (Bangkok, Thailand) for the homogeneity study are shown in Figure 3.9.

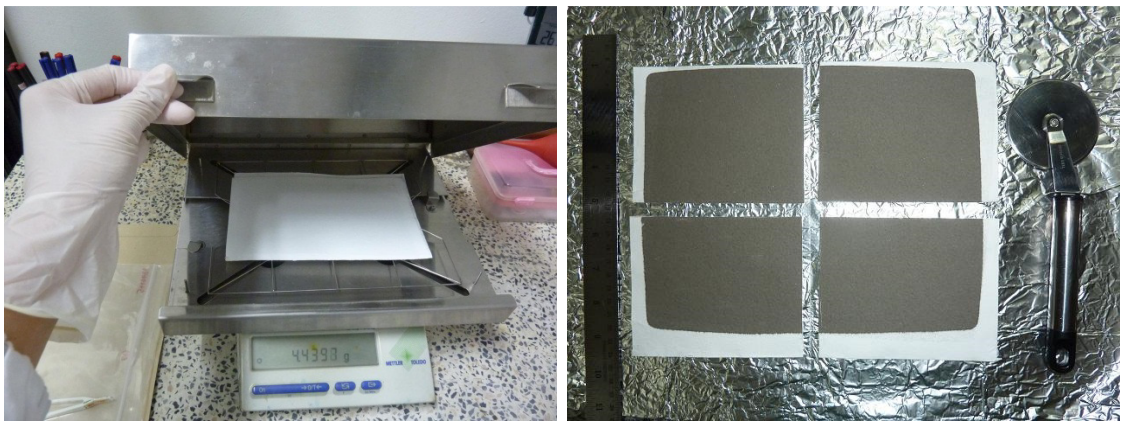

Figure 3.9 Filter weighing and preparation of PM_{10} filter sample for the homogeneity study.

3.2.3.2 Sample evaporation

Sample extracts were concentrated to the volume of approximately 1 mL using a Syncore® Analyst (Büchi UK Ltd., Oldham, UK). The equipment has a capacity of 12 vessels with the working volume of 120 mL per vessel. Evaporation of 12 samples can be performed simultaneously. Major components of the sample evaporation system composed of the Syncore® Analyst platform, condenser unit, vacuum pump V-700, vacuum controller V-855 and recirculating chiller B-740. The Syncore® Analyst system is shown in Figure 3.10. The concentration of sample extracts was performed under vacuum. Sample temperature and shaking speed were controlled. Solvent vapour was condensed into the receiver vessel.

For trace analysis of environmental samples, concentration of the sample can enhance method detection limits. The concentration should be done carefully if target compounds can be volatilised. Extracts of mixed hexane and toluene were concentrated under vacuum conditions to allow a rapid solvent evaporation at relatively low temperature to prevent the loss of volatile compounds. Sample rack and vacuum lid temperatures were maintained at 60°C and 70°C. The sample rack contains the Flushback module which assists the condensation of solvent vapour to improve the recovery by flushing back sample adhered to the glass vessel wall. The cooling temperature was set to 8°C. The heating and cooling units were switched on 15 minutes prior to use to achieve temperature set points. The vacuum controller was

programmed as follows: 400 mbar to 40 mbar in 5 minutes, maintained at 40 mbar for 3 minutes and then reduced to 20 mbar and maintained for 42 minutes or until a sample volume of less than 1 mL remained in the vessel. The final sample volume was adjusted to 1.5 mL with toluene. Samples were spiked with deuterated PAHs standards prior to the GC-MS analysis.

Figure 3.10 Buchi Syncore® Analyst concentrator used for parallel evaporation of samples with the maximum capacity of 12 samples.

3.2.4 Methods for PAHs analysis

3.2.4.1 Qualitative analysis

The preliminary study of PAHs in dust and particulate samples was done using the Trace Ultra GC connected with a DSQ II quadrupole mass spectrometer (Thermo Scientific, Hertfordshire, UK). Chromatographic separation conditions were optimised to separate 16 US EPA priority PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene,

benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene. A solution of mixed alkylated PAHs including methylnaphthalene, ethylnaphthalene and dimethylnaphthalene isomers was prepared and mixed with the stock standard solution while preparing calibration standard solutions. All standard solutions and samples were prepared in toluene and preserved at -80°C between analyses to prevent evaporation of any sample and solvent. Target compounds were identified by comparing the mass spectra of PAHs mixed standard with the National Institute of Standards and Technology (NIST) Mass Spectral Library (Gaithersburg, MD, USA). Target PAHs and deuterated standards are classified into groups as shown in Table 3.2.

Deuterated PAHs standards used during sample extraction and analysis were naphthalene-d_8, fluorene-d_{10}, pyrene-d_{10}, anthracene-d_{10}, acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12}. Retention times and deuterated standard mass spectrum were identified by injecting the single standard to the GC-MS and comparing the resulting mass spectrum with the NIST library where available. Data analysis of GC-MS results were performed by the Xcalibur® software Version February 2007 (Thermo Scientific, Hertfordshire, UK). Retention times and peaks identification of all target compounds were determined in the mixed standard solution prior to environmental sample analysis.

Table 3.2 Molecular masses of target PAHs and deuterated standards and classification.

No.	Compounds (Abbreviations)	MW	Classification
1	Naphthalene (N)	128.17	2-ring
2	Acenaphthylene (ACY)	152.19	3-ring
3	Acenaphthene (ACE)	154.21	3-ring
4	Fluorene (FLU)	166.22	3-ring
5	Phenanthrene (PHE)	178.23	3-ring
6	Anthracene (ANT)	178.23	3-ring
7	Fluoranthene (FLT)	202.25	4-ring
8	Pyrene (PYR)	202.25	4-ring
9	Benz[a]anthracene (BaA)	228.29	4-ring
10	Chrysene (CHR)	228.29	4-ring
11	Benzo[b]fluoranthene (BbF)	252.31	5-ring
12	Benzo[k]fluoranthene (BkF)	252.31	5-ring
13	Benzo[a]pyrene (BaP)	252.31	5-ring
14	Dibenz[a,h]anthracene (DBA)	278.35	5-ring
15	Indeno[1,2,3-cd]pyrene (IP)	276.33	6-ring
16	Benzo[g,h,i]perylene (BP)	276.33	6-ring
17	1-Methylnaphthalene (1MN)	142.20	C1-naphthalene

No.	Compounds (Abbreviations)	MW	Classification
18	2-Methylnaphthalene (2MN)	142.20	C1-naphthalene
19	1-Ethylnaphthalene (1EN)	156.22	C2-naphthalene
20	2-Ethylnaphthalene (2EN)	156.22	C2-naphthalene
21	1,5-Dimethylnaphthalene (1,5-DMN)	156.22	C2-naphthalene
22	2,3-Dimethylnaphthalene (2,3-DMN)	156.22	C2-naphthalene
23	Naphthalene-d_8 (D8-N)	136.22	deuterated standard
24	Fluorene-d_{10} (D10-FLU)	176.28	deuterated standard
25	Pyrene-d_{10} (D10-PYR)	212.31	deuterated standard
26	Acenaphthene-d_{10} (D10-ACE)	188.29	deuterated standard
27	Phenanthrene-d_{10} (D10-PHE)	188.29	deuterated standard
28	Chrysene-d_{12} (D12-CHR)	240.36	deuterated standard

Analytical conditions for qualitative analysis

The qualitative analysis was performed using the GC-MS scan mode. Sample extracts were brought to room temperature and spiked with internal standards prior to analysis. The analysis was performed by the Trace Ultra GC equipped with a split/splitless injector connected with a DSQ II quadrupole mass spectrometer. All samples were analysed in triplicate. PAHs were separated on a 30 m x 0.25 mm ID 5% phenylmethylsiloxane column with 0.25 µm film thickness. Each sample was injected at 1 µL using splitless mode. The inlet temperature was set at 230°C. Helium carrier gas was set at 1 mL min^{-1} throughout the run. The temperature programme was 60°C with 3 minutes isothermal then increased at the rate of 5°C min^{-1} to 310°C hold for 1.50 minutes. The total run time was 54.5 minutes. The mass spectrometer

was set for full scan from mass 50 to 650 amu at the scan rate of 500 amu s^{-1}. Transfer line and ion source temperatures were set at 320 and 220°C respectively.

3.2.4.2 Quantitative analysis

Quantification of target 16 PAHs was performed by the GC-QMS in selected ion monitoring mode (SIM mode). Characteristic ions of each PAH were selectively monitored in a time window encompassing a group of adjacent peaks instead of scanning all masses throughout the acquisition time. The SIM mode increased the sensitivity of MS by allowing longer time to monitor fewer ions. The dwell time was set for each time window section resulted in the higher the abundance of ions. Thus limit of detections determined from SIM mode were lower than those of scan mode. The quantitative analysis of relatively low concentration air samples was performed under SIM mode.

Analytical conditions for quantitative analysis

The quantitative analysis of 16 PAHs in PM_{10} samples was performed using the GC-MS selected ion monitoring mode. Extracts were adjusted to the final volume of 1.5 mL in toluene and spiked with internal standards prior to the analysis. All samples were analysed in triplicate. PAHs were separated on a 30 m x 0.25 mm i.d. 5% phenylmethylsiloxane column with 0.25 µm film thickness. Each sample was injected at 1 µL using splitless mode at the inlet temperature of 250°C. Helium carrier gas was set at 1 mL min^{-1} throughout the run. The temperature programme was 60°C with 3 minutes isothermal, increased at the rate of 1°C min^{-1} to 80°C, increased at the rate of 5°C min^{-1} to 230°C and finally increased at the rate of 10°C min^{-1} to 310°C hold for 6.50 minutes. The total run time was 67.5 minutes. The transfer line and ion source temperatures were set at 320 and 230°C respectively.

The concentration of each PAH was determined from the area ratio of standard and the concentration ratio of the target analyte to the internal standard. PM_{10} filter samples containing trace level of PAHs were analysed in selected ion monitoring (SIM) mode. Selected masses of each PAH used for quantification are listed in Table 3.3. Calibration curves for target compounds were determined from the analysis of at

least five concentration levels of PAHs mix standard. A linear regression line is acceptable when the coefficient of determination (r^2) is higher than 0.95.

Table 3.3 Selected SIM masses and time windows for PAHs analysis using an Rxi®-5Sil MS capillary column (30m x 0.25 mm i.d. x 0.25 µm df).

Segment	Start time (min)	SIM masses	Compounds
1	8.00	127, 128, 134, 136	naphthalene, naphthalene-d_8
2	25.50	115, 141, 142	1-methylnaphthalene, 2-methylnaphthalene
3	31.50	115, 141, 151, 152, 153, 154, 155, 156	1-ethylnaphthalene, 2-ethylnaphthalene, 1,2-dimethylnaphthalene, 1,3-dimethylnaphthalene, acenaphthylene, acenaphthene
4	37.00	165, 166	fluorene
5	40.50	94, 176, 178, 187, 188, 189	phenanthrene, anthracene, phenanthrene-d_{10}, anthracene-d_{10}
6	46.00	101, 200, 202	fluoranthene, pyrene
7	52.00	226, 228, 229, 236, 240, 241	benz[a]anthracene, chrysene, chrysene-d_{12}
8	56.80	126, 132, 250, 252, 253, 264, 265	benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene
9	60.30	137, 138, 139, 276, 278, 279	dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene

3.2.4.3 Limit of detection and limit of quantification

For the trace measurement, it is essential to demonstrate that there is a significant difference between a signal peak and random noise peaks of the analytical system. This can be shown as the lowest concentration of an analyte that can be detected by

the method or the limit of detection (LOD) or detection limit (DL). Another important limit that needs to be established is the lowest level at which the method can measure an analyte concentration confidently or the limit of quantification (LOQ). The limit of quantification is often used as a threshold to report the analyte concentration. The concentration found lower than LOQ value can be report as a value <LOQ or not detected (ND). For chromatographic technique, LOD and LOQ can be calculated from standard deviation (S) of replicate measurements of reagent blanks spiked with low concentrations of analytes to obtain a non-zero standard deviation. The instrument LOD and LOQ were estimated according to the EURACHEM Guide for method validation (Magnusson and Örnemark, 2014).

LOD and LOQ were determined from standard deviation of replicate measurements according to following equations.

$$S = \sqrt{\frac{1}{N-1}\sum_{i-1}^{N}(x_i - \bar{x})} \qquad \text{Equation 3.5}$$

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} \qquad \text{Equation 3.6}$$

$$LOD = 3S \qquad \text{Equation 3.7}$$

$$LOQ = 10S \qquad \text{Equation 3.8}$$

Instrument LOD and LOQ values of an analytical method need to be determined for the quality control of trace analysis. The report value of an analyte concentration found below LOQ can be justified from the usage of measurement data.

3.3 Data Analysis

Qualitative and quantitative analysis of GC-QMS data were performed by the Xcalibur® software with the National Institute of Standards and Technology (NIST) Mass Spectral Library. The quantification of 16 US EPA PAHs were done for dust

samples. The quartz fibre filter used for PM_{10} collection has a low water affinity. The filter could not retain naphthalene–the most volatile PAH. This was confirmed during the extraction method development when naphthalene-d_8 was spiked onto a blank filter in order to determine the extraction efficiency. Due to the limitation of the filter property, 15 PAHs were quantified in ambient particulate matter (PM_{10}) samples.

The screening data obtained by the GCxGC TOFMS were processed using ChromaTOF® software (Leco). GCxGC TOFMS is a powerful tool for screening of non-targeted analysis at the trace level. However, the identification of unknowns was limited by the mass spectrum available in the library database. Compounds identified by library search need to be manually re-examined to ensure the quality of data.

3.4 Results and Discussion

3.4.1 Extraction efficiency

Extraction of dust and particulate samples were performed by an accelerated solvent extraction system Dionex ASE350. Recoveries of surrogate PAHs were used to determine the efficiency of ASE methods. An aliquot of deuterated PAHs standard solution was spiked onto the sample and left to dry for approximately 15-30 minutes prior to the ASE extraction. For dust samples, naphthalene-d_8 and chrysene-d_{12} were used to represent volatile (2-ring) and semi-volatile (4-ring) PAHs in the sample. Samples were extracted, concentrated and then analysed for target 16 PAHs. The amount of surrogate D-PAHs measured was compared with the initially spiked amount. The extraction efficiency of the method was determined according to the equation 3.9.

$$\%R = \frac{C_{observe}}{C_{spiked}} \times 100 \qquad \text{Equation 3.9}$$

Where:

%R = recovery percentage

$C_{observed}$ = amount of surrogate D-PAH measured

C_{spiked} = amount of surrogate D-PAH spiked

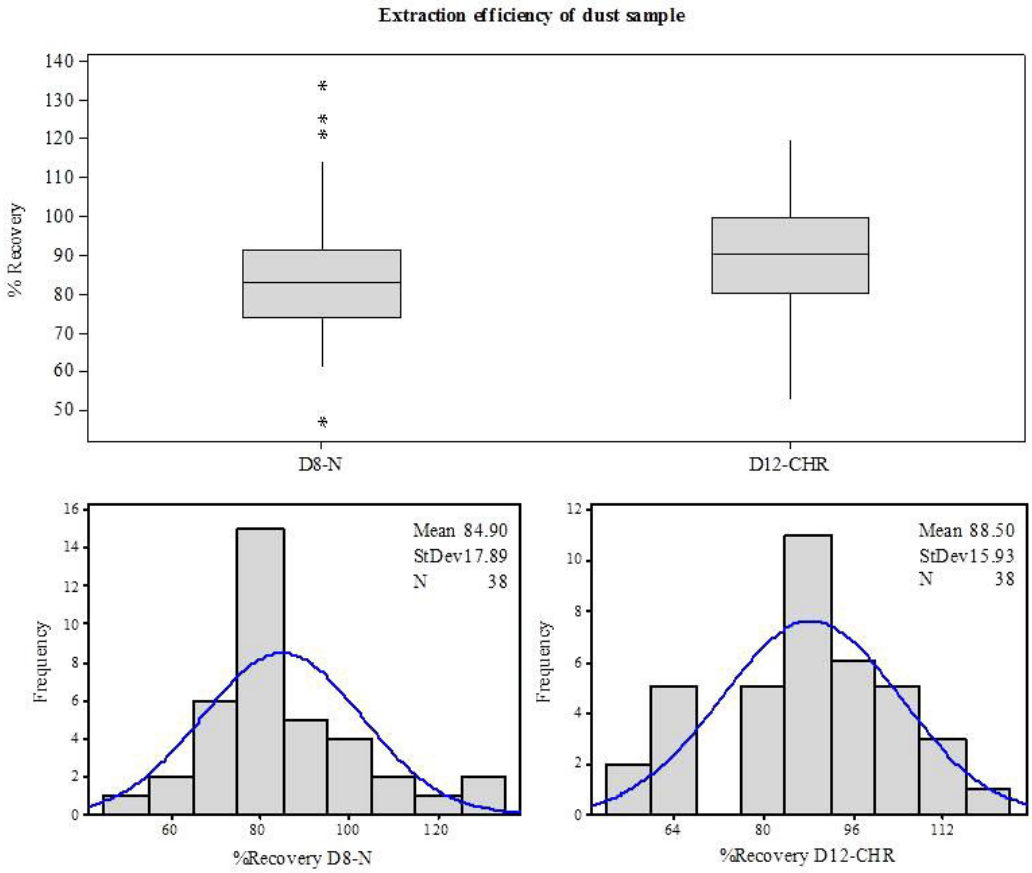

Figure 3.11 Boxplots and histograms of recovery percentages of naphthalene-d_8 and chrysene-d_{12} in dust samples.

Figure 3.11 illustrates the boxplot and histograms of recovery percentages of surrogate D-PAHs spiked onto dust samples collected from 38 households in the south of Malawi. It is shown that surrogate D-PAHs adsorbed by dust particles were extracted at high recoveries for both 2-ring and 4-ring PAHs. The mean recovery of naphthalene-d_8 was 85% ± 18% whereas higher mean recovery was found at 89% ± 16% for chrysene-d_{12}. Recoveries of naphthalene-d_8 in 21 samples (55% of all samples) and chrysene-d_{12} in 30 samples (79% of all samples) were found in the range between 80% and 120%. The ASE extraction method gave satisfactory results for dust samples although higher variations were observed for naphthalene-d_8.

The extraction method used for dust samples was then verified using spiked blank filters prior to extraction of PM_{10} filter. A quartz micro fibre filter 20.3 x 25.4 cm (Whatman Inc., Fairfield, NJ) used for PM_{10} sampling was spiked with a 40 µL

surrogate D-PAHs solution containing naphthalene-d_8, anthracene-d_{10} and chrysene-d_{12} at the concentration of 1218.0, 1064.4 and 1100.0 µg mL^{-1}, respectively. D-PAHs were used to represent 2-ring, 3-ring, and 4-ring PAHs in the filter sample. Spiked samples were extracted using four different ASE methods with different settings summarised in Table 3.4. All samples were extracted at 110°C with 6 minute static time. Each sample was extracted in three cycles and the system pressure was maintained above 1500 psi.

Table 3.4 ASE conditions tested for the extraction of PAHs in PM_{10} filter sample.

Method	Solvent	Solvent ratio	Purge time (s)
ASE1	Toluene/Hexane	4 : 1	60
ASE2	Toluene/Hexane	4 : 1	100
ASE3	Toluene/Hexane	4 : 1	120
ASE4	Toluene/Methanol	4 : 1	120

Extraction conditions were tested with a spiked blank quartz fibre filter and recoveries of surrogate standards were calculated as shown in Figure 3.12. It is found that the quartz fibre filters used as PM_{10} sampling media fail to retain volatile 2-ring naphthalene-d_8 while moderate recovery percentage was found for 3-ring anthracene-d_{10} and good recovery percentage was found for 4-ring chrysene-d_{12}. This is consistent with a previous study that demonstrated poor recovery percentage of less than 30% for naphthalene from 4 filter media including quartz, glass fibre, PTFE and nylon (Borrás and Tortajada-Genaro, 2007). ASE2 method was selected for the extraction of PAHs in PM_{10} as anthracene-d_{10} recovery was 71% ± 7% and chrysene-d_{12} recovery was 95% ± 10%. The extraction method may result in an underestimation of low molecular weight 3-ring PAHs while high molecular weight from 4-ring PAHs can be reliably recovered from PM_{10} filter samples.

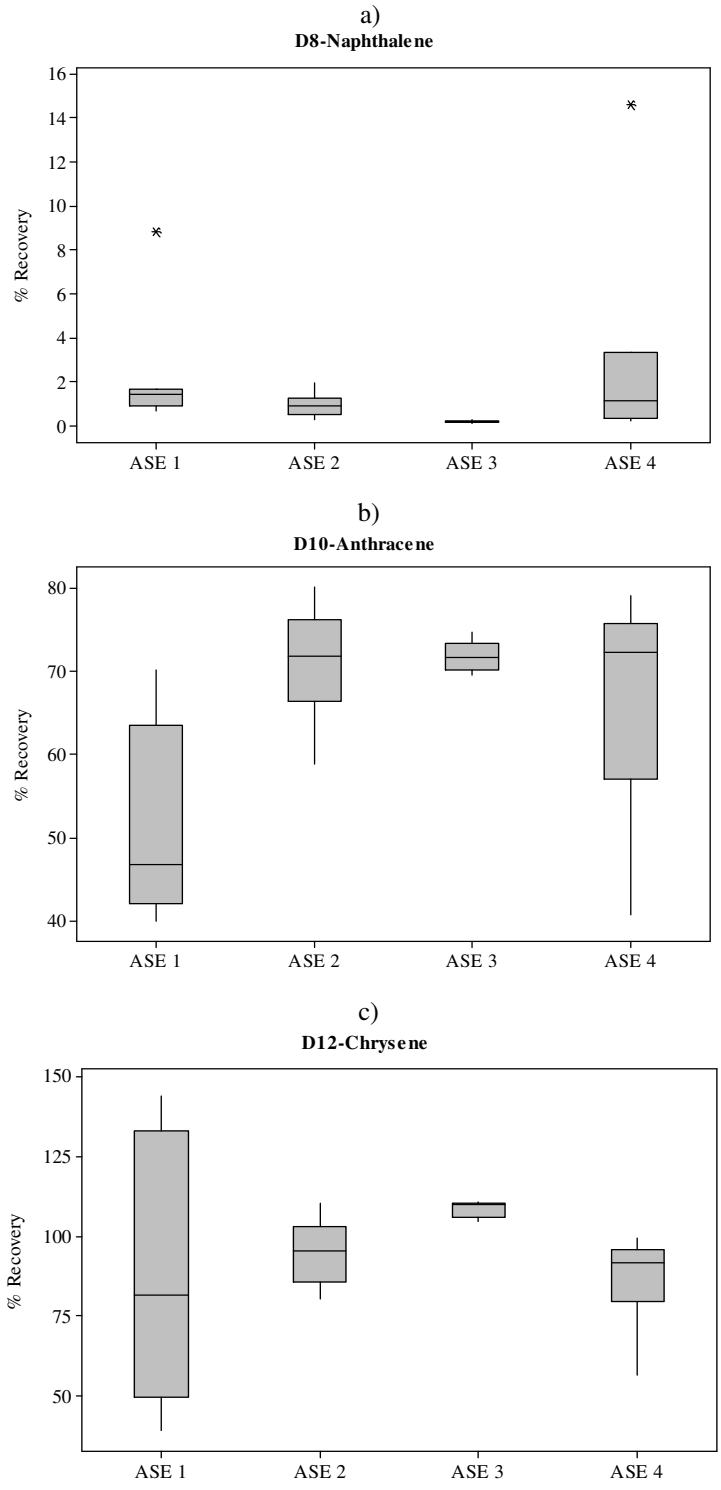

Figure 3.12 Recovery percentages of surrogate D-PAHs in quartz fibre filters extracted under four ASE conditions: a) naphthalene-d_8, b) anthracene-d_{10} and c) chrysene-d_{12}.

3.4.2 Identification of target PAHs

GC-MS methods were optimised for separation of 16 US EPA priority PAHs using columns with similar dimensions of 30 m x 0.25 mm i.d. x 0.25 µm film thickness. A method developed using a HP-5MS had a total chromatogram run time of 54 minutes (Borrás and Tortajada-Genaro, 2007). Firstly, an Rxi-5Sil MS, a low polarity capillary column with Crossbond® 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane stationary phase was used to analyse PAHs in dust samples. A method was optimised with a total chromatogram run time of 67.50 minutes. Then the column with more specific stationary phase for semi-volatile compound was tested in order to improve the sample throughput. The Zebron™ ZB-SemiVolatiles column is coated with 5% phenyl-arylene 95% dimethylpolysiloxane. Both columns were tested and methods were optimised in order to separate out 16 US EPA priority PAHs. The latter column resulted in a dramatic improvement of the run time from 67.50 to 18.30 minutes. Retention times of 16 PAHs on the two columns were compared in Table 3.5.

Table 3.5 Quantification masses and retention times of 16 US EPA priority PAHs under optimised conditions for Rxi-5Sil MS and Zebron™ ZB-SemiVolatiles columns.

PAH	Quantification mass	Retention time (min)	
		Rxi-5Sil MS	ZB-SemiVolatiles
Naphthalene	128	22.39	5.49
Acenaphthylene	152	34.77	6.62
Acenaphthene	153	35.74	6.74
Fluorene	166	38.45	7.11
Phenanthrene	178	43.04	7.83
Anthracene	178	43.28	7.87
Fluoranthene	202	48.62	9.02
Pyrene	202	49.60	9.31

PAH	Quantification mass	Retention time (min)	
		Rxi-5Sil MS	ZB-SemiVolatiles
Benz[a]anthracene	228	55.00	11.39
Chrysene	228	55.16	11.46
Benzo[b]fluoranthene	252	55.28	13.91
Benzo[k]fluoranthene	252	55.34	13.97
Benzo[a]pyrene	252	59.04	14.71
Indeno[1,2,3-cd]pyrene	276	61.42	17.37
Dibenz[a,h]anthracene	278	61.48	17.44
Benzo[g,h,i]perylene	276	61.95	17.79

The chromatographic separation of 16 PAHs on the Rxi-5Sil MS column is demonstrated in Figure 3.13a. The separation of 16 PAHs and some alkylated naphthalene isomers on the Zebron™ ZB-SemiVolatiles column is shown in Figure 3.13b. Alkylated naphthalene derivatives including C1-naphthalenes and C2-naphthalenes were quantified using the Zebron™ ZB-SemiVolatiles column. However, the results were not reported in this study due to poor separation of some C2-naphthalene derivatives that caused difficulties in the determination of detection limits. This research focused on the characterisation of targeted 16 PAHs which will be used in the health risk assessment.

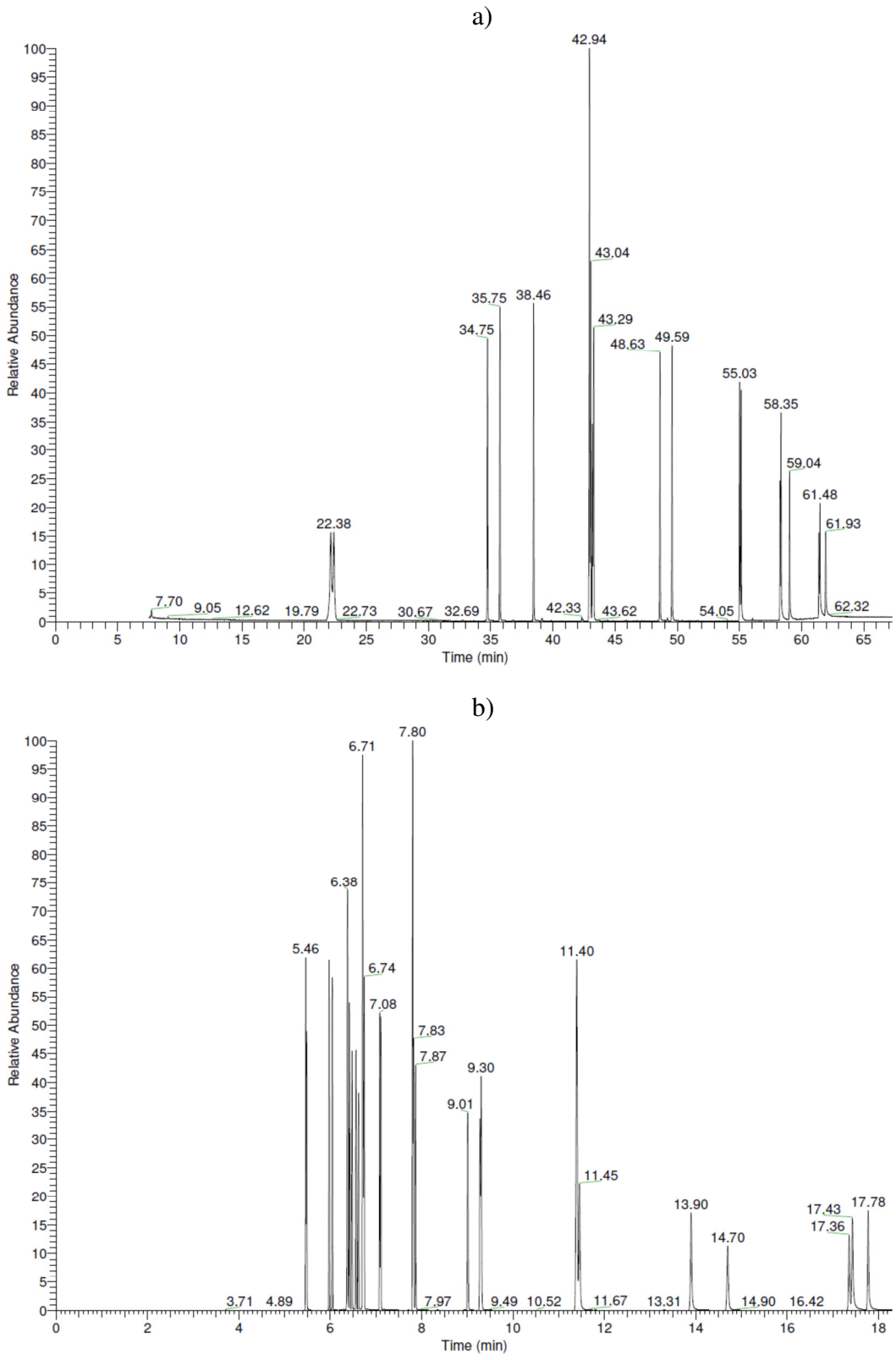

Figure 3.13 Separation of PAHs calibration standard solution on a) Rxi-5Sil MS and b) Zebron™ ZB-SemiVolatiles.

3.4.3 Limit of detection and quantification (LOD and LOQ)

LOD and LOQ of target 16 PAHs were calculated from standard deviation of 10 replicate measurements of reagent blank spiked with low concentrations PAHs standard solution. GC-MS was operated under selected ion monitoring (SIM) mode to maximise the instrument sensitivity. All target compounds were previously identified by comparing mass spectrum of the standard solution with the mass spectrum of the NIST database. The calculation of LOD and LOQ of a GC-MS method is shown in Table 3.6. Detection limits ranged from 0.001 to 0.004 ng and quantification limits were 0.004 to 0.012 ng for the injection of 1 µL liquid sample.

The LOD was determined from liquid injection while samples analysed were soil and air particles and therefore unit conversion to either weight of sample or volume of air were performed to report the analyte concentration accordingly.

For example, an aliquot of 5 grammes of dust was extracted and the final volume of sample was adjusted to 1.5 mL. LOD of BaP at 0.004 µg mL^{-1} is converted to a weight of BaP per gramme of dust as follows.

LOD of BaP = LOD (µg mL^{-1}) * Injection volume (mL) / Dust weight (g)

= 0.004 µg mL^{-1} * 0.001 mL / 5 g

= $8 * 10^{-4}$ ng g^{-1}

For particulate matter (PM_{10}) collected on a quartz fibre filter, the total air volume is used to convert the LOD to the weight of a PAH in a cubic metre of air. GC-MS methods were developed using 2 columns of different stationary phases including a Restek Rxi®-5Sil MS and a Zebron™ ZB-SemiVolatiles with similar column dimensions (30 m x 0.25 mm i.d. x 0.25 µm df). The Restek Rxi®-5Sil MS column is a low polarity column generally used for the analysis of compounds in volatile to semi-volatile ranges. The GC-MS method was modified from the previous study in the analysis of soot and dust samples from Malawi (Chidziwisano, 2012). The Zebron™ ZB-SemiVolatiles column was later developed for the analysis of compounds in semi-volatile range. LOD and LOQ of 2 analytical methods were summarised in Table 3.7.

Table 3.6 Calculation of LOD and LOQ from replicate analysis of 0.01 µg mL^{-1} 16 PAHs standard solution.

Sample	Amount (ng)															
	N	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IP	DBA	BP
Rep 1	0.010	0.012	0.009	0.011	0.011	0.014	0.012	0.011	0.011	0.012	0.012	0.012	0.014	0.011	0.013	0.014
Rep 2	0.010	0.010	0.008	0.010	0.010	0.014	0.011	0.010	0.010	0.011	0.010	0.010	0.012	0.009	0.011	0.011
Rep 3	0.009	0.009	0.008	0.010	0.009	0.013	0.011	0.010	0.010	0.011	0.010	0.010	0.011	0.009	0.010	0.011
Rep 4	0.009	0.009	0.008	0.010	0.009	0.013	0.010	0.009	0.011	0.011	0.010	0.009	0.011	0.009	0.009	0.010
Rep 5	0.009	0.009	0.007	0.010	0.009	0.013	0.011	0.009	0.010	0.010	0.009	0.010	0.011	0.009	0.010	0.010
Rep 6	0.009	0.008	0.008	0.010	0.009	0.013	0.010	0.009	0.009	0.010	0.009	0.009	0.011	0.008	0.009	0.010
Rep 7	0.009	0.009	0.007	0.010	0.009	0.012	0.010	0.009	0.010	0.011	0.009	0.009	0.010	0.007	0.009	0.010
Rep 8	0.009	0.008	0.007	0.009	0.009	0.012	0.010	0.009	0.009	0.011	0.009	0.009	0.010	0.008	0.009	0.010
Rep 9	0.008	0.008	0.007	0.010	0.010	0.012	0.010	0.009	0.009	0.010	0.009	0.009	0.010	0.008	0.009	0.010
Rep 10	0.009	0.008	0.007	0.010	0.010	0.013	0.010	0.009	0.009	0.011	0.009	0.009	0.010	0.009	0.009	0.010
Average	0.009	0.009	0.008	0.010	0.010	0.013	0.010	0.009	0.010	0.011	0.010	0.010	0.011	0.009	0.010	0.011
S	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
DL (3S)	0.002	0.004	0.002	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.004	0.003	0.004	0.004
QL (10S)	0.006	0.012	0.007	0.004	0.007	0.007	0.006	0.007	0.007	0.005	0.009	0.010	0.013	0.009	0.012	0.012

Table 3.7 Limits of detection and limits of quantification for the analysis of PAHs in PM_{10} using different capillary columns.

PAH	Rxi-5Sil MS		ZB-SemiVolatiles	
	LOD (ng m^{-3})	LOQ (ng m^{-3})	LOD (ng m^{-3})	LOQ (ng m^{-3})
N	1.0E-05	3.4E-05	1.1E-06	3.7E-06
ACY	9.6E-06	3.2E-05	2.3E-06	7.6E-06
ACE	9.1E-06	3.0E-05	1.2E-06	4.1E-06
FLU	9.8E-06	3.3E-05	7.2E-07	2.4E-06
PHE	7.9E-06	2.6E-05	1.2E-06	4.1E-06
ANT	2.0E-05	6.6E-05	1.3E-06	4.3E-06
FLT	2.9E-05	9.8E-05	1.2E-06	3.9E-06
PYR	3.5E-05	1.2E-04	1.3E-06	4.3E-06
BaA	2.3E-06	7.5E-06	1.4E-06	4.5E-06
CHR	4.9E-05	1.6E-04	1.0E-06	3.3E-06
BbF	4.1E-06	1.4E-05	1.6E-06	5.4E-06
BkF	1.6E-05	5.2E-05	1.8E-06	5.9E-06
BaP	5.1E-05	1.7E-04	2.4E-06	7.9E-06
IP	3.2E-05	1.1E-04	1.7E-06	5.7E-06
DBA	1.1E-05	3.6E-05	2.2E-06	7.4E-06
BP	1.5E-05	5.0E-05	2.2E-06	7.2E-06

3.4.4 Homogeneity of PM_{10} filter sample

PM_{10} filter samples were randomly selected to investigate homogeneity of sample. Filters were cut into 2 pieces and 4 pieces then each section was analysed for PAHs concentrations as an individual sample. A total of 22 filters were tested, 16 samples were cut into two halves and 6 samples were cut into 4 sections. Analysis of variance

and paired t-test for sample means were perform by Microsoft Excel version 11.0 to determine the significant difference in PAHs concentrations in split samples.

Analysis of variance (ANOVA two-factor without replication) were performed for PAHs concentrations obtained from 4-split samples to determine the difference between sample means. There were significant differences between the sample means determined by ANOVA ($F(3,22) = 3.34$, $p = 0.024$; $F(3,22) = 4.41$, $p = 0.007$; $F(3,23) = 3.78$, $p = 0.014$ and $F(3,23) = 3.73$, $p = 0.015$). Mean concentrations showed statistically significant differences in 4 out of 6 samples split into 4 sections (67% of all samples). This suggested that PM_{10} filter samples should not be subdivided into multiple sections as this may cause errors in the PAHs quantification.

The significant mean differences of samples split into 2 pieces were analysed using paired t-test. All samples split into 2 pieces showed no significant difference of PAH mean concentrations ($p > 0.05$). Thus PM_{10} filter samples can be split into 2 pieces for the duplicate analysis. However, the use of partial samples is not recommended due to the low level of analytes in the ambient particulate sample.

3.5 Summary

This chapter presented general background of the analytical method development for particulate-bound PAHs in two sample matrices including dust and particulate matter collected on a quartz fibre filter. Extraction methods were optimised for the extraction of PAHs from dust and PM_{10} filter samples. GC-MS methods were developed for the identification of non-targeted PAHs as well as the quantification of trace amount of PAHs in samples. General purpose low polarity capillary column is adequate for the separation of US EPA 16 priority PAHs. However, the application of specific column stationary phase dramatically improved the chromatographic method in terms of separation, run time and limits of detection. In the next chapters, analytical methods were applied for the determination of pPAHs in environmental samples. The quantification of PAHs in dust samples aimed to evaluate potential exposure to indoor air pollution in the rural household of Malawi. Particulate-bound

PAHs in urban areas of Thailand were determined to assess the associated health risks from long-term inhalation exposure.

Chapter 4

A Case Study of Malawi Household Dust

4.1 Background

Biomass fuels have been a common source of indoor air pollution in developing countries as they are cheap and abundant. The use of biomass fuels is a regular practice in rural areas of developing countries for both cooking and residential heating. This results in many low-income residents being exposed to a wide range of toxic air pollutants including carbon monoxide, benzene and polycyclic aromatic hydrocarbons. PAHs are products of incomplete combustion emitted during the burning of biomass (Ramdahl, 1985). A study on PAH emissions from agricultural burning revealed that high molecular weight 5-ring and 6-ring PAHs were associated with ultrafine particles with sizes less than 0.1 μm while more volatile 3-ring and 4-ring PAHs were predominant in larger particles (Keshtkar and Ashbaugh, 2007). Home cooking and heating using biomass fuels is a threat to human health that half of the world's population is exposed to in daily life. The exposure to smoke from indoor use of solid fuels is associated with lower respiratory tract infections, chronic obstructive pulmonary disease and trachea, bronchus and lung cancers (WHO, 2002).

Frequent use of biomass fuels for cooking has been associated with chronic obstructive pulmonary disease and interstitial lung disease (Lisouza, Owuor and Lalah, 2011). A study in Kenya showed the association between indoor exposure to biomass smoke and childhood asthma (Mohamed, 1995). A recent study in rural Nigeria observed significant reductions of health symptoms related to exposure of indoor biomass burning smoke after one year of stoves being introduced (Oluwole *et al.*, 2013). Low-emission stoves substantially reduced indoor carbon monoxide and $PM_{2.5}$ concentrations measured during the peak cooking period thus substantially reduced the indoor exposure of women and children in the household.

Women were exposed to higher indoor air pollution than men owing to time spent at home (Smith, Mehta and Maeusezahl-Feuz, 2004). It was noted that out of the deaths of 1.3 million women globally from chronic obstructive pulmonary disease (COPD), more than 500,000 were attributable to indoor air pollution, compared to only 171,000 of 1.4 million COPD deaths linked to indoor air pollution amongst men. WHO (2005) reported that women and children in the developing countries are exposed on a daily basis to indoor cooking smoke pollution up to 20 times higher than the guideline levels of World Health Organization and other environmental agencies around the world. In India, men and women who had frequent exposure to the biomass burning smoke were at a high risk of tuberculosis (Gupta and Mathur, 1997).

In Malawi, it is estimated that only 2% of households cook with electricity and that the majority of residents are daily exposed to air pollution through the use of open fires. PM_{10} has been found to be significantly correlated with mortality rates of children under 5 years old in low-income countries and was found at the rate of 52.9 per 1,000 live births in 2011 in Malawi (Gani, 2015). Exposure to particles emitted from cooking activities in poorly ventilated households is very likely to result in an elevated health risk for residents especially children and women who spend more time indoors than men. Exposure to PAHs is associated with lung inflammatory and carcinogenic health effects in humans (Vineis *et al.*, 2004; Brook *et al.*, 2010).

A study on biomass fuel emissions in Malawi observed high concentrations of respirable dust in both urban (Blantyre) and rural (Chikwawa) homes with 24-hour average total inhalable dust concentrations of 185 µg m^{-3} and 268 µg m^{-3}, respectively (Fullerton *et al.,* 2014). The study showed high concentrations of household air pollution associated with biomass burning during the peak cooking period particularly carbon monoxide and particulate matter, whereas transition metal levels found in filters were low. Despite the high particle concentration, PAHs were not analysed in this study. Traditional households in rural Malawi are constructed of mud walls, dirt floors, small wooden windows and doors and traditional grass thatched roofs. These conditions enhance the exposure of residents to air pollutants

including both fine inhalable soot particles and re-suspended coarse particles through poor ventilation.

Indoor air pollution has the potential to contribute to child, adolescent and adult morbidity and mortality; and in turn negatively affects Malawi in achieving the Millennium Development Goals (MDGs) to reduce infant and child mortality rates. In 2010, the under-five child and infant mortality rates were at 122 per 1,000 and 69 per 1,000 live births, respectively (Malawi-Government, 2010). These are relatively high when compared to developed countries e.g. Scotland where the infant mortality rate is 3.7 per 1,000 (Scottish-Government, 2010). In addition, a survey study on indoor environments pointed out the link between solid fuel burning and respiratory illnesses of children under 5 years old in the peri-urban area of Abidjan city in Ivory Coast (Sackou *et al.,* 2014). Recently WHO reported that currently almost 3 billion of the world's population relied on solid fuels which resulted in approximately 4 million annual premature deaths of children and adults from respiratory related diseases and cancer (WHO, 2014).

The concentration of particulate matter and PAHs from indoor cooking and other sources in households vary due to a number of different factors including the season of the year, type of fuel burnt, fuelling rate, kitchen size, ventilation efficiency and type of cook stove used (Gachanja and Worsfold, 1993). A number of different organisations currently promote the use of improved cook stoves (ICS) in rural Malawi. The introduction of ICS aimed to reduce indoor air pollution through a more efficient means of combustion. Five ICS brands with different designs were investigated in the previous study including PCI mud stove, Chitetzo Mbaula, Briquette, Aleva and Esperanza stoves (Chidziwisano, 2012). ICS are generally simple to construct, with charity organisations training locals in their production, meaning that the new designs can be easily adopted by residents. The Chitetzo Mbaula stove is the only portable design which could ideally be used outside (or at least in the most ventilated area of a residence) to limit the build-up of indoor smoke. On the other hand, the Aleva and PCI mud stoves are produced using compacted soil and mud respectively, to prevent problems in sourcing clay which may constrain the distribution and positioning of stoves. The Esperanza stove is a larger and more

expensive ICS with ceramic-lined air and combustion chambers and thus has been less popular. Soot and dust samples collected from households using biomass fuels in rural Malawi were investigated for the evaluation of improved cook stoves (Chidziwisano, 2012). Samples were collected from households equipped with improved cook stoves. Chidziwisano (2012) demonstrated high PAHs concentrations in soot samples collected from households in Balaka district with the range of 13.7 to 815.0 µg per gramme of soot.

The objective of this study is to verify analytical methods for particulate-bound PAHs using house dust samples. These analytical methods were adopted from Chidziwisano's study (2012). Dust samples preserved under -80°C were extracted and analysed using the same set of instruments. In addition to the 15 PAHs measured in the previous study, acenaphthene (3-ring PAH) can be identified and quantified in this study. Methods were further optimised for the analysis of US EPA 16 priority PAHs. Targeted 16 PAHs were measured in household dust in order to evaluate the deposition of these PAHs in the indoor environment of Chikwawa households. Measurement of PAHs concentrations in indoor dust provided information related to PAHs exposure and the potential health risks to people living in such households. The evaluation of health risks may give rise to a better practice for biomass fuel burning in order to prevent adverse health effects from indoor particulate exposure.

4.2 Methodology

4.2.1 Study area

The study was conducted in rural areas in the south of Malawi where biomass fuels were generally used for cook stoves. Dust samples were collected from 38 random households in Chikwawa district in the southern region of Malawi (Figure 4.1). Main biomass sources in the study areas were indigenous and exotic trees, including bush species. Biomass fuels are used for cooking with traditional three stone stoves. The majority of residents are farmers. While women and children were subjected to the indoor smoke exposure, men workers were exposed to outdoor particulate matter from the open burning of agricultural residues.

Figure 4.1 Map of Malawi showing sampling locations in Balaka and Chikwawa.

4.2.2 Samples and standards

Dust samples were collected from indoor residential dust of 38 households in Chikwawa by floor sweeping. Dust samples were collected and placed in clean polythene bags. After transport to the laboratory, samples were transferred to clean glass vials and stored at -80°C until extraction and analysis.

All solvents used (n-hexane, dichloromethane, toluene) were of analytical grade, purchased from Fisher Scientific (Loughborough, U.K) and used without further purification. All PAHs and deuterated PAHs were purchased from Sigma–Aldrich (Gillingham, U.K). Accelerated solvent extraction method with in-cell clean-up was adopted from the previous study without further adjustment (Chidziwisano, 2012). Anhydrous sodium sulphate, silica gel 60 (both from Sigma–Aldrich) and diatomaceous earth (Dionex, Camberley, UK) were baked at 450°C for 4 hours prior to use. Silica gel 60 was then deactivated by 10% water (w/w) after baked.

4.2.3 Sample preparation

The extraction of PAHs from dust was performed using an accelerated solvent extraction system (ASE 350, Dionex, Camberley, UK) equipped with 34 mL extraction cells. Dust samples were extracted at 110°C with a heating time of 6 minutes and a static time of 6 minutes. Each sample was extracted in 3 cycles. The extraction solvent was a mixture of hexane and toluene (4:1 v/v). A flush volume of 60% cell volume and a purge time of 60 seconds were used. The approximate solvent volume of 3-cycle combined extract was 70 mL per sample.

Surrogate deuterated PAHs standards (naphthalene-d_8 and chrysene-d_{12} prepared as a 500 μg mL^{-1} stock solution in dichloromethane) were added to each sample to determine the extraction efficiency. ASE extraction cells were prepared by lining the lower lid with two filter papers to prevent particles entering the ASE system, then filling the cell with approximately 3 g of silica gel and 3 g of anhydrous sodium sulphate. Approximately 5 g of dust sample was weighed and spiked with surrogate PAHs and then added to the sample cell. The remaining cell volume was packed with diatomaceous earth (as an inert packing agent). A method blank cell was prepared by filling an extraction cell with packing agents. The method blank cell was then extracted and analysed with each batch of samples. The method blank of at least one or 10% of the sample, whichever is greater, should be analysed in every batch of samples.

A Büchi Syncore Analyst (Oldham, UK) was used for solvent evaporation under vacuum. Sample volume was reduced to approximately 1 mL and then adjusted to

the final volume of 1.5 mL with toluene. All samples were spiked with internal standard, phenanthrene-d_{10}, prior to the GC-MS analysis. The quantification of 16 US EPA priority PAHs was performed by a quadrupole gas chromatograph-mass spectrometer. All samples and standard solutions were stored at -80°C between analyses.

Dust samples were analysed by using a ThermoScientific Trace Ultra GC equipped with a DSQ II quadrupole mass spectrometer and a Triplus autosampler (Thermo Scientific, Hertfordshire, U.K.). Helium (BOC Ltd., 99.999% purity) was used as the carrier gas at a flow rate of 1 mL min^{-1}. A J&W Scientific DB-5MS column with dimensions of 30 m x 0.25 mm i.d. x 0.25 μm film thickness was used for all dust analyses. The inlet temperature was set at 230°C, with 1 μL of each sample extract injected under the splitless mode. Helium carrier gas was held constant at 1 mL min^{-1} through the GC run time. All standards and extracts were analysed with the oven temperature programme at 60°C with 3 minutes isothermal then increased at the rate of 5°C min^{-1} to 310°C (maintained for 1.5 min). The MS was operated in full scan mode with the mass range of 50-650 amu at the scan rate of 500 amu s^{-1}. The ion source temperature was set at 220°C. Target PAHs in dust extracts were quantified by GC-MS using a calibration series containing 16 PAHs. All samples and standards were analysed in triplicate.

4.3 Results and Discussion

4.3.1 Concentrations of PAHs

Dust samples from 38 households in Chikwawa district were analysed for 16 US EPA priority PAHs using the Trace Ultra GC coupled with the DSQ II quadrupole MS. PAHs concentrations were detected in the range of 0.005 – 6.52 μg g^{-1}. The sum of all 16 PAHs ranged from 0.36 – 7.07 μg g^{-1} in dust samples which was in similar order of 0.07 – 9.35 μg g^{-1} found in previous study (Chidziwisano, 2012). PAHs content in dust samples were compared with soot samples collected during the same period in Balaka district. Soot samples collected from the inside wall of kitchens equipped with improve cook stoves were found to contain high concentration of 4-

ring PAHs. Chidziwisano (2012) reported high concentrations of PAHs in the range of 13.7 – 815.0 μg g^{-1} in soot suggesting that higher health effects might occur from soot exposure than dust exposure. Low molecular weight 2-ring and 3-ring PAHs were found to constitute more than 80% of PAHs weight in 33 out of 38 dust samples (87% of dust samples). The composition of PAHs may be influenced by types of biomass fuels used in households. The results of dust analysis implied that in biomass fuels contributing to the emission of low molecular weight PAHs that composed of 2-ring and 3-ring formed during low temperature burning and associated with coarse particles. Concentrations of PAHs in soot and dust samples are summarised in Table 4.1.

Table 4.1 PAH concentrations (μg g^{-1}) in soot and dust samples.

PAH	Concentration in soot [a] (μg g^{-1})			Concentration in dust (μg g^{-1})		
	Range	Mean	SD	Range	Mean	SD
N	0.10 - 4.40	1.36	1.47	0.16 - 6.52	1.80	1.28
ACY	N/A	N/A	N/A	0.01 - 0.18	0.06	0.04
ACE	0.40 - 15.70	3.98	4.51	0.01 - 0.11	0.03	0.02
FLU	0.30 - 9.50	2.67	2.82	0.01 - 0.22	0.04	0.04
PHE	1.70 - 117.8	39.07	40.21	0.03 - 0.32	0.13	0.08
ANT	1.00 - 31.1	9.81	9.86	0.005 - 0.06	0.02	0.01
FLT	2.90 - 216.7	63.29	63.72	0.01 - 0.17	0.06	0.04
PYR	2.50 - 256.9	69.43	72.17	0.005 - 0.15	0.05	0.04
BaA	1.90 - 60.9	20.25	18.33	<0.002	N/A	N/A
CHR	0.60 - 51.3	18.18	15.85	0.02 - 0.08	0.04	0.02
BbF	0.80 - 43.2	15.47	12.42	0.02 - 0.08	0.04	0.02
BkF	0.30 - 16.4	5.71	5.02	<0.003	N/A	N/A
BaP	1.20 - 26.4	9.67	8.30	0.01 - 0.07	0.03	0.02

PAH	Concentration in soot [a] (µg g^{-1})			Concentration in dust (µg g^{-1})		
	Range	Mean	SD	Range	Mean	SD
IP	0.80 - 24.6	7.28	6.15	0.01 - 0.07	0.04	0.02
DBA	0.70 - 2.50	1.37	0.53	<0.003	N/A	N/A
BP	0.90 - 15.0	4.11	3.75	0.02 - 0.06	0.03	0.02
Total	13.7 - 815.0	270.21	256.28	0.36 - 7.07	2.22	1.39

N/A = not available

[a] Chidziwisano, 2012

A large variation in PAH concentrations was observed in soot samples which was associated with smaller particle size range compared with dust samples. Major components of PAHs in soot samples were approximately 60% 4-ring PAHs while naphthalene contributed to approximately 70% of PAHs weight in dust. The sum of 2-ring and 3-ring PAHs accounted for more than 80% of total PAHs weight in all dust samples. High concentration of high molecular weight PAHs suggested that exposure to soot may cause a significant impact to the health of residents. On the contrary, dust samples which were associated with low molecular weight PAHs are less harmful to health. PAHs composition by total weight of PAHs measured in dust and soot samples are shown in Figure 4.2 and 4.3.

Major components of PAHs in soot were 4-ring PAHs including PYR, FLT and CHR that comprised approximately 54% of total PAHs weight. PHE, 3-ring PAH, was found at approximately 13% of total PAHs weight. BaP, marker of carcinogenic PAHs, contributed to 4% of total PAHs weight in soot. While PHE, FLT and PYR have not been classified as carcinogenic to humans (Group 3), CHR is possibly carcinogenic to humans (Group 2B) (IARC, 2010). On the contrary, low molecular weight PAHs, N and ACY, were the most abundant components in dust samples. Combined weight of N and ACY contributed to 91% of total PAHs weight in dust samples while BaP was found at 2% of total PAHs weight.

The comparison of pPAHs associated with indoor air pollution in the rural household of Malawi indicated that high PAHs concentrations were found in small size particles represented by soot samples. Most soot associated PAHs were distributed in the 3-ring and 4-ring PAHs range. Coarse dust particles contained mostly 2-ring and 3-ring PAHs. Concentrations of PAHs in dust samples were significantly lower than in soot samples. The exposure to indoor PAHs is most likely associated with the inhalation of soot particles. In addition, the ingestion of dust may occur more in children than in adults.

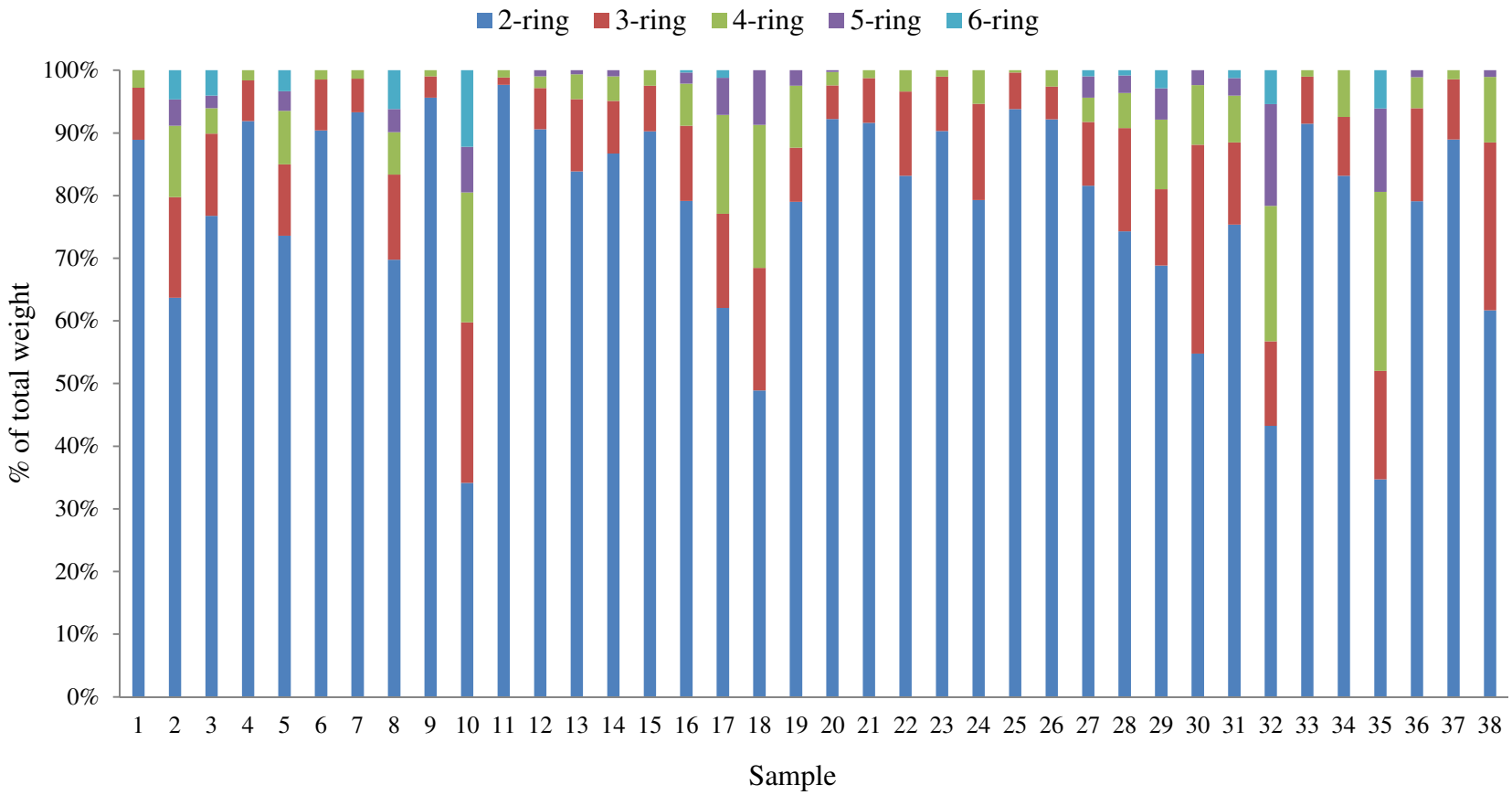

Figure 4.2 Composition of PAHs in dust samples classified by number of rings in the molecule by total weight of 16 PAHs measured (2-ring: N; 3-ring: ACY, ACE, FLU, PHE, ANT; 4-ring: FLT, PYR, BaA, CHR; 5-ring: BbF, BkF, BaP, DBA; 6-ring: IP, BP).

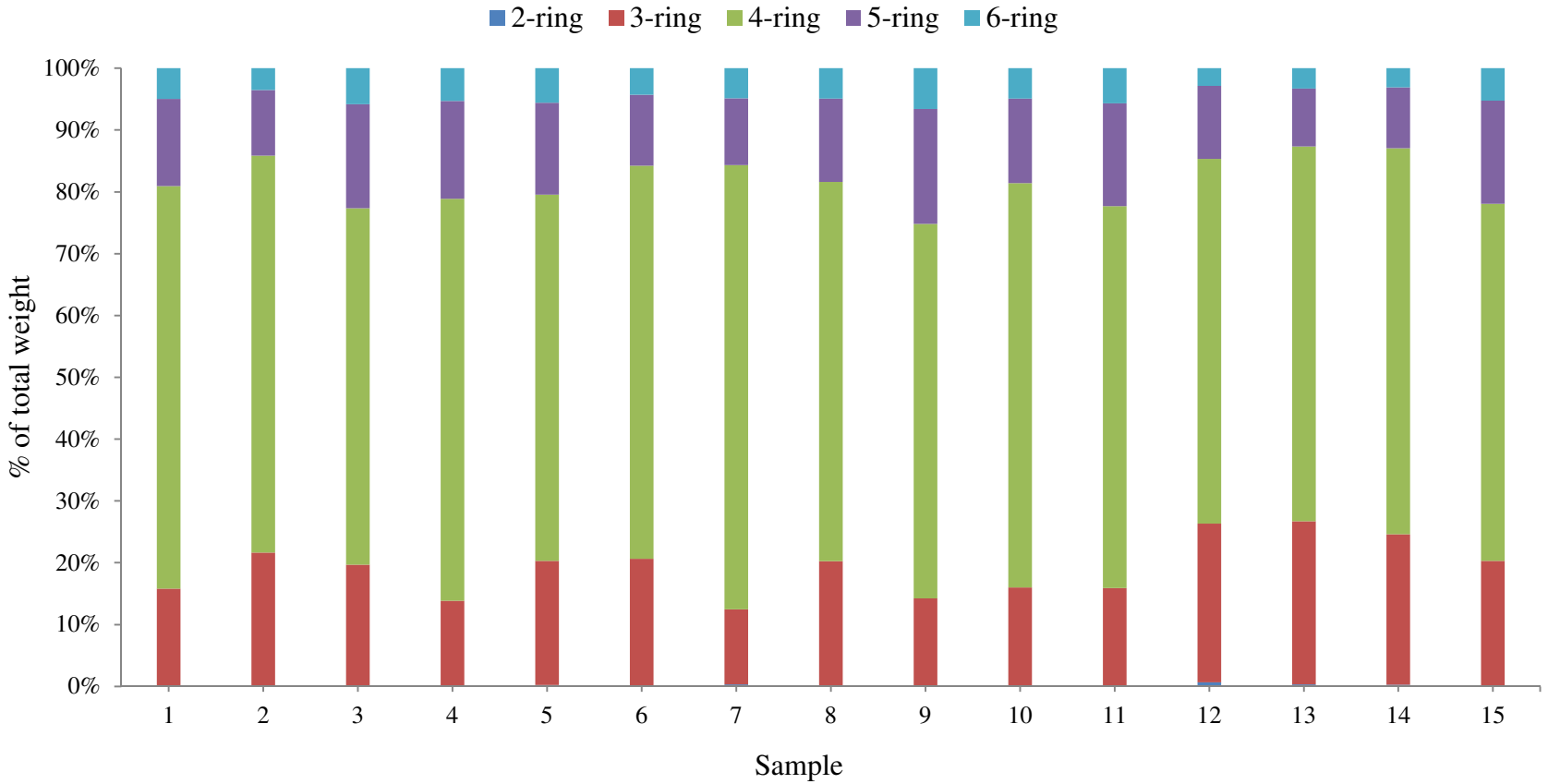

Figure 4.3 Composition of PAHs in soot samples categorised by weight of PAHs with same numbers of rings by total weight of 15 PAHs (Chidziwisano, 2012).

4.3.2 Hazards to human health

The exposure to PAHs occurs mainly via inhalation and ingestion including the inhalation of smoke from cooking activities. Ingestion can be a major pathway in which contaminated house dust is transferred in children from hand to mouth behaviour. PAHs attract attention due to their potential adverse health effects; many are known to exhibit carcinogenic and/or mutagenic properties (IARC, 2010). Human health effects of PAHs exposure depend on factors such as concentration, frequency and duration of exposure, the innate toxicity of the particular PAHs and the route of exposure e.g. oral, inhalation, eyes and skin absorption. Other determinants including health conditions and age also influence PAHs health effects (OSU, 2012).

It is known that exposure to organic material combustion products such as PAHs has been associated with the causation of eye problems such as cataracts, cancerous conditions, liver damage and renal failure (Brune, 1981). Brune (1981) also documented that exposure to PAHs is one of the major factors contributing to the development of tumours of the lungs, bladder, kidney, pelvis, mouth, pharynx, larynx and oesophagus. Ezzati (2002) suggested that indoor air pollution from biomass combustion is the fourth leading risk factor of disease burden in under developed countries experiencing high-mortality rates killing 1.6 million people globally, and contributing to 39 million of disease prevalence. It is important to investigate indoor air pollution particularly PAHs which are produced during incomplete combustion of biomass fuels on a daily basis.

Fuel woods and biomass were used to start and make cooking fires in many households in Chikwawa and Balaka districts of Malawi. Houses were constructed from mud walls, dirt floors, tiny wooden windows and doors, with traditional grass thatched roofs; all these conditions increased the risk to household members of expose to indoor air pollutants particularly PAHs from cooking and heating. Cooking areas in most rural Malawian households tend to be poorly ventilated which promotes the accumulation of indoor particles. In addition, cooking areas were attached, or closely located to the main house thus increasing the risk of exposure.

Women and children spent time working around the cooking area where cooking is often made on traditional three stone stoves. This situation exposes them on a daily basis to substantial air pollutants such as carcinogenic PAHs that were mostly adsorbed on inhalable particles.

Indoor and outdoor air quality standards have been established to safeguard human health against hazardous situations. WHO recommended guidelines for ambient PM_{10} are 50 μg m^{-3} and 20 μg m^{-3} for 24-hour and annual means, respectively (WHO, 2005). The first step in the air quality evaluation, and eventual improvement of its quality, is the monitoring of the ambient air and the identification of potential emission sources. However, air quality monitoring requires high investment and operational costs that limit most monitoring networks within urban areas. Developing countries are struggling to come up with effective air quality standards to safeguard public health against PAH emissions. For instance, it is reported that air pollution exposures in India from solid fuel cook smoke had surpassed appropriate health-based standards by a factor of 20 or more (Mishra, Retherford, and Smith, 1999). This is extremely high in comparison to particulate matter levels in developed countries. PAHs occur in a mixture, which makes it difficult to develop guidelines, the known carcinogen benzo(a)pyrene was chosen as an indicator of carcinogenic PAHs. However, considering that PM_{10} as well as several PAHs are classified as human carcinogens, no safe threshold can be determined and all indoor exposures are considered significant to health (WHO, 2010).

The results of this preliminary survey show that distributions of indoor PAHs from cook stoves in rural Malawi were predominantly 4-ring PAHs such as FLT, PYR, BaA and CHR that were found predominantly in soot particles. More volatile 2-ring and 3-ring PAHs were associated with larger particles that settled faster and deposited on the floor. PAHs measured in dust were found at significantly lower concentrations than soot and composed mainly of 2-ring and 3-ring PAHs. Nevertheless, the residents are still likely to be exposed to more volatile PAHs via both smoke inhalation and dust ingestion. Further studies may be required to show the cumulative effect of multiple routes of exposure to PAHs of the residents of Malawi, whether it be skin absorption, ingestion or inhalation, especially for

susceptible group such as children and people having respiratory diseases. It is necessary to further clarify the indoor air quality situation in rural communities of Malawi since more than half of the population lives in these conditions. The preliminary study results provided the characterisation of PAHs associated with indoor particulate matter in rural household of Malawi. Addressing the indoor air pollutant issue is a challenge in health promotion particularly in developing countries where biomass fuels are widely used.

4.4 Conclusion

Combustion of biomass fuels can generate a wide range of air pollutants in both gaseous and particulate phases. Solid fuels used for cooking and heating were found to be the major source of indoor particulate matter. Most PAHs that pose a risk to human health are high molecular weight PAHs that associate with particulate matter. The survey on indoor air quality based on surrogate samples collected from biomass utilising households in 2 rural areas of Malawi showed potentially high exposure to carcinogenic PAHs in soot particles while dust particles contained much lower PAHs levels mostly distributed in 2-ring and 3-ring PAHs (Chidziwisano, 2012). Carcinogenic PAHs appearing in semi-volatile ranges containing 4-ring to 6-ring structures were associated with soot particles adhered to the kitchen walls. The use of biomass fuels is the major indoor air pollution source in remote areas of developing countries which resulted in adverse health effects particularly in women and children who spend more time indoors (Gachanja and Worsfold, 1993; Ezzati, 2002). Attempts to reduce indoor air pollution exposure have been to encourage the use of more efficient combustion stoves, however, more study is required to optimise the stove design that can significantly reduce particulate emission.

4.5 Summary

This chapter explained the characteristic of 16 US EPA priority PAHs quantified within 38 household dust samples collected from rural Malawi households in Chikwawa districts. The results were compared with the previous study on soot samples collected in Balaka district of Malawi (Chidziwisano, 2012). It is shown that higher PAH concentrations were found in the kitchen soot samples and higher

molecular weight PAHs were associated with smaller size particles. Indoor PAHs emitted from biomass fuel burning mostly accumulated in soot collected from kitchen walls implying the accumulation of indoor particulate matter. Dust particles may contribute to exposure to low molecular weight PAHs which are less toxic compared to the high molecular weight PAHs. The study results implied that particulate matter emitted from cooking activities may contribute to adverse health effects of people in rural Malawi households. The main exposure route of indoor PAHs from cooking activities is inhalation of small particles.

The exposure to particulate-bound PAHs in rural environments mostly involved biomass burning particularly from cooking and agricultural activities. Women and children are daily exposed to indoor air pollution while men experience more outdoor air pollution. In rural areas where resources for air sampling are limited, environmental samples such as soot can be utilised to investigate potential pPAHs exposure from the indoor smoke. A more extensive study would be useful to compare the PAH emissions of traditional open fires with improved cook stoves so as to encourage the use of more efficient cook stove in order to reduce indoor air pollution exposure.

The analysis of dust samples used in this study replicated and verified methods used in the previous study. Remaining dust samples were analysed for the US EPA priority 16 PAHs using modified ASE extraction and GC-MS methods. Results showed that the ASE method is a highly efficient technique for particulate-bound PAHs extraction. The extraction time is approximately 30 minutes per sample which significantly shortens the sample preparation time when compared with the 18-hour reflux of the conventional Soxhlet extraction. The extraction and analysis of dust samples conducted in this research also provided training for vital laboratory skills prior to performing the particulate matter analysis.

Analytical methods for PAHs in dust investigated in this preliminary study were applied for the analysis of PAHs in ambient particulate matter samples. The methods were further optimised in the next chapter to provide sensitive quantitative methods for trace level of PAHs in airborne particles. The outdoor pPAHs situation is

investigated in the Bangkok Metropolitan Administration area of Thailand through a long-term collection of ambient particulate matter (PM_{10}) samples. In urban environments, fossil fuels are main sources of energy in the transportation sector. The composition of pPAHs is expected to be significantly different from the rural area of Malawi. This study can give rise to a better understanding of pPAHs composition from the different environmental settings including biomass fuels used in rural areas of Malawi and other fuels and combustion activities in urban areas of Thailand.

Chapter 5

Spatial Variation of Particulate-bound Polycyclic Aromatic Hydrocarbons in the Bangkok Metropolitan Administration

5.1 Background

In Chapter 4, the composition of PAHs in household dust was investigated and analytical methods were tested. Major constituents of PAHs in dust particles were low molecular weight 2-ring and 3-ring PAHs which can be formed under low temperature burning of biomass fuel used in Malawi households. In this chapter, PAHs in airborne particulate matter from urban area of the Bangkok Metropolitan Administration were characterised. PM_{10} samples were collected from three study areas where ambient air quality was monitored.

Air quality has been a major environmental issue in mega-cities worldwide due to its impact on a large population. Particulate matter, one of criteria air pollutants, is responsible for a range of adverse health effects from acute short-term exposure to chronic exposure. Bangkok, the capital city of Thailand, has faced a prolonged air pollution problem due to high levels of airborne particles including total suspended particulate, particulate matter size smaller than 10 µm (PM_{10}) and particulate matter size smaller than 2.5 µm ($PM_{2.5}$). To protect public health, WHO has recommended guidelines for outdoor PM_{10} concentration at 50 µg m^{-3} for 24-hour mean and 20 µg m^{-3} for annual mean (WHO, 2006). Roadside PM_{10} concentrations in Bangkok occasionally exceeded the 24-hour average National Ambient Air Quality Standard (NAAQS) of 120 µg m^{-3} (PCD, 2013). In 2013, concentrations of PM_{10} at 2 Bangkok roadside air monitoring stations were found in the top five highest areas nationwide. Highest PM_{10} concentrations at Phaholyothin and Rama VI sites were measured at 303 and 178 µg m^{-3} for daily means and 82 and 74 µg m^{-3} for annual means with

15% and 7% of days exceeded the NAAQS. Peak PM_{10} levels in Bangkok were six times higher than WHO guideline values and, thus, posed a threat of health risks to people spending a long time travelling or working near roadside areas.

Since people residing in mega-cities are continuously exposed to high PM concentrations over a long time period, adverse health outcomes can develop over long-term exposure. The most concerning health issue caused by chronic exposure to PM_{10} and PAHs is the development of lung cancer. The International Agency for Research on Cancer (IARC) evaluation on cancer in humans concluded that sufficient evidence was found for the carcinogenicity of particulate matter and the exposure to outdoor particulate matter is a cause of lung cancer (IARC, 2013). Evidence found in animal studies pointed out the carcinogenicity of organic solvent-extracted materials from outdoor particles.

Studies on adverse health effects of PM_{10} exposure focusing on PAHs carcinogenicity have been carried out in many countries (Ruchirawat *et al.,* 2002; Adonis *et al.,* 2003; Amador-Muñoz *et al.,* 2010; Jung *et al.*, 2010; Anastasopoulos *et al.,* 2012). Semi-volatile high molecular weights PAHs such as benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[g,h,i]perylene were accounted for more than 80% of PM_{10}-bound PAHs in Malaysia (Jamhari *et al.*, 2014). Some of these particulate-bound high molecular weight PAHs were identified carcinogens and mutagens. It is shown that PAHs are major constituents of organic mixtures in air-borne particles, thus recurrent exposure to respirable particles poses a health risk concern owing to their physical properties and toxic contaminants. The European Commission adopted benzo[a]pyrene as a single marker for carcinogenic PAHs mixture in ambient air and specified the target annual mean value of 1 ng m^{-3} (EC, 2004) while the UK implemented more stringent standard of 0.25 ng m^{-3} per year (DEFRA, 2007).

In Thailand, although a PM_{10} monitoring network was established for more than 10 years, systematic PAHs measurements have not been carried out. Previous studies on the exposure of carcinogenic PAHs focused on highly polluted areas, in high exposure population groups and specific occupational exposure identified the need to

mitigate carcinogenic PAHs as they resulted in a significant health risk to the exposed population (Norramit *et al.,* 2005; Ruchirawat *et al.,* 2007). Recent studies indicated problematic areas with high seasonal particulate concentration during haze episodes in the northern region of Thailand (Pengchai *et al.*, 2009; Phoothiwut and Junyapoon, 2013; Ponpiachan, 2013; Ponpiachan, 2015). The establishment of an ambient air quality guideline or standard requires collection of accurate information on the pollutant situation and its potential adverse health effect on the general public. While BaP is regulated in European countries (EC, 2004), the ambient PAHs situation in Thailand needs to be investigated in order to establish an appropriate guideline.

Particulate-bound PAHs major components are high molecular weight (MW ≥ 228), low volatility PAHs that are more carcinogenic than low molecular weight ones. Chemical characterisation of PM_{10} can give rise to a better understanding of the ambient PAHs situation that is vital for the health risk assessment. The determination of long-term PAHs concentration is also required for the estimation of the health risk from chronic pPAHs exposure. Published research on particle-bound PAHs from archived $PM_{2.5}$ filters showed that high molecular weight PAHs composed of 5-ring and 6-ring compounds were reliably quantified, however, the more volatile 3-ring and 4-ring PAHs tend to be lost when stored at room temperature (Pleil *et al.*, 2004).

The monitoring of PM_{10} in the Bangkok Metropolitan Administration contains long-term information of PAHs concentrations that can be utilised to assess the health risk from pPAHs exposure. The sampling duration of one year encompassed the seasonal variation which may influence PM_{10}-bound PAHs concentrations. This study aimed to quantify the ambient pPAHs in three study areas with different environmental surroundings to understand spatial variations of pPAHs from different sources. The three sampling sites representing roadside, industrial and urban background environments were designated in urban areas of the Bangkok Metropolitan Administration. All sampling sites are operated by the Pollution Control Department to monitor the ambient air quality in compliance with the Thailand National Ambient

Air Quality Standards. The sampling of PM_{10} for gravimetric analysis is also carried out at these three locations. Properties of targeted PAHs are shown in Table 5.1.

Table 5.1 Properties of the US EPA 16 priority PAHs.

Compound	CAS	FW	Number of rings	MW (Da)	IARC [a] Carcinogenicity	Vapour pressure [a] (Pa)	Boiling point [b] (°C)
Naphthalene	91-20-3	$C_{10}H_8$	2	128.17		11	218
Acenaphthylene	208-96-8	$C_{12}H_8$	3	152.19		9.0×10^{-1}	280
Acenaphthene	83-32-9	$C_{12}H_{10}$	3	154.21	Group 3	3.0×10^{-2}	279
Fluorene	86-73-7	$C_{13}H_{10}$	3	166.22	Group 3	9.0×10^{-2}	295
Phenanthrene	85-01-8	$C_{14}H_{10}$	3	178.23	Group 3	2.0×10^{-2}	340
Anthracene	120-12-7	$C_{14}H_{10}$	3	178.23	Group 3	1.0×10^{-3}	342
Fluoranthene	206-44-0	$C_{16}H_{10}$	4	202.25	Group 3	1.2×10^{-3}	375
Pyrene	129-00-0	$C_{16}H_{10}$	4	202.25	Group 3	6.0×10^{-4}	393
Benz[a]anthracene	56-55-3	$C_{18}H_{12}$	4	228.29	Group 2B	2.8×10^{-5}	400
Chrysene	218-01-9	$C_{18}H_{12}$	4	228.29	Group 2B	1.4×10^{-6}	448
Benzo[b]fluoranthene	205-99-2	$C_{20}H_{12}$	5	252.31	Group 2B	6.7×10^{-5}	481
Benzo[k]fluoranthene	207-08-9	$C_{20}H_{12}$	5	252.31	Group 2B	5.2×10^{-8}	480
Benzo[a]pyrene	50-32-8	$C_{20}H_{12}$	5	252.31	Group 1	7×10^{-7}	496

Compound	CAS	FW	Number of rings	MW (Da)	IARC [a] Carcinogenicity	Vapour pressure [a] (Pa)	Boiling point [b] (°C)
Dibenz[a,h]anthracene	53-70-3	$C_{22}H_{14}$	5	278.35	Group 2A	3.7×10^{-8}	524
Indeno[1,2,3-cd]pyrene	193-39-5	$C_{22}H_{12}$	6	276.33	Group 2B	1.3×10^{-8}	536
Benzo[g,h,i]perylene	191-24-2	$C_{20}H_{12}$	6	276.33		1.4×10^{-8}	550

[a] IARC, 2010 (Group 1: carcinogenic to humans, Group 2A: probably carcinogenic to humans, Group 2B: Possibly carcinogenic to humans, Group 3: not classifiable as to its carcinogenicity to humans)

[b] Stogiannidis and Laane, 2015

Atmospheric PAHs measurement

Conventional methods for ambient PAHs measurement specified the sampling of both gas and particulate phase PAHs using a sorbent cartridge and quartz filter followed by gas chromatography-mass spectrometry analysis (US EPA, 1999). Volatile PAH such as naphthalene can be found more in gas phase than particulate phase and required a sorbent i.e. Tenax®, XAD-2® and polyurethane foam (PUF) to adsorb whereas non-volatile PAHs (vapour pressure $<10^{-8}$ mm Hg) can be trapped on a filter. Sample was extracted using Soxhlet apparatus that required a large volume of solvent up to 700 mL and a period of 18 hours reflux. Alternative methods for sample preparation have been developed to reduce difficulties in sample preparation and analysis time of PAHs in various matrices including sediment, soil and airborne particle (Björklund *et al*., 1999; Björklund, Nilsson and Søren, 2000; Delgado-Saborit *et al.*, 2010; Karthikeyan, Balasubramanian, and See, 2006).

Determination of PAHs is influenced by the concern of their carcinogenicity as well as high concentrations of PM_{10} in the study area that led to a prolonged exposure to pPAHs. The development of GC-MS methods aimed to increase sensitivity and speed of a routine PAHs quantification. In this study, particulate-bound PAHs were determined from archived PM_{10} filter samples. PAHs were extracted from a filter by means of accelerated solvent extraction which is a faster and less complicated alternative sample preparation technique than the Soxhlet extraction (Schantz, Nichols and Wise, 1997; Björklund *et al*., 1999; Björklund and Nilsson and Søren, 2000).

5.2 Experimental

5.2.1 Sample collection

Sampling sites for PM_{10} monitoring were located in Bangkok Metropolitan Administration which comprises of Bangkok and five adjacent provinces including Nakhon Pathom, Pathum Thani, Nonthaburi, Samut Prakan and Samut Sakhon. PM_{10} concentrations in Thailand are routinely monitored at ambient air monitoring stations

operated by the Pollution Control Department (PCD). All PCD ambient air quality monitoring stations were equipped with automatic analysers for measuring criteria air pollutants i. e., carbon monoxide, sulphur dioxide, oxides of nitrogen, ozone and PM_{10}. Hourly PM_{10} concentrations were measured with automatic beta ray attenuation monitoring. In addition to automatic analysers, gravimetric measurement of PM_{10} is carried out at three monitoring sites to validate automatic PM_{10} data. The sampling of PM_{10} onto a quartz fibre filter is done using a high volumetric air sampler. PM_{10} filters were collected every 6 days to obtain data from all days of the week.

Sampling sites representing roadside, urban background and industrial environments were located at the National Housing Authority Dindaeng (NHAD), the Public Relations Department (PRD) and the Electricity Generating Authority of Thailand-Nonthaburi (EGAT). Sites were classified according to major emission sources existing in the immediate vicinity. The roadside site is located approximately 2 meters away from the kerbside of the 6-lane Din Daeng road. The industrial site is located in the Electricity Generating Authority of Thailand where the North Bangkok Power Plant is operated. The natural gas power plant is located at the side of the Chao Phraya River. The urban background site is situated in the residential area of the Public Relations Department adjacent to a small recreation area. Sampling site details were shown in Table 5.2.

Table 5.2 Sampling site characteristics.

Sampling site	Coordinate	District (Province)	Population [a]	Site category	Sampling duration	Number of samples
National Housing Authority Dindaeng (NHAD)	N 13° 45' 45.36" E 100° 33' 1.44"	Dindaeng (Bangkok)	134,480 (5,701,394)	Roadside	2 May 2013 – 27 May 2014	43
Public Relations Department (PRD)	N 13° 46' 59.16" E 100° 32' 25.78"	Phaya Thai (Bangkok)	74,693	Urban background	2 May 2013 – 15 May 2014	46
Electricity Generating Authority of Thailand-Nonthaburi (EGAT)	N 13° 48' 25.92" E 100° 30' 22.68"	Bang Kruai (Nonthaburi)	108,266 (1,101,743)	Industrial	2 May 2013 – 27 May 2014	37

[a] National Statistical Office, 2010

Airborne particles were collected onto a quartz fibre filter (Whatman QMA, 20.3 x 25.4 cm) using a high volume air sampler equipped with a PM_{10} inlet (Graseby GMW high volume air sampler, Andersen Instruments, Inc., USA). The sampling flow rate was maintained between 1.1 – 1.7 m^3 min^{-1} throughout the 24-hour sampling period. PM_{10} filter samples were collected from sampling sites every 6 days in order to obtain data from different days of a week. Three sampling sites were chosen to monitor ambient air pollutants influenced by different source types including the roadside site, urban background site and industrial site as shown in Figure 5.1 and 5.2.

Figure 5.1 Map of particulate matter (PM_{10}) sampling sites showing urban background and roadside sites in Bangkok and the industrial site in Nonthaburi province in the north of Bangkok.

a) Roadside site (National Housing Authority Dindaeng: NHAD)

b) Industrial site (Electricity Generating Authority of Thailand-Nonthaburi: EGAT)

c) Urban background site (Public Relations Department: PRD)

Figure 5.2 Ambient air quality monitoring stations where PM_{10} samples were collected by high volumetric samplers in addition to automatic analysers.

All filters were equilibrated in desiccators under temperatures between 15 – 30°C ± 3°C and humidity of 20 – 45%RH ± 5%RH at least 24 hours before and after sampling. After sampling, PM_{10} filters were folded in half, put in a polythene bag and transferred to the laboratory for PM_{10} mass analysis. Filters were weighed under controlled conditions under the temperature of 23°C ± 3°C and humidity of 44%RH ± 5%RH using an electronic balance AB-204 (Mettler Toledo, Thailand). PM_{10} mass concentrations were calculated at standard conditions (25°C, 760 mmHg). After PM_{10} analysis, filters were wrapped in aluminium foil, put in polythene bags and stored at -20°C until transportation to the Civil and Environmental Engineering Department laboratory (University of Strathclyde, UK) where filters were preserved at -80°C until extraction and analysis.

5.2.2 Chemicals and materials

Organic solvents used for PAHs extraction and analysis were of HPLC grade purchased from Fluka Chemicals Ltd. (Gillingham, UK). Deuterated PAHs standards including naphthalene-d_8, fluorene-d_{10}, anthracene-$d_{10,}$ phenanthrene-$d_{10,}$ pyrene-d_{10} and chrysene-d_{12} were obtained from Sigma-Aldrich Company Ltd. (Gillingham, UK). Certified US EPA priority 16 PAHs (TCL Polynuclear Aromatic Hydrocarbons Mix) standards at 2000 µg mL^{-1} were obtained from Supelco Analytical (Pennsylvania, USA). Ambient PM_{10} samples were collected using quartz fibre filters from Whatman Inc. (New Jersey, USA) and prepared at the Environmental Laboratory, Pollution Control Department (Thailand).

5.2.3 Pressurised fluid extraction

PAHs extraction was done under a high pressure and high temperature conditions using an accelerated solvent extraction ASE350 system (Dionex, Camberley, UK). Prior to the extraction, filter samples were spiked with surrogate deuterated PAHs standards containing naphthalene-d_8, anthracene-d_{10} and chrysene-d_{12} to determine the extraction efficiency. All ASE packing agents were baked at 450°C for 8 hours before use. Silica gel was deactivated with 10% w/w deionised water. A filter sample was cut into small pieces and packed into the extraction cell with approximately 3 g

of silica gel and 3 g of anhydrous sodium sulphate as in-cell clean-up agents while the remaining cell volume was filled with pelletised diatomaceous earth. Samples were extracted in 3 cycles with a solvent mixture of toluene-hexane volume ratio 4:1 at 110°C with 6 min static time and 100 sec purge time. Extraction pressure was maintained over 1500 psi while sample cells were heated up and held at the extraction temperature. Extracted samples were transferred into cleaned glass vessels and evaporated under vacuum using a Büchi Syncore® Analyst (Oldham, U.K). Samples with high moisture content were dried with anhydrous sodium sulphate and filtered before solvent removal. The final volume of each sample was adjusted to 1.5 mL with toluene. Sample extracts were spiked with a 40 µL of 964.3 µg mL^{-1} phenanthrene-d_{10} internal standard prior to the GC-MS analysis. US EPA priority 16 PAHs were identified and quantified by a quadrupole gas chromatograph-mass spectrometer (Thermo Scientific, Inc.). All samples and standard solutions were stored at -80°C between analyses.

5.2.4 GC-MS analysis

During the method development, 2 fused silica capillary columns were tested for target PAHs analysis. GC-MS conditions were optimised for the quantification of 16 US EPA priority PAHs. The first conditions were developed using a low-polarity general purpose column namely Restek Rxi®-5Sil MS. The second conditions were further optimised using a specific column for semi-volatile compounds known as Phenomenex Zebron ZB-SemiVolatiles column.

Sample collected during 2nd May 2013 – 19th July 2013 were analysed using a fused silica column with Crossbond® 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane stationary phase, Rxi®-5Sil MS. Sample collected after 19th July 2013 were analysed using the Zebron ZB-SemiVolatiles with 5% phenyl-arylene, 95% dimethylpolysiloxane stationary phase. Both conditions were optimised to separate US EPA 16 priority PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene. GC-MS

was operated in selected ion monitoring mode for the quantification of targeted PAHs.

5.2.4.1 Condition 1

Samples were analysed for 16 PAHs using a gas chromatograph (Trace Ultra GC) equipped with a quadrupole mass spectrometer (DSQ II) and an autosampler (TriPlus) (Thermo Scientific, Inc.). PAHs were separated with the Rxi®-5Sil MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Each sample was injected at 1 μL using splitless mode at the inlet temperature of 250°C. Helium carrier gas was set at 1 mL min^{-1} throughout the run. The oven temperature programme was operated at 60°C with 3 min isothermal then increased at 1°C min^{-1} to 80°C then increased at 5°C min^{-1} to 230°C and finally increased 10°C min^{-1} to 310°C and hold for 6.50 min. The transfer line and ion source temperatures were set at 320 and 230°C respectively. Solvent delay was set to 8.0 min. Target PAHs were identified by comparing mass spectrum of authentic mix standards (Supelco Analytical, USA) acquired under MS scan mode with the NIST Mass Spectral Database (Gaitherburg, MD, USA). Quantitative analysis of PAHs in PM_{10} extracts was performed in the SIM mode. Detailed analytical conditions are given in Table 5.3.

Table 5.3 Target compounds, target ions, qualifier ions, dwelling time and retention time for GC-MS condition 1 and condition 2.

Compound	Target Ion	Q1	Q2	Dwell Time (ms)		Retention Time (min)		LOD (pg m^{-3})	
				Condition 1	Condition 2	Condition 1	Condition 2	Condition 1	Condition 2
Naphthalene	128	127		50	100	22.39	5.48	0.010	0.001
Acenaphthylene	152	151		50	40	34.77	6.61	0.010	0.002
Acenaphthene	153	154		50	40	35.74	6.73	0.009	0.001
Fluorene	166	165		100	50	38.45	7.10	0.010	0.001
Phenanthrene	178	176		70	55	43.04	7.82	0.008	0.001
Anthracene	178	176		70	55	43.28	7.86	0.020	0.001
Fluoranthene	202	200		100	80	48.62	9.01	0.029	0.001
Pyrene	202	200		100	80	49.60	9.29	0.035	0.001
Benz[a]anthracene	228	226	229	50	55	55.00	11.37	0.002	0.001
Chrysene	228	229	229	50	55	55.16	11.45	0.049	0.001
Benzo[b]fluoranthene	252	250		55	55	55.28	13.89	0.004	0.002

Compound	Target Ion	Q1	Q2	Dwell Time (ms)		Retention Time (min)		LOD (pg m^{-3})	
				Condition 1	Condition 1	Condition 1	Condition 2	Condition 1	Condition 2
Benzo[k]fluoranthene	252	126		55	55	55.34	13.95	0.016	0.002
Benzo[a]pyrene	252	250		55	100	59.04	14.69	0.051	0.002
Dibenz[a,h]anthracene	278	279	139	100	55	61.42	17.35	0.011	0.002
Indeno[1,2,3-cd]pyrene	276	138		100	55	61.84	17.42	0.032	0.002
Benzo[g,h,i]perylene	276	138	137	100	55	61.95	17.77	0.015	0.002

5.2.4.2 Condition 2

A ThermoScientific Trace Ultra GC equipped with a TriPlus autosampler and a Zebron ZB-SemiVolatiles capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). 1 µL of sample was injected in a split mode (split ratio 10:1) at the inlet temperature of 280°C. Oven temperature was held at 50°C for 2 min and then ramped at 35°C min^{-1} to 240°C and then ramped at 6°C min^{-1} to 295°C and finally ramped at 25°C min^{-1} to 325°C and held for 0.50 min. The helium carrier gas flow rate was held constant at 1.4 mL min^{-1} throughout the run time. The transfer line and ion source temperatures were set at 325°C and 230°C respectively. Solvent delay was set to 3.5 minute. The quadrupole mass spectrometer was set to quantify target compounds in the selected ion monitoring mode. Detail analytical conditions are given in Table 5.4.

Chromatograms were processed using Xcalibur® software (Xcalibur® version 2.0.7, Thermo Fisher Scientific Inc.). Quantification of target PAHs was done using linear regression of a six point calibration curve calculated from the concentration ratio of analyte to internal standard and the peak area ratio between analyte and internal standard.

Table 5.4 Optimised GC-MS programme parameters.

Parameter	Condition 1	Condition 2
Inlet Temperature (°C)	230	280
Injection Mode	Splitless	Split (Ratio 10:1)
Initial GC Temperature (°C)	60	50
Initial GC Time (min)	3	2
Ramp 1 Rate (°C min^{-1})	1	35
Ramp 1 Temperature (°C)	80	240
Ramp 1 Hold Time (min)	0	0

Parameter	Condition 1	Condition 2
Ramp 2 Rate (°C min^{-1})	5	6
Ramp 2 Temperature (°C)	230	295
Ramp 2 Hold Time (min)	0	0
Ramp 3 Rate (°C min^{-1})	10	25
Ramp 3 Temperature (°C)	310	325
Ramp 3 Hold Time (min)	6.50	0.50
Run Time (min)	67.50	18.30
GC Column	Rxi®-5Sil MS	Zebron ZB-SemiVolatiles
GC Column Dimensions	30 m x 0.25 mm i.d. x 0.25 µm film thickness	
Carrier Flow (mL min^{-1})	1.0	1.4
Transfer Line Temperature (°C)	320	325
Detector Temperature (°C)	230	230
Solvent Delay (min)	8.00	3.50

5.2.5 Statistical analysis

Statistical analysis was performed by statistical software packages including Microsoft Excel 2010 Version 14.0 (Microsoft Corporation, Washington, USA) and Minitab 16 Version 16.2.4 (Minitab Inc., Coventry, UK). Descriptive statistics e.g. mean, standard deviation and t-test were calculated using data analysis features of Microsoft Excel software. Multivariate statistics and more complicate graphical illustrations e.g. boxplot and cluster observation were performed in Minitab 16.

5.3 Results and Discussion

5.3.1 Particulate-bound PAHs concentrations

Ambient concentrations of 15 particulate-bound PAHs were measured to assess air quality related to pPAHs in the Bangkok Metropolitan Administration (BMA) during May 2013 – May 2014. PM_{10} sampling was carried out at roadside, urban background and industrial sites in urban areas of the BMA. The annual mean PM_{10} was highest at 56.44 µg m^{-3} at the roadside site, followed by the industrial site PM_{10} concentration at 50.69 µg m^{-3} and lowest at the urban background site at 39.80 µg m^{-3}. Total 15 PAHs in PM_{10} ranged from 1.09 – 13.10 ng m^{-3}, 1.49 – 9.39 ng m^{-3} and 0.77 – 5.20 ng m^{-3} at the roadside, industrial and urban background sites, respectively. Annual mean concentrations of BaP during the sampling period were found well below the EC limit value of 1 ng m^{-3} (EC, 2004). Annual mean BaP concentrations were 0.47 ± 0.39 ng m^{-3} at the roadside site, 0.35 ± 0.27 ng m^{-3} at the industrial site and 0.24 ± 0.19 ng m^{-3} at the urban background site. Although PM_{10} concentrations were significantly higher than WHO recommended guideline value of 20 µg m^{-3} for annual mean, levels of BaP in PM_{10} in 3 study areas were below the EC guideline value. Annual mean concentration and standard deviation of 15 PAHs measured in PM_{10} samples are illustrated in Figure 5.3.

Among 15 PAHs measured, PHE was the most abundant low molecular weight 3-ring PAHs found at all sampling sites while ACE was the least abundant of all pPAHs. Concentrations of 3-ring PAHs were likely to be underestimated due to their volatility which was as anticipated from the method development. The analysis of 16 PAHs in PM_{10} samples in Malaysia showed that only PHE and ANT were found while other 2-ring and 3-ring PAHs were not detected in particulate phase (Jamhari *et al.,* 2014). PAHs recovered from PM_{10} filter samples were mostly in the range from 4-ring to 6-ring PAHs with high molecular weights. The 3 most abundant PAHs in the BMA were BP, IP and BbF while BaP ranked fourth in all sampling sites. Although higher annual mean concentrations of PAHs were observed in the Thongsanit *et al.* (2003) study, their rankings were similar implying that compositions of roadside PAHs have not significantly changed in the past 10 years.

Mean concentrations of all PAHs except IP and DBA were highest at the roadside site indicating a strong influence from vehicular emissions. Annual IP and DBA mean concentrations were highest at the industrial site indicating source specific emissions. Annual mean concentrations of PM_{10} and PAHs were summarised in Table 5.5. The lowest pPAHs concentrations were found at the urban background site as expected. Traffic related emissions were the most prominent sources of pPAHs and most abundance PAHs were IP, BP, BbF and BaP which were consistent with studies previously conducted in the BMA (Kim Oanh *et al.,* 2000; Thongsanit *et al.,* 2003). In addition, results from previous studies showed high concentrations of benzo[e]pyrene and coronene at roadside sites. BP, coronene and PHE were markers for motor vehicle emissions (Ravindra *et al.,* 2008). In this study, BP and PHE concentrations were significantly higher at the roadside than other sites indicating traffic emissions.

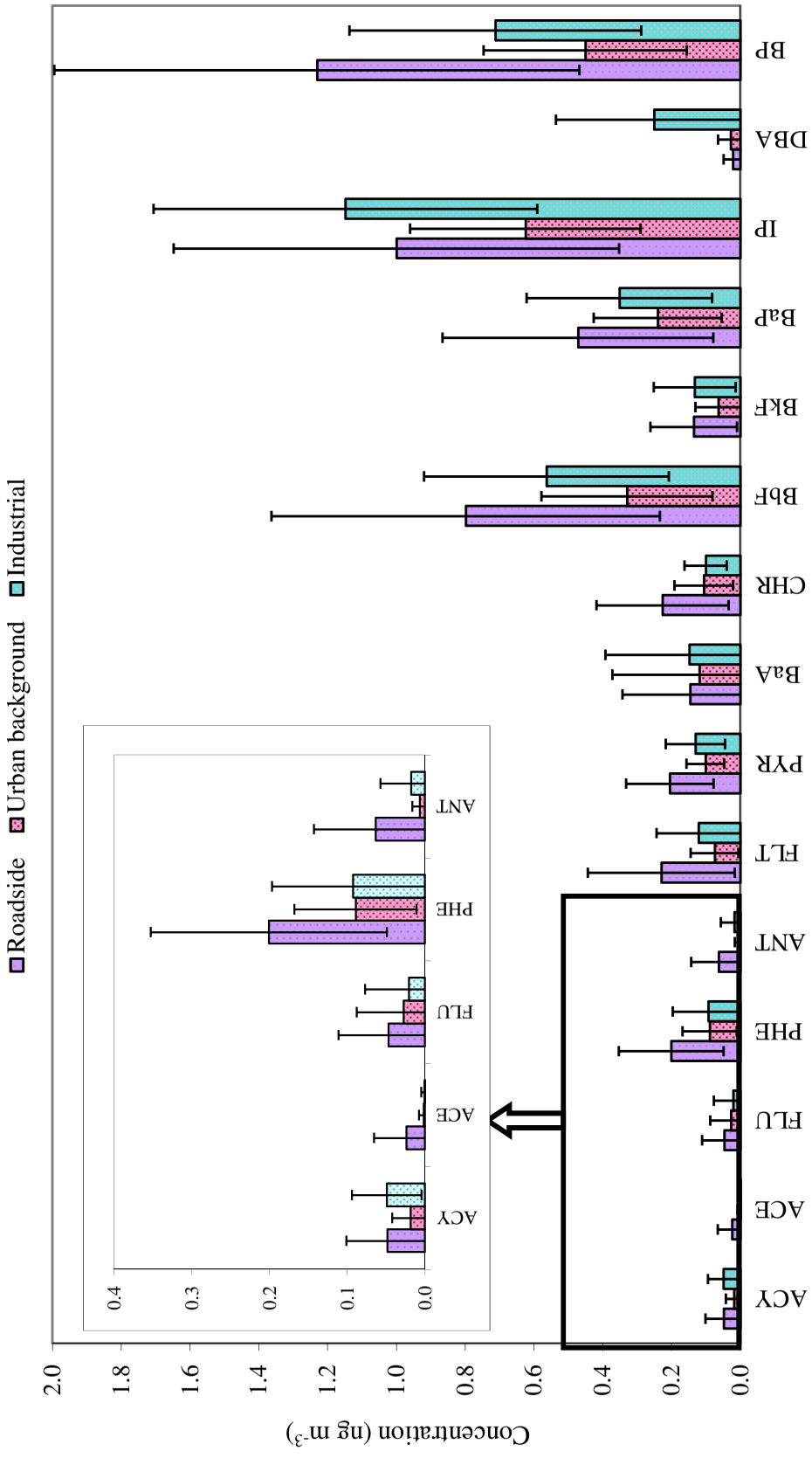

Figure 5.3 Comparison of annual mean pPAH concentrations (±standard deviation) at roadside, urban background and industrial sites.

Table 5.5 Annual mean concentrations of PM_{10} (µg m^{-3}), PAHs, total carcinogenic PAHs (∑7PAHs: BaA, CHR, BbF, BkF, BaP, IP and DBA) and total PAHs (∑15PAHs).

Pollutant	Annual mean concentration (ng m^{-3})											
	Roadside (n = 43)				Industrial (n = 37)				Urban background (n = 46)			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
PM_{10} (µg m^{-3})	26.6	162.6	56.4	27.3	18.4	156.4	51.0	31.1	18.9	124.2	39.8	22.2
ACY	<QL	0.18	0.05	0.05	<QL	0.15	0.05	0.04	<QL	0.14	0.02	0.02
ACE	<QL	0.14	0.02	0.04	<QL	0.02	0.001	0.004	<QL	0.03	0.001	0.01
FLU	<QL	0.38	0.05	0.06	<QL	0.33	0.02	0.06	<QL	0.35	0.03	0.06
PHE	0.03	0.70	0.20	0.15	0.02	0.60	0.09	0.10	0.02	0.40	0.09	0.08
ANT	<QL	0.28	0.06	0.08	<QL	0.23	0.02	0.04	<QL	0.04	0.01	0.01
FLT	0.03	0.81	0.23	0.21	<QL	0.62	0.12	0.12	<QL	0.40	0.07	0.07
PYR	0.06	0.54	0.20	0.13	<QL	0.40	0.13	0.09	0.04	0.30	0.10	0.06
BaA	<QL	0.98	0. 15	0.20	<QL	0.94	0.15	0.24	<QL	0.97	0.12	0.25
CHR	0.03	0.87	0.23	0.19	<QL	0.19	0.10	0.06	<QL	0.36	0.11	0.09

Pollutant	Annual mean concentration (ng m^{-3})											
	Roadside (n = 43)				Industrial (n = 37)				Urban background (n = 46)			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
BbF	<QL	2.38	0.80	0.56	0.13	1.63	0.56	0.36	<QL	0.81	0.33	0.25
BkF	<QL	0.43	0.14	0.13	<QL	0.46	0.13	0.12	<QL	0.25	0.06	0.07
BaP	0.05	1.74	0.47	0.39	0.11	1.56	0.35	0.27	<QL	1.15	0.24	0.19
IP	<QL	2.88	1.00	0.65	0.60	2.82	1.15	0.56	<QL	1.97	0.62	0.34
DBA	<QL	0.08	0.02	0.03	<QL	0.95	0.25	0.28	<QL	0.19	0.03	0.04
BP	<QL	3.98	1.23	0.76	<QL	2.00	0.71	0.42	0.08	1.27	0.45	0.30
∑7PAHs	0.58	7.00	2.80	1.60	1.11	6.48	2.69	1.42	0.36	3.73	1.51	0.79
∑15PAHs	1.09	13.10	4.85	2.74	1.49	9.39	3.84	2.01	0.77	5.20	2.28	1.16

5.3.2 Composition of pPAHs

Concentrations of PM_{10}, individual PAHs and compositions of pPAHs categorised by number of rings were illustrated in Figure 5.4. Although PAHs concentrations at the roadside site were significantly higher than those at the urban background site, the percentage compositions of both sites were similar. This implied that prevalent sources of PAHs at the urban background site could be substantially sourced from traffic emissions. Photochemical reaction and dilution of pPAHs may occur during the transportation of PM_{10} from emission sources to the sampling site. This inferred that the profile of pPAH at the urban background site should be less prominent compared with other sites.

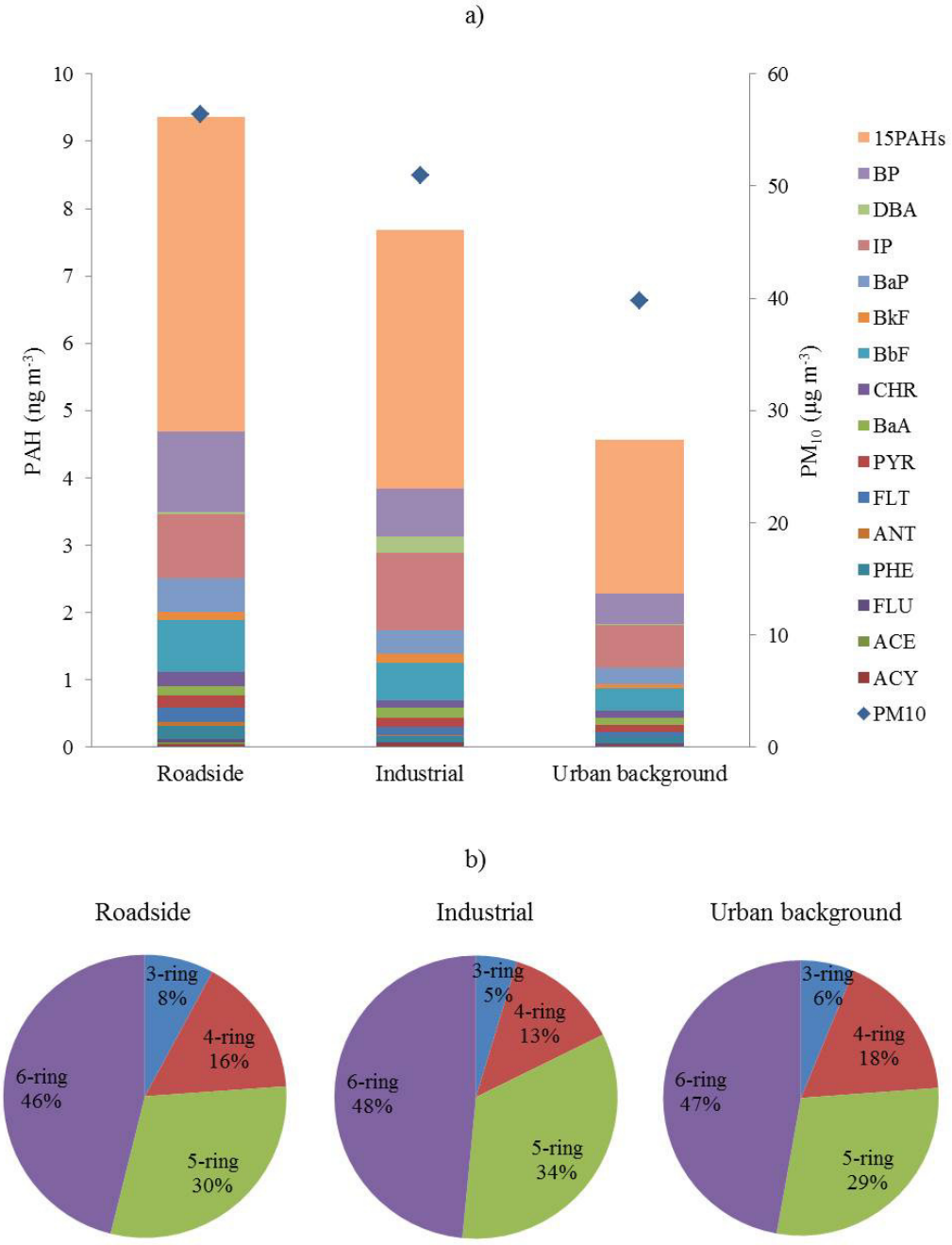

Figure 5.4 PM_{10} and PAHs composition at the roadside, industrial and urban background sites shown as a) annual mean concentrations and b) percentage of total PAHs weight.

Mass distribution of pPAH grouping by number of rings showed that 6-ring PAHs (IP and BP) are most abundant and contributed to 44 – 50% weight of total 15 PAHs weight in PM_{10}. Carcinogenic PAHs found at all sampling sites were major

compositions of pPAH as shown in Figure 5.5. The sum of 7 carcinogenic PAHs including BaA, BbF, BkF, BaP, CHR, DBA and IP accounted for 60%, 66% and 70% of total PAHs at the roadside, urban background and industrial site, respectively. BaP contributed to approximately 9 – 11% of total PAHs weight. PM_{10}-bound PAHs were predominantly high molecular weight 5-ring and 6-ring PAHs that were main contributors to the carcinogenicity of pPAHs. Thus, exposure to high ambient PM_{10} may result in the high exposure to carcinogenic PAHs. It is important to understand the chemical composition of pPAHs in order to conduct the appropriate health risk assessment.

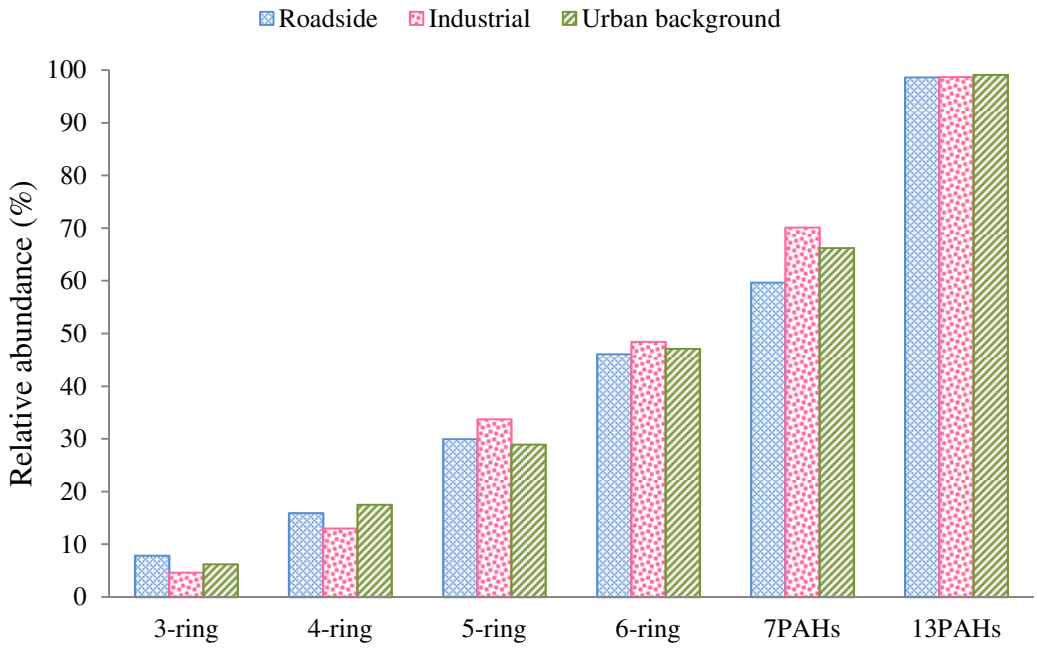

Figure 5.5 Relative abundance of pPAHs (% of total PAHs) at 3 sampling sites presented as groups of PAHs with different numbers of rings, sum of carcinogenic PAHs and sum of 13 PAHs used to calculate the exposure risk according to BaP toxic equivalency factors (Larsen and Larsen, 1992).

In general, concentration of annual mean PM_{10}, total PAHs and BaP were highest at the roadside site where vehicle emission was the most prevalent source. Annual mean PM_{10} concentration was 56.4 ± 27.3 µg m^{-3}, 51.0 ± 31.1 µg m^{-3} and 39.8 ± 22.2 µg m^{-3} at the roadside, industrial and urban background sites, which were approximately 2.8, 2.5 and 2.0 times higher than WHO annual guideline values.

Levels of PM_{10} in the BMA were comparable to those measured during June to September 2010 in urban, industrial and semi-urban areas of Malaysia which ranged from 31.86 ± 4.1 μg m^{-3} to 51.52 ± 19.9 μg m^{-3} (Jamhari *et al.,* 2014). Mean PM_{10} concentrations at roadside and industrial sites breached the Thailand National Ambient Air Quality Standards of 50 μg m^{-3} for annual mean. Relatively high ambient PM_{10} concentrations compared with the WHO guideline value underlined the need for health risk assessment as the exposure to ambient particulate matter is unavoidable.

In contrast to the previous long-term measurements conducted at the same roadside site, concentrations of PM_{10} and BaP in this study were significantly lower than those reported by Thongsanit *et al.* (2003). PM_{10} mean concentration measured at the roadside site (Dindaeng) during November 1999 to November 2000 was 72 ± 27 μg m^{-3} and the mean BaP concentration was 4 ng m^{-3}. The reduction in both PM_{10} and PAHs roadside emissions might be the result of vehicle emission standards that have changed from the Euro II to Euro IV over the past 10 years (PCD, 2016). Thailand emission standards for motor vehicles comply with these EC standards; however, they are usually enforced at the later stage due to the age of in-use vehicles. Concentrations of BaP in the industrial area were comparable with those found in Malaysia industrial areas while the urban background concentrations in the BMA were approximately three times higher than in the urban area of Kuala Lumpur (Jamhari *et al.,* 2014). Concentrations of PM_{10} and BaP measured in different cities are shown in Table 5.6.

In order to reduce the complications from 27 parameters measured at each sampling site, cluster analysis was performed by Minitab 16 statistical software. Similarities between variables were determined by correlation coefficients and distances between clusters were calculated using the average linkage. Hierarchical cluster analysis of all parameters including meteorological data, concentrations of individual PAHs and groups of PAHs were illustrated with dendrograms in Figure 5.6, 5.7 and 5.8. Two closest clusters were the most similar variables connected by the horizontal dendrogram line at the corresponding similarity level.

Table 5.6 Concentrations of PM_{10} ($\mu g\ m^{-3}$) and BaP ($ng\ m^{-3}$) in different cities.

Country	Sampling area (type)	Sampling duration	PM_{10} ($\mu g\ m^{-3}$)	BaP ($ng\ m^{-3}$)	Reference
Argentina	Buanos Aires	13 August – 15 September 2008	61 ± 49	1.0 ± 0.1	Vasconcellos *et al.* (2011)
Brazil	Sãl Paolo	7 – 29 August 2008	64 ± 19	2.2 ± 2.1	Vasconcellos *et al.* (2011)
Chile	Santiago (urban)	7 – 9 July 2002	129.4 ± 28.1	5.28	Del Rosario Sienra *et al.*
		27 September – 7 October 2002	64.2 ± 17.1	0.93	(2005)
Colombia	Bogotá	24 November – 9 December 2008	47 ± 12	0.7 ± 0.2	Vasconcellos *et al.* (2011)
Finland	Virolahti (background)	January 2007 – September 2008	9.91	0.23	Vestenius *et al.* (2011)
India	Raipur region	January – December 2006	115 ± 36	0.04 - 29.7[a]	Giri *et al.* (2013)
Italy	Milan	Winter 2007	92 ± 12	1.4 ± 0.33	Belis *et al.* (2011)
Italy	Milan	Winter 2009	85 ± 16	1.2 ± 0.35	Belis *et al.* (2011)
Mexico	Mèxico City	October 1998 – October 1999	-	0.69 ± 0.41	Amador-Muñoz *et al.* (2010)
Malaysia	Kuala Lumpur (urban)	June – September 2010	51.52 ± 19.9	0.11 ± 0.03	Jamhari *et al.* (2014)

Country	Sampling area (type)	Sampling duration	PM_{10} (μg m^{-3})	BaP (ng m^{-3})	Reference
Malaysia	Petaling Jaya (industrial)	June – September 2010	31.86 ± 4.1	0.32 ± 0.13	Jamhari *et al.* (2014)
Malaysia	Bangi (semi-urban)	June – September 2010	47.95 ± 8.0	0.11 ± 0.02	Jamhari *et al.* (2014)
Spain	Zaragoza	February 2010 – January 2011	34.4 ± 29.0	0.09 ± 0.11	Callén *et al.* (2013)
Thailand	Chiang Mai (urban)	June – November 2004	40.0 ± 14.0	0.99 ± 0.31	Chantara and Sangchan (2009)
	Chiang Mai (background)	June – November 2004	29.6 ± 13.1	0.92 ± 0.46	
	Chiang Mai (roadside)	June – November 2004	88.8 ± 21.6	1.70 ± 0.55	
	Chiang Mai (roadside)	June – November 2004	106.8 ± 32.0	1.64 ± 0.41	
Thailand	Bangkok (roadside)	November 2002 – April 2003	N/A	1.30 ± 0.72	Norramit *et al.* (2005)
Thailand	Bangkok (roadside)	November 1999 – November 2000	76 and 72	5 and 4	Thongsanit *et al.* (2003)
Thailand	Bangkok (roadside)	2 May 2013 – 27 May 2014	56.4 ± 27.3	0.47 ± 0.39	This study
Thailand	Bangkok (urban background)	2 May 2013 – 15 May 2014	39.8 ± 22.2	0.24 ± 0.19	This study
Thailand	Nonthaburi (industrial)	2 May 2013 – 27 May 2014	50.1 ± 31.1	0.35 ± 0.27	This study

[a] Concentration reported as a range

N/A: not available

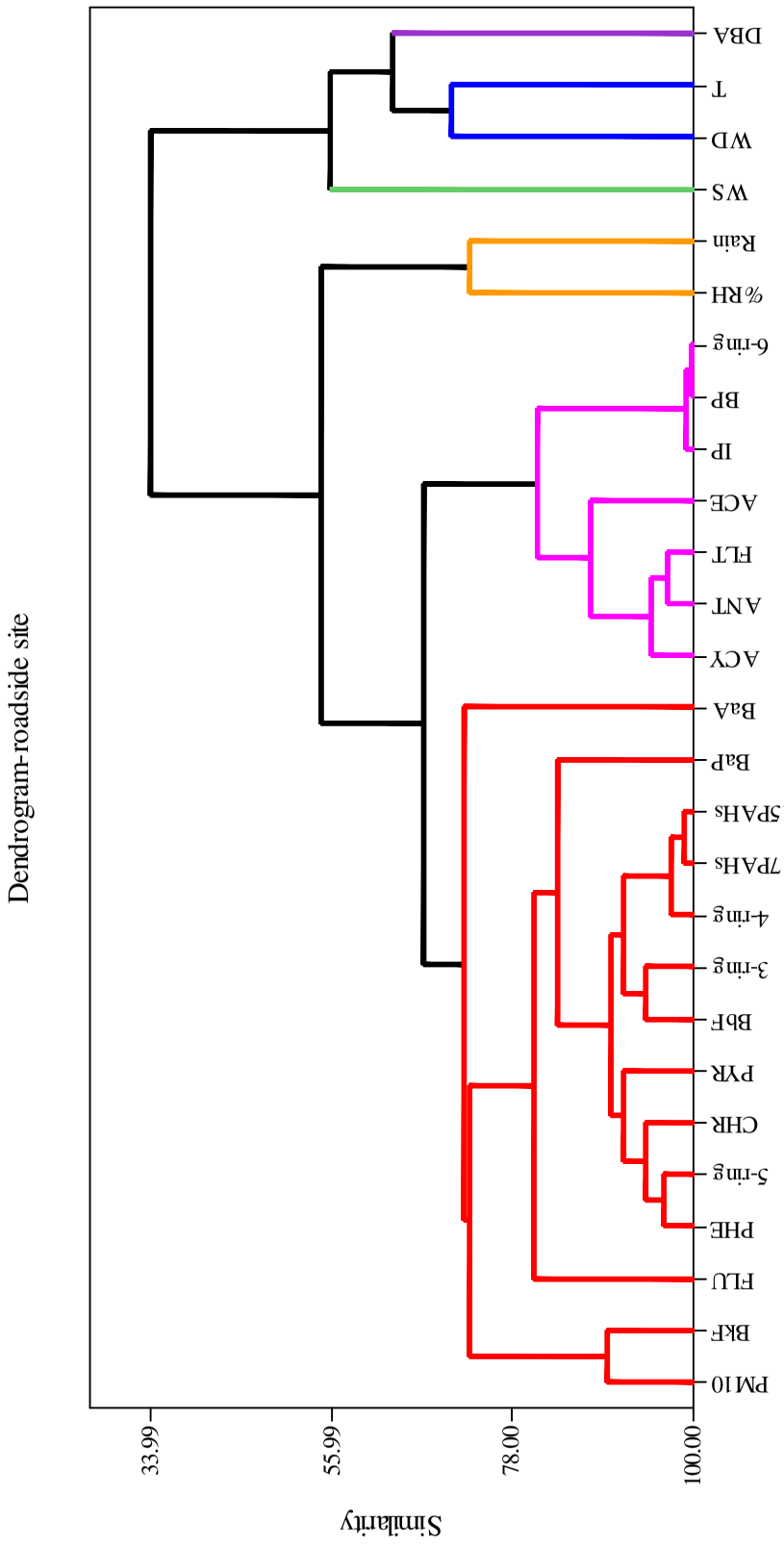

Figure 5.6 A dendrogram of cluster observation of all parameters at the roadside site showing high similarities (close to 100) of PAHs while most meteorological parameters were clustered together with less similarity.

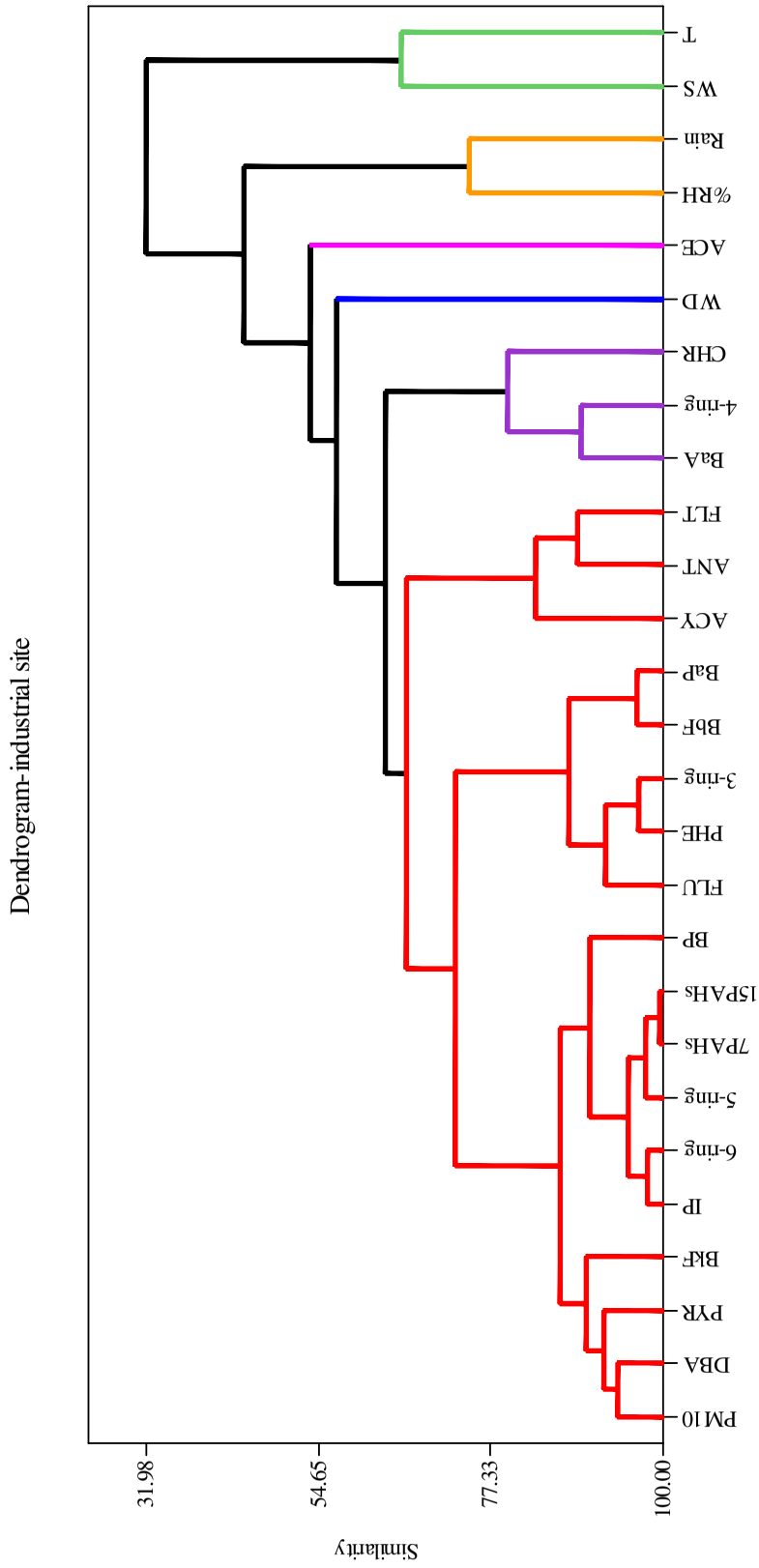

Figure 5.7 A dendrogram of cluster observation of all parameters at the industrial site showing high similarities of PAHs grouped by number of rings.

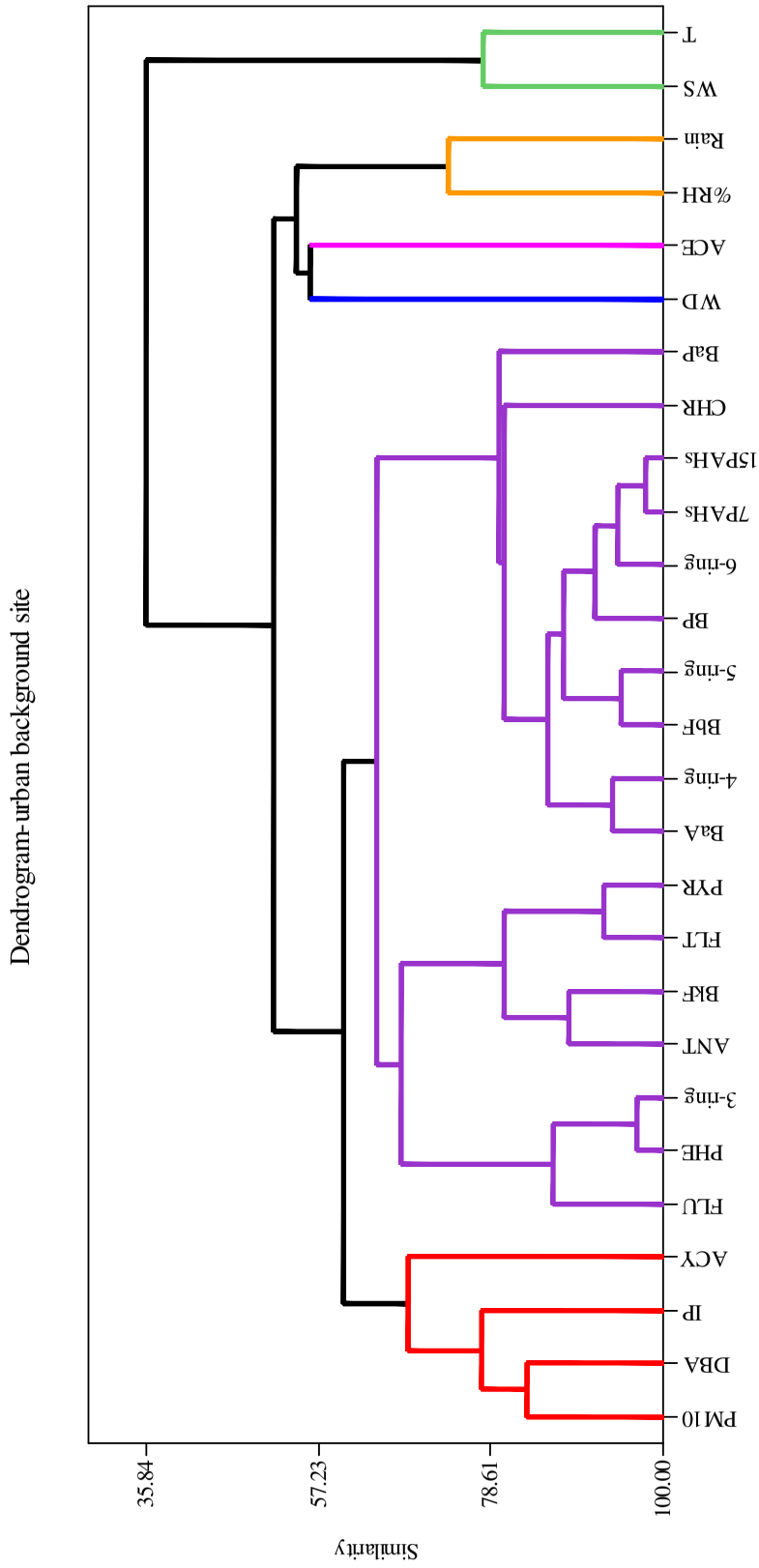

Figure 5.8 A dendrogram of cluster observation of all parameters at the urban background site showing similarities among PAHs while meteorological parameters tend to cluster together.

The roadside site dendrogram showed two clusters with very high similarity (>95). One of the clusters consisted of 6-ring PAHs, BP and IP, the other cluster consisted of 4-ring PAHs, 7 PAHs and 15 PAHs. BaP joined together with the cluster containing PHE, CHR and PYR those also exhibited good linear correlation. The high similarity (>91) between PHE and PYR supported the traffic profile measured in Birmingham which indicated that PHE and PYR were indicators of traffic source (Alam *et al.*, 2013). The industrial site dendrogram revealed slightly different patterns while high molecular weights including 5-ring PAHs, 6-ring PAHs, 7 PAHs and 15 PAHs, IP and BP were clustered together at high similarity (>90). BP and IP were the predominant PAHs at the industrial site. For the urban background site, the cluster of high molecular weight PAHs including 7 PAHs, 15 PAHs, 6-ring PAHs and BP; 5-ring PAHs and BbF; 4-ring PAHs and BaA were observed at a lower similarity (>86) compared with the other sites. This might be the result of distance from sources where both roadside and industrial sites were located close to emission sources, whereas the urban background site had no prominent nearby sources.

Results of hierarchical cluster analysis inferred that pPAHs were more likely to distribute in the smaller size particulate matter than PM_{10}. PAHs from traffic emissions including PHE, PYR and BaP observed in the same cluster of the roadside dendrogram showed moderate linear correlations. Similarly, BaP and BbF clustered with a high similarity at the industrial site showed a high linear correlation.

All dendrograms showed moderate similarities among meteorological parameters. Relative humidity was the closest variable to the rainfall while wind speed clustered with temperature. PM_{10} was not closely associated with most high molecular weight PAHs which implied that pPAHs distributed mostly in high molecular weight range were associated with smaller size particles. A study on size-segregation of PM and PAHs in Bangkok also found that more than 97% of PAHs load were from ultrafine particles ($PM_{<0.95}$) and fine particles ($PM_{1.5}$) composed 60% of PM_{10} weight (Thongsanit *et al.,* 2003).

Pearson correlation coefficients between pollutants and meteorological parameters were calculated and displayed in Table 5.7, 5.8 and 5.9 for the roadside, industrial and urban background sites, respectively. All meteorological factors were not positively correlated with pollutants but some showed negative correlations, i.e. WD and PYR (r^2 = -0.66) at the roadside site, T and PYR (r^2 = -0.65) at the industrial site, WS and ANT (r^2 = 0.65) and WS and PYR (r^2 = -0.68) at the urban background site. At the industrial site, high correlations were observed between PM_{10} and PHE (r^2 = 0.86) as well as some high molecular weight PAHs including BkF (r^2 = 0.83), IP (r^2 = 0.83), DBA (r^2 = 0.88) and BP (r^2 = 0.68). These pollutants also clustered closely in the dendrogram showing high similarity (86.47). At the roadside site, BP and IP, indicators of fuel combustion, were highly correlated (r^2 = 0.98), thus strongly supporting the cluster analysis result (similarity = 99.20). Combination of cluster observations and correlation coefficients showed some source specific characteristics of pPAHs particularly at roadside and industrial sites.

Table 5.7 Correlation coefficients between pollutants and meteorological parameters at the roadside site.

	PM_{10}	WS	WD	T	%RH	Rain	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IP	DBA	BP	3-ring	4-ring	5-ring	6-ring	7PAHs	15PAHs
PM_{10}	1																										
WS	-0.178	1																									
WD	-0.540	0.084	1																								
T	-0.485	0.057	0.398	1																							
%RH	-0.180	-0.493	-0.226	-0.250	1																						
Rain	-0.038	-0.089	-0.326	-0.211	0.461	1																					
ACY	-0.033	-0.207	0.020	-0.148	0.160	0.003	1																				
ACE	-0.272	-0.145	0.198	-0.158	0.300	0.107	**0.731**	1																			
FLU	0.363	-0.270	-0.285	-0.413	0.161	0.140	-0.008	-0.030	1																		
PHE	**0.657**	-0.242	-0.547	-0.522	0.128	0.091	0.076	-0.114	**0.842**	1																	
ANT	-0.070	-0.182	0.039	-0.192	0.208	0.069	**0.916**	**0.825**	0.024	0.086	1																
FLT	0.133	-0.163	-0.098	-0.327	0.112	0.026	**0.877**	**0.693**	0.137	0.311	**0.935**	1															
PYR	**0.736**	-0.194	**-0.662**	-0.497	0.083	0.130	0.144	-0.107	0.492	**0.860**	0.134	0.390	1														
BaA	0.418	-0.249	-0.514	-0.292	0.190	0.154	0.362	-0.027	0.134	0.350	0.080	0.178	0.532	1													
CHR	0.410	-0.315	-0.580	-0.369	0.295	0.213	0.267	0.033	**0.693**	**0.851**	0.226	0.437	**0.793**	0.466	1												
BbF	0.497	-0.313	-0.473	-0.460	0.249	0.114	0.549	0.282	**0.654**	**0.767**	0.491	0.600	**0.658**	0.552	**0.785**	1											
BkF	**0.790**	0.020	-0.558	-0.369	-0.130	0.032	-0.172	-0.378	0.294	**0.602**	-0.180	-0.046	**0.701**	0.345	0.283	0.364	1										
BaP	0.411	-0.271	-0.377	-0.296	0.081	0.023	-0.034	-0.195	**0.615**	**0.775**	-0.068	0.212	**0.712**	0.235	**0.825**	0.459	0.247	1									
IP	0.383	-0.187	-0.158	-0.363	0.011	-0.144	**0.620**	0.409	-0.015	0.333	0.586	**0.762**	0.568	0.383	0.446	0.492	0.119	0.444	1								
DBA	-0.240	0.100	0.264	0.270	0.067	0.166	-0.358	-0.047	-0.140	-0.357	-0.289	-0.494	-0.382	-0.213	-0.481	-0.369	0.017	-0.447	-0.537	1							
BP	0.387	-0.238	-0.234	-0.373	0.118	-0.065	**0.684**	0.465	0.017	0.362	**0.652**	**0.791**	**0.604**	0.482	0.487	0.590	0.170	0.384	**0.975**	-0.487	1						
3-ring	0.388	-0.317	-0.331	-0.503	0.249	0.122	**0.619**	0.468	**0.714**	**0.788**	**0.654**	**0.762**	**0.654**	0.320	**0.769**	**0.884**	0.265	0.527	0.541	-0.397	**0.606**	1					
4-ring	0.508	-0.303	-0.570	-0.469	0.231	0.167	0.589	0.244	0.451	**0.733**	0.496	**0.686**	**0.840**	**0.704**	**0.858**	**0.846**	0.362	**0.611**	**0.711**	-0.518	**0.780**	**0.820**	1				
5-ring	**0.618**	-0.321	-0.552	-0.479	0.182	0.095	0.307	0.039	**0.744**	**0.929**	0.254	0.465	**0.843**	0.510	**0.913**	**0.902**	0.496	**0.776**	0.523	-0.410	0.569	**0.842**	**0.866**	1			
6-ring	0.387	-0.216	-0.200	-0.371	0.069	-0.102	**0.659**	0.442	0.002	0.351	**0.626**	**0.782**	0.591	0.439	0.471	0.549	0.147	0.414	**0.993**	-0.513	**0.995**	**0.580**	**0.753**	0.551	1		
7PAHs	0.591	-0.318	-0.497	-0.487	0.162	0.038	0.494	0.187	0.497	**0.784**	0.412	**0.635**	**0.848**	**0.611**	**0.853**	**0.851**	0.393	**0.728**	**0.790**	-0.524	**0.821**	**0.808**	**0.948**	**0.927**	**0.812**	1	
15PAHs	0.534	-0.304	-0.425	-0.485	0.164	0.024	**0.614**	0.333	0.398	**0.699**	0.565	**0.761**	**0.803**	0.560	**0.779**	**0.824**	0.331	**0.632**	**0.870**	-0.536	**0.906**	**0.827**	**0.942**	**0.856**	**0.895**	**0.979**	1

Table 5.8 Correlation coefficients between pollutants and meteorological parameters at the industrial site.

	PM_{10}	WS	WD	T	%RH	Rain	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IP	DBA	BP	3-ring	4-ring	5-ring	6-ring	7PAHs	15PAHs
PM_{10}	1																										
WS	-0.380	1																									
WD	0.190	-0.339	1																								
T	-0.498	0.303	-0.081	1																							
%RH	-0.290	-0.433	-0.006	-0.094	1																						
Rain	-0.257	0.089	-0.315	-0.050	0.488	1																					
ACY	**0.646**	-0.518	0.101	-0.520	0.092	-0.004	1																				
ACE	0.141	-0.212	-0.068	-0.062	0.132	-0.078	0.051	1																			
FLU	0.027	-0.126	-0.092	-0.172	0.185	-0.053	-0.055	0.217	1																		
PHE	0.350	-0.206	-0.093	-0.399	0.049	-0.114	0.250	**0.077**	**0.892**	1																	
ANT	0.141	-0.318	0.213	-0.066	-0.024	-0.134	**0.617**	0.046	-0.030	0.107	1																
FLT	0.445	-0.351	0.115	-0.450	-0.254	-0.260	**0.716**	**0.092**	-0.054	0.241	**0.774**	1															
PYR	**0.865**	-0.339	0.043	**-0.646**	-0.201	-0.240	0.563	0.175	0.246	0.576	0.020	0.458	1														
BaA	-0.009	-0.450	0.015	-0.175	0.371	0.076	0.109	-0.031	-0.097	-0.086	-0.124	-0.019	0.037	1													
CHR	0.296	-0.449	0.226	-0.143	-0.079	-0.303	0.338	0.084	-0.163	-0.006	0.251	0.492	0.344	0.435	1												
BbF	0.492	-0.509	0.119	-0.259	0.140	-0.216	0.340	0.082	**0.608**	**0.759**	0.145	0.264	**0.624**	0.224	0.481	1											
BkF	**0.834**	-0.360	0.134	-0.347	-0.061	-0.120	0.566	0.133	-0.029	0.279	0.112	0.318	**0.794**	-0.106	0.137	0.474	1										
BaP	0.276	-0.351	0.066	-0.190	0.191	-0.144	0.147	-0.023	**0.783**	**0.853**	0.043	0.099	0.449	0.150	0.263	**0.929**	0.261	1									
IP	**0.834**	-0.502	0.215	-0.423	-0.021	-0.183	0.567	0.005	0.187	0.518	0.171	0.419	**0.821**	0.073	0.374	**0.746**	**0.851**	0.594	1								
DBA	**0.879**	-0.283	0.177	-0.490	-0.300	-0.361	**0.604**	0.112	0.052	0.345	0.168	0.426	**0.824**	-0.089	0.176	0.382	**0.768**	0.170	**0.692**	1							
BP	**0.684**	**-0.631**	0.404	-0.263	-0.029	-0.305	0.555	0.012	-0.146	0.131	0.295	0.482	0.596	0.354	**0.786**	**0.636**	0.594	0.383	**0.788**	0.533	1						
3-ring	0.401	-0.355	-0.013	-0.423	0.105	-0.114	0.506	0.155	**0.803**	**0.933**	0.420	0.465	0.552	-0.079	0.085	**0.738**	0.317	**0.774**	0.531	0.401	0.230	1					
4-ring	0.419	**-0.607**	0.102	-0.465	0.112	-0.150	0.530	0.069	-0.055	0.167	0.235	0.541	0.498	**0.785**	**0.743**	0.492	0.259	0.299	0.470	0.324	**0.707**	0.261	1				
5-ring	**0.723**	-0.488	0.153	-0.391	0.017	-0.281	0.483	0.085	0.530	**0.763**	0.150	0.338	**0.812**	0.100	0.372	**0.932**	**0.696**	**0.821**	**0.874**	**0.674**	**0.667**	**0.753**	0.458	1			
6-ring	**0.812**	-0.592	0.316	-0.376	-0.026	-0.251	0.594	0.009	0.045	0.370	0.237	0.471	**0.765**	0.205	0.583	**0.737**	**0.782**	0.532	**0.960**	**0.659**	**0.929**	0.423	**0.605**	**0.829**	1		
7PAHs	**0.763**	-0.584	0.187	-0.433	0.065	-0.237	0.540	0.050	0.360	**0.635**	0.145	0.381	**0.820**	0.278	0.483	**0.898**	**0.730**	**0.752**	**0.934**	**0.659**	**0.796**	**0.640**	**0.620**	**0.963**	**0.924**	1	
15PAHs	**0.783**	**-0.617**	0.226	-0.458	0.025	-0.270	**0.611**	0.065	0.303	0.599	0.250	0.493	**0.825**	0.264	0.559	**0.877**	**0.722**	**0.706**	**0.934**	**0.675**	**0.848**	**0.642**	**0.665**	**0.943**	**0.947**	**0.989**	1

Table 5.9 Correlation coefficients between pollutants and meteorological parameters at the urban background site.

	PM_{10}	WS	WD	T	%RH	Rain	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IP	DBA	BP	3-ring	4-ring	5-ring	6-ring	7PAHs	15PAHs
PM_{10}	1																										
WS	-0.420	1																									
WD	-0.091	0.112	1																								
T	-0.351	0.562	0.117	1																							
%RH	-0.286	-0.237	0.141	-0.411	1																						
Rain	0.016	-0.305	0.017	-0.218	0.460	1																					
ACY	0.301	-0.058	-0.035	0.011	-0.026	-0.052	1																				
ACE	-0.129	0.068	0.124	0.009	0.179	0.027	-0.159	1																			
FLU	0.038	-0.227	-0.002	0.060	0.050	0.232	-0.138	-0.068	1																		
PHE	0.577	-0.362	-0.055	-0.211	-0.261	0.012	0.124	-0.096	**0.631**	1																	
ANT	**0.658**	**-0.650**	-0.033	-0.360	0.066	0.216	0.060	-0.138	0.153	0.346	1																
FLT	0.486	-0.567	0.011	-0.424	-0.120	0.217	0.050	0.039	0.207	0.512	**0.633**	1															
PYR	**0.757**	**-0.678**	-0.075	-0.443	-0.150	0.137	0.237	-0.077	0.337	**0.769**	**0.735**	**0.855**	1														
BaA	-0.069	-0.121	0.165	-0.225	0.277	0.016	0.261	0.259	-0.081	-0.081	-0.095	0.202	0.100	1													
CHR	0.028	-0.342	0.141	-0.196	0.111	0.174	-0.065	0.262	0.348	0.380	0.211	0.591	0.462	0.472	1												
BbF	0.165	-0.461	0.076	-0.414	0.281	0.207	0.102	0.243	-0.092	-0.007	0.431	**0.616**	0.456	**0.631**	**0.668**	1											
BkF	0.373	-0.504	-0.147	-0.162	-0.054	0.269	0.052	-0.132	0.045	0.150	**0.764**	0.540	0.520	-0.158	0.092	0.382	1										
BaP	0.060	-0.215	0.096	-0.198	0.140	0.185	0.046	0.187	0.567	0.492	0.015	0.314	0.407	0.433	0.500	0.403	-0.070	1									
IP	0.520	0.020	-0.156	-0.206	-0.219	-0.247	0.436	-0.003	-0.390	0.088	0.053	0.043	0.237	0.323	-0.159	0.206	0.008	0.120	1								
DBA	**0.664**	-0.367	-0.275	-0.289	-0.268	-0.055	0.368	-0.137	-0.089	0.435	0.381	0.207	0.525	-0.183	-0.157	0.050	0.416	0.001	0.581	1							
BP	0.240	-0.343	0.170	-0.325	0.161	0.166	0.123	0.198	0.372	0.507	0.225	0.490	0.561	**0.608**	**0.763**	**0.663**	0.063	**0.826**	0.272	0.141	1						
3-ring	0.461	-0.377	-0.037	-0.123	-0.126	0.125	0.187	-0.083	**0.825**	**0.937**	0.356	0.460	**0.711**	-0.035	0.405	0.014	0.170	0.576	-0.046	0.308	0.524	1					
4-ring	0.170	-0.384	0.142	-0.358	0.178	0.100	0.216	0.242	0.118	0.252	0.220	**0.612**	0.503	**0.876**	**0.761**	**0.797**	0.096	0.551	0.236	-0.045	**0.796**	0.272	1				
5-ring	0.259	-0.519	0.043	-0.415	0.212	0.266	0.131	0.208	0.210	0.296	0.446	**0.651**	**0.621**	0.562	**0.663**	**0.896**	0.418	**0.719**	0.244	0.197	**0.837**	0.340	**0.780**	1			
6-ring	0.487	-0.185	-0.006	-0.326	-0.053	-0.069	0.362	0.114	-0.042	0.356	0.167	0.316	0.487	0.572	0.341	**0.526**	0.042	0.564	**0.825**	0.470	**0.768**	0.277	**0.624**	**0.653**	1		
7PAHs	0.331	-0.321	0.023	-0.385	0.111	0.047	0.327	0.213	-0.050	0.199	0.236	0.470	0.491	**0.787**	0.521	**0.806**	0.170	**0.601**	**0.632**	0.269	**0.809**	0.182	**0.850**	**0.852**	**0.895**	1	
15PAHs	0.403	-0.415	0.051	-0.405	0.088	0.105	0.289	0.185	0.182	0.437	0.331	0.597	**0.655**	**0.703**	**0.651**	**0.777**	0.208	**0.722**	0.508	0.291	**0.919**	0.431	**0.872**	**0.899**	**0.877**	**0.957**	1

Relatively high linear correlations were observed between BaP vs. PHE, PYR and CHR at the roadside area where PAHs concentrations varied considerably. At the industrial site where most PHE and FLU concentrations distributed in lower concentrations ranged below 0.02 ng m^{-3}, maximum concentrations of BaP, PHE, FLU and BbF were found on 7th July 2013 suggesting the similar source origin. High BbF, BaP and IP concentrations were found in the sample while PM_{10} concentration was relatively low (21.2 µg m^{-3}) emphasising the significance of source type instead of the particulate amount. A strong linear correlation was found between BaP vs. BbF at the industrial area indicated a consistent emission source of both PAHs. Linear plots of BaP vs. selected PAHs at the roadside and industrial sites are illustrated in Figure 5.9.

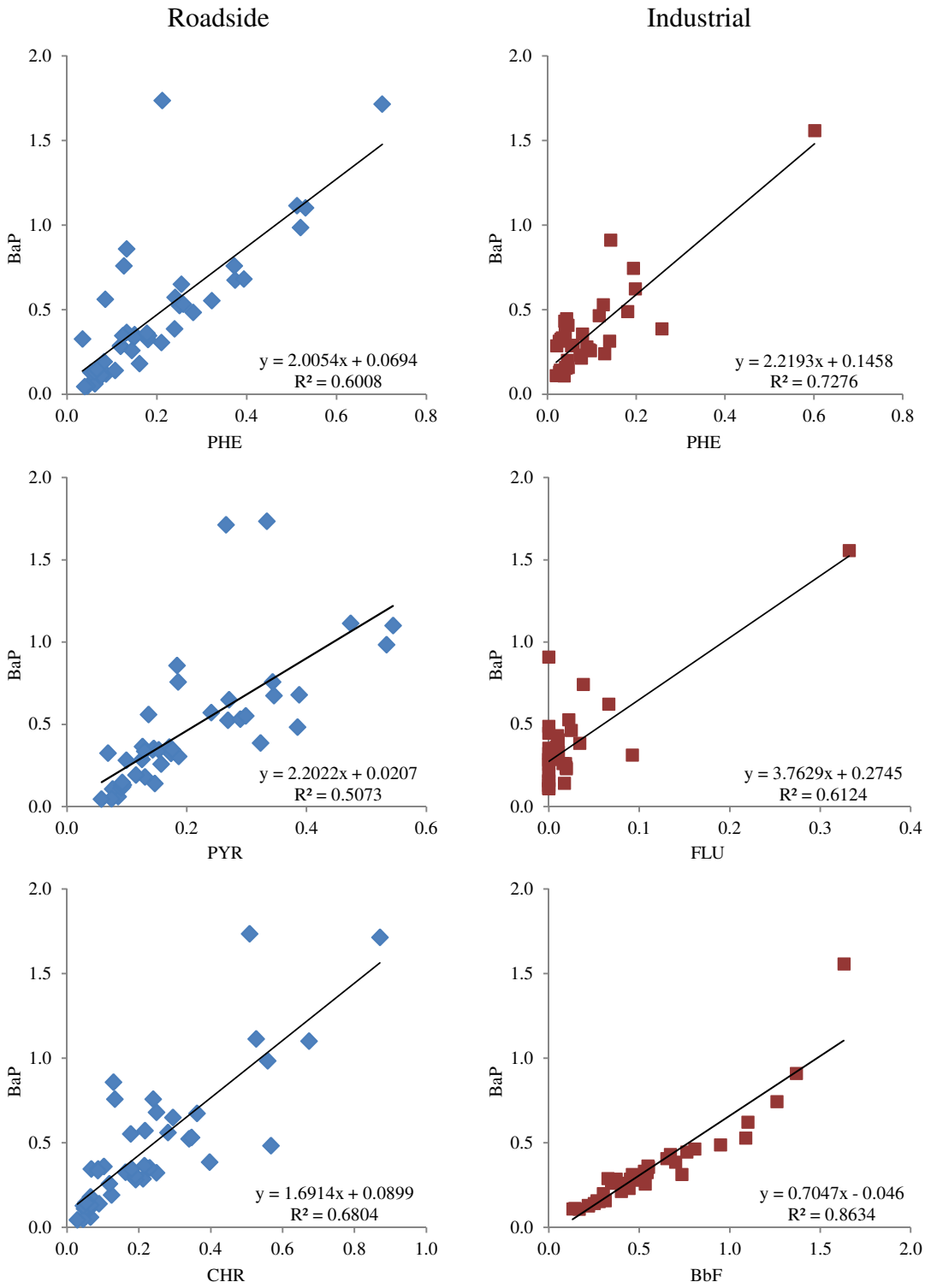

Figure 5.9 Linear plots between daily mean concentrations (ng m^{-3}) of BaP vs. PHE, PYR and CHR at the roadside site and BaP vs. PHE, FLU and BbF at the industrial site.

5.4 Conclusion

This study utilised PM_{10} filter samples collected and archived by the Pollution Control Department Thailand to investigate consistent long-term pPAHs concentrations. Fifteen PM_{10}-bound PAHs were measured at 3 ambient air monitoring sites in the Bangkok Metropolitan Administration representing the roadside, industrial and urban background environments. Methods for chemical characterisation of pPAHs were successfully applied for the analysis of PAHs in PM_{10} taking into account the proper sample preservation to maintain sample integrity. PM_{10} samples used in this study were preserved under -20°C after the analysis of PM_{10} masses. Samples were kept refrigerated until their transportation to the University of Strathclyde where they were stored at -80°C until their chemical characterisation. PAHs were identified and quantified during the sampling period from 2nd May 2013 to 27th May 2014. The results showed that high molecular weight 4-ring to 6-ring PAHs were reliably recovered from PM_{10} filter samples. High molecular weight PAHs dominated PM_{10} compositions with the highest proportion being 6-ring PAHs followed by 5-ring and 4-ring PAHs, respectively. More volatile 3-ring PAHs were less than 10% of the total PAHs weight while 2-ring naphthalene cannot be recovered from the quartz fibre filter used for PM_{10} sampling.

PM_{10} and total PAHs were highest at the roadside site (56.4 ± 27.3 µg m^{-3} and 4.85 ± 2.74 ng m^{-3}), slightly lower at the industrial site (51.0 ± 31.1 µg m^{-3} and 3.84 ± 2.01 ng m^{-3}) and lowest at the urban background site (39.8 ± 22.2 µg m^{-3} and 2.28 ± 1.16 ng m^{-3}). Most PAHs found in particulate matter were high molecular weight 4-ring to 6-ring that comprised more than 92% of total PAHs. IP, BP, BbF and BaP were the most abundance pPAHs found at all sampling sites and comprised 72 – 73% of the total PAH weight. Carcinogenic and mutagenic PAHs including BaA, CHR, BbF, BkF, BaP, DBA and IP contributed to more than 60% of the total pPAHs weight which may pose health risks through long-term exposure. Therefore, it is important to investigate pPAHs in order to evaluate adverse health effects on the exposed population.

BaP concentration ranked fourth among 15 PAHs measured and the highest concentration was at the roadside site indicating risk of exposure to commuters and people spending a lot of time near roadside areas. However, BaP concentrations in this study were significantly lower than previous long-term measurement data at the same roadside site (Thongsanit *et al.,* 2003). This implied that the change in vehicle emission standards had resulted in a significant emission reduction from on-road vehicles during the past decade.

BaP annual mean concentrations at all sampling sites were below the 1 ng m^{-3} EC guideline implying an acceptable health risk when using BaP as a single marker for carcinogenic PAHs. On the contrary, when WHO guideline is applied, the corresponding concentration for an excess lifetime cancer risk of 1/1,000,000 is at 0.012 ng m^{-3} (WHO, 2010). The big gap between the two guideline values indicated the need to assess the cancer risk of PAHs exposure not only to BaP but measurement data should be considered as much as possible.

5.5 Summary

PM_{10}-bound PAHs in urban areas of Thailand showed a different pattern in composition in contrast with PAHs in soot collected from Malawi's households. Biomass fuels burned in cook stoves generated more volatile low molecular weight PAHs while vehicle and industrial combustion processes led to the emission of higher molecular weight PAHs. The environmental and living conditions are the most important influence on pPAHs exposure.

The result of this study showed high proportions of carcinogenic PAHs in ambient PM_{10} measured at all sampling sites. The chemical characterisation of pPAHs is essential for the quantification of carcinogenic PAHs that are associated with the development of lung cancer from chronic exposure. Ambient BaP concentration alone may not be adequate to represent a PAHs mixture. It is found that components measured in PM_{10} at different sampling sites composed of various carcinogenic PAHs. In areas where high particulate matter is concerned, the study on pPAHs composition can lead to a better health risk evaluation.

The spatial variation of pPAHs among different source types were found in roadside and industrial areas as anticipated. A strong variation in the spatial concentrations of PAHs in PM_{10} was observed in the roadside and industrial site samples as illustrated by linear regression. Although concentrations of most individual and total PAHs were relatively higher at the roadside site, DBA and IP showed a strong influence from industrial sources. The relationship of pPAHs and source contribution will be further investigated in the next chapter. Chapter 6 will focus on the analysis of time series data and seasonal variations of PM_{10} and pPAHs.

Chapter 6

Temporal Variation of Particulate-bound Polycyclic Aromatic Hydrocarbons in the Bangkok Metropolitan Administration

6.1 Background

Climate conditions play an important role on the fate of air pollution such as occurrence, transportation and removal. Concentrations of atmospheric pollutants can be influenced by climate conditions and seasonal anthropogenic activities. Other than weathering, seasonal variations of atmospheric PAHs are highly associated with local activities that cause changes in a number of sources such as residential heating, and agricultural land clearing. These activities involve combustions of both fossil fuel and biomass that give rise to differences in PAHs profile and concentration. Anthropogenic activities associated with particulate-bound PAHs emissions vary in different seasons causing a fluctuation in particulate and PAHs concentrations throughout the year. In Chapter 5, the hypothesis that spatial location and local sources would affect PAHs profiles in the BMA was tested. The measurement results revealed that pPAHs were strongly influenced by local emission sources at roadside and industrial sites. In this chapter, weekly data were further investigated to identify seasonal variations of pPAHs in the Bangkok Metropolitan Administration region of Thailand.

Previous studies showed dramatic increases in PM_{10} and PAHs emissions in winter in rural areas owing to the increase in burning of firewood and biomass fuels for residential heating (Del Rosario Sienra, Rosazza and Préndez, 2005; Bari *et al.,* 2011; Cvetković *et al.,* 2015). Measurement data in the UK pointed out influences of industrial and traffic emissions on local PAHs concentrations (Mari *et al.,* 2010). The study found that home heating in winter was the major seasonal emission source in

Northern Ireland. Similar increasing trends of PAHs from residential heating during winter were observed in European countries (Bari *et al.,* 2011; Vestenius, *et al.,* 2011). Apparent seasonal variations of particulate matter and PAHs concentrations were observed in the winter as a result of increasing fuel consumption for residential heating and dry weather conditions (Teixeira *et al.,* 2012; Amador-Muñoz *et al.,* 2013). Furthermore, emissions from burning different types of firewood can give rise to different PAHs mixture profiles and associate toxicity. It is suggested that fast burning conditions that generate lower toxic PAHs should be used for domestic wood heaters (Zou *et al.,* 2003).

Previous studies indicated significant human health risks from exposure to pPAHs in northern and central regions of Thailand (Ruchirawat, *et al.,* 2007; Tuntawiroon *et al.,* 2007; Pengchai, *et al.,* 2009). Studies were carried out in the northern part of Thailand which had been experiencing seasonal haze from large-scale open burning of agricultural residues and forest fires. The haze period known as the burning season mostly occurs in the dry and cool weather conditions that promote the suspension of particles in the atmosphere. Without precipitation, haze of open burning smoke can persist for weeks causing environmental health effects as well as economic loss. Temporal variations of PM_{10}-bound PAHs observed in Chiang Mai and Lamphun, provinces in the north of Thailand, showed that pPAHs concentrations were highest in dry season during December 2005 – March 2006 (Chantara *et al.,* 2010). The study revealed positive correlations between PM_{10} and total PAHs as well as carcinogenic PAHs. Carcinogenic PAHs compositions ranged between 73% and 79% which were comparable to results from roadside and industrial sites found in this study. However, climate conditions in Thailand are different from previously mentioned European countries. The study on seasonal variation of pPAH in urban areas of the BMA where seasonal sources are not recognisable is still scarce.

This study aimed to investigate temporal variations of PM_{10}-bound PAHs concentrations at three sampling sites located in urban areas of the BMA to better understand factors that may influence ambient pPAH concentrations. Target PAHs were 3-ring to 6-ring semi-volatile PM_{10}-bound including acenaphthylene,

acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene. Seasonal pPAHs variations at each site were investigated to identify influences of climate conditions on PM_{10} and pPAHs concentrations.

6.2 Experimental

Fifteen PAHs were quantified in PM_{10} samples collected on quartz fibre filters at three sampling sites in the Bangkok Metropolitan Administration. A 24-hour integrated sample was collected from each site every six days throughout the sampling campaign. This allowed the PM_{10} concentration to be measured from all days of the week. Details of sample collection and analytical methods are given in Chapter 5 section 5.2. PM_{10} samples collected during 2nd May 2013 to 27th May 2014 were analysed in order to obtain year-long data of ambient pPAHs concentrations. Missing data were caused by the failure of sampling equipment. According to the Thai Meteorological Department, the climate in the central part of Thailand can be divided into three seasons namely summer, rainy season and winter (TMD, 2014). PM_{10} sampling was started in the summer of 2013 and ended in the rainy season of 2014. The tropical climate in the central part of Thailand is composed of a hot and humid summer, a wet rainy season and a dry and cool winter. Numbers of samples collected from each sampling site in each season are summarised in Table 6.1.

Meteorological data were provided by the Pollution Control Department including temperature (T), wind speed (WS), wind direction (WD), relative humidity (RH) and rainfall.

Statistical analyses were performed by Microsoft Excel Version 14.0 (Microsoft Cooperation, Washington, USA) and Minitab 16 Version 16.2.4 (Minitab Inc., Coventry, UK). Seasonal mean concentrations of summer and rainy seasons were calculated by combining samples collected in 2013 and 2014.

Table 6.1 Sampling duration and number of samples collected from three sampling sites (Rd: roadside site, Ind: industrial site, Bg: urban background site).

Season	Sampling duration	Number of samples (n)		
		Rd	Ind	Bg
Summer 2013	2 May 2013 – 15 May 2013	3	3	2
Rainy season 2013	16 May 2013 – 15 October 2013	19	14	19
Winter 2013/2014	16 October 2013 – 15 February 2014	8	11	12
Summer 2014	16 February 2014 – 15 May 2014	11	8	13
Rainy season 2014	16 May 2014 – 27 May 2014	2	1	0
Total		43	37	46

6.3 Results and Discussion

PM_{10} samples were collected from 2nd May 2013 to 27th May 2014 during which 126 filters were analysed for 15 PAHs. A year-long sampling period was selected to encompass seasonal climate conditions that may influence air pollutant concentrations. Climate conditions in the central part of Thailand are divided into three seasons: summer, rainy season and winter. Winter and summer are sometimes referred to as dry season. They are governed by the Northeast monsoon blowing from China and Mongolia during mid-October to mid-February. The transition between winter and summer is not distinct in the central part of Thailand. From mid-May to mid-October, the Southwest monsoon carries the moist air from the Indian Ocean resulting in the rainy season in most parts of the country (TMD, 2014). Mean seasonal temperatures based on a 30-year period (1981 – 2010) in the central part of Thailand were 26.2°C, 29.7°C and 28.2°C in the winter, summer and rainy season, respectively (TMD, 2015b). The seasonal rainfall was lowest in the winter and average annual rainy days were 116 days. Seasonal rainfall and relative humidity (%) were 127.3 mm (70%) in the winter, 205.4 mm (68%) in the summer and 942.5 mm (78%) in the rainy season.

In this study, analysed data was acquired during five months of the rainy season (2013), three months of the winter (2013/2014) and four months of the summer (2014). TMD reported of the climate conditions of 2013 that the monthly and average annual temperatures were higher than the 1981 – 2010 normal temperature (TMD, 2014). Monthly temperatures were above normal from January to November 2013, while the temperature in December 2013 was 1.4°C below normal. The monthly average rainfall amounts were higher than normal in during June to December 2013 with the exception of below normal rainfall in August 2013. In 2014, winter temperatures during January and February were below normal for the 1981 – 2010 period (TMD, 2015a). Monthly temperatures in other months were warmer than normal. The rainy season started late in May 2014 and the total rainfall for 2014 was 4% below normal. Meteorological conditions and seasonal concentrations of 15 PAHs at three sampling sites are summarised in Table 6.2.

PM_{10} concentrations were considerably higher in winter at all sampling sites with the highest winter mean concentration of 92.03 ± 35.27 µg m^{-3} at the roadside site. Winter mean concentrations at industrial and background sites were 79.03 ± 32.45 µg m^{-3} and 55.18 ± 28.93 µg m^{-3}, respectively. Total PAHs and sum of 7 carcinogenic PAHs trends followed the PM_{10} concentrations showing higher concentrations in the winter than in other seasons.

Table 6.2 Meteorological parameters and seasonal concentration of PM_{10} (μg m^{-3}) and PAHs (mean ± standard deviation).

Parameter	Summer			Rainy season			Winter		
	Roadside	Industrial	Urban background	Roadside	Industrial	Urban background	Roadside	Industrial	Urban background
Sampling duration	2 May 2013 to 14 May 2013 21 February 2014 to 14 May 2014			20 May 2013 to 11 October 2013 21 May 2014 to 27 May 2014			17 October 2013 to 14 February 2014		
Sample (n)	14	11	15	21	15	19	8	11	12
T (°C)	33.0 ± 1.3	31.4 ± 1.3	30.8 ± 2.3	30.7 ± 1.4	29.5 ± 1.2	27.9 ± 3.1	29.3 ± 2.5	27.3 ± 2.7	26.9 ± 2.3
Relative Humidity (%)	64 ± 6	64 ± 6	61 ± 9	70 ± 7	72 ± 7	75 ± 6	60 ± 10	65 ± 13	67 ± 10
PM_{10} (μg m^{-3})	44.98 ± 14.96	67.91 ± 15.31	37.56 ± 18.33	50.52 ± 18.66	39.96 ± 26.24	31.85 ± 15.07	92.03 ± 35.27	79.03 ± 32.45	55.18 ± 28.93
PAHs (ng m^{-3})									
ACY	0.02 ± 0.04	0.02 ± 0.03	0.02 ± 0.02	0.07 ± 0.06	0.05 ± 0.05	0.02 ± 0.03	0.04 ± 0.02	0.08 ± 0.03	0.01 ± 0.01
ACE	0.007 ± 0.010	<LOQ	<LOQ	0.04 ± 0.05	<LOQ	0.004 ± 0.009	<LOQ	0.002 ± 0.007	<LOQ
FLU	0.004 ± 0.009	0.003 ± 0.006	0.01 ± 0.03	0.07 ± 0.08	0.03 ± 0.09	0.04 ± 0.08	0.07 ± 0.03	0.03 ± 0.02	0.03 ± 0.05
PHE	0.09 ± 0.03	0.04 ± 0.02	0.07 ± 0.07	0.22 ± 0.15	0.10 ± 0.15	0.08 ± 0.08	0.35 ± 0.13	0.14 ± 0.05	0.13 ± 0.07
ANT	0.03 ± 0.06	0.004 ± 0.008	<LOQ	0.09 ± 0.10	0.02 ± 0.06	0.01 ± 0.01	0.05 ± 0.02	0.03 ± 0.01	0.02 ± 0.01
FLT	0.12 ± 0.16	0.05 ± 0.02	0.03 ± 0.03	0.28 ± 0.25	0.12 ± 0.15	0.08 ± 0.03	0.29 ± 0.12	0.19 ± 0.11	0.12 ± 0.11

Parameter	Summer			Rainy season			Winter		
	Roadside	Industrial	Urban background	Roadside	Industrial	Urban background	Roadside	Industrial	Urban background
PYR	0.11 ± 0.04	0.07 ± 0.03	0.07 ± 0.03	0.21 ± 0.11	0.11 ± 0.08	0.10 ± 0.04	0.35 ± 0.14	0.22 ± 0.08	0.15 ± 0.07
BaA	0.04 ± 0.04	0.04 ± 0.03	0.02 ± 0.03	0.18 ± 0.25	0.25 ± 0.36	0.23 ± 0.37	0.23 ± 0.13	0.12 ± 0.04	0.07 ± 0.03
CHR	0.09 ± 0.06	0.06 ± 0.06	0.05 ± 0.10	0.28 ± 0.20	0.12 ± 0.07	0.15 ± 0.07	0.33 ± 0.20	0.12 ± 0.04	0.11 ± 0.06
BbF	0.39 ± 0.26	0.31 ± 0.15	0.11 ± 0.16	0.95 ± 0.60	0.65 ± 0.41	0.45 ± 0.24	1.13 ± 0.47	0.70 ± 0.30	0.41 ± 0.16
BkF	0.08 ± 0.06	0.07 ± 0.05	0.03 ± 0.05	0.11 ± 0.12	0.11 ± 0.15	0.06 ± 0.07	0.29 ± 0.11	0.22 ± 0.08	0.11 ± 0.05
BaP	0.24 ± 0.26	0.19 ± 0.09	0.15 ± 0.09	0.55 ± 0.44	0.45 ± 0.36	0.34 ± 0.27	0.68 ± 0.28	0.38 ± 0.16	0.20 ± 0.08
IP	0.61 ± 0.36	0.75 ± 0.08	0.77 ± 0.39	1.11 ± 0.75	1.21 ± 0.57	0.51 ± 0.32	1.38 ± 0.43	1.46 ± 0.60	0.61 ± 0.22
DBA	0.03 ± 0.02	0.14 ± 0.20	0.03 ± 0.05	0.02 ± 0.03	0.11 ± 0.22	0.02 ± 0.02	<LOQ	0.55 ± 0.21	0.05 ± 0.02
BP	0.76 ± 0.35	0.42 ± 0.21	0.27 ± 0.22	1.39 ± 0.90	0.77 ± 0.42	0.60 ± 0.32	1.65 ± 0.50	0.93 ± 0.45	0.43 ± 0.20
7PAHs[a]	1.49 ± 0.63	1.57 ± 0.34	1.17 ± 0.54	3.20 ± 1.53	2.89 ± 1.47	1.76 ± 0.98	4.04 ± 1.50	3.55 ± 1.36	1.55 ± 0.56
15PAHs	2.63 ± 1.20	2.18 ± 0.53	1.64 ± 0.77	5.56 ± 2.69	4.09 ± 1.95	2.68 ± 1.34	6.84 ± 2.41	5.15 ± 1.97	2.44 ± 0.98

[a] 7PAHs: total carcinogenic PAHs concentration (BaA, CHR, BbF, BkF, BaP, DBA and IP)

Seasonal mean concentrations of 15 pPAHs are shown in Figure 6.1. Most PAHs concentrations at roadside and industrial sites were highest in the winter and lowest in the summer. PM_{10} concentrations were highest in winter at all sampling sites implying higher emissions in the winter than other seasons. While PM_{10} concentrations were not significantly different in the summer and rainy season, mean concentrations of most PAHs were noticeably lower in the summer than rainy season except for IP at the urban background site and DBA at the roadside and industrial sites. At the roadside site, all pPAHs except DBA were higher in the winter and rainy season than in the summer. Similarly, most pPAHs concentrations in the winter and rainy season at the industrial site were higher than summer concentrations. At the background site, some pPAHs including BaA, BaP and BP were found at higher concentrations in the rainy season than in the winter.

BP, IP and BbF were the three most abundant pPAHs at all sampling sites. Annual average BaP concentrations were the 4^{th} highest among 15 PAHs concentrations measured but appeared to be significantly lower than the top three PAHs. Previous studies in Bangkok also found that IP and BP were the highest pPAHs found in ambient PM_{10} during November 1999 – November 2000 (Thongsanit *et al.,* 2003). Ambient profiles of 20 PAHs were measured and the most concentrated pPAHs in PM_{10} were BP, IP, BeP, BbF, coronene and BaP, respectively. BP, IP, BbF and BaP appeared in the same order in this study, however, at significantly lower concentration ranges despite similar PM_{10} levels. The current roadside PAHs concentrations pointed to a significant reduction of traffic related pPAHs over the past decade. Annual mean BaP concentrations in 2000 were reported between 3 – 5 ng m^{-3} from 6 sampling sites in Bangkok and were found at 4 – 5 ng m^{-3} at roadside sites. In this study, the roadside annual mean BaP was found at 0.47 ± 0.39 ng m^{-3}. Measurement results showed that BaP concentrations in roadside PM_{10} samples of 2013/2014 were almost 10 times lower than those measured in 1999/2000.

Daily PM_{10} concentrations were plotted against BaP, carcinogenic PAHs (7PAHs: BaA, CHR, BbF, BkF, BaP, IP and DBA), PAHs classified by ring number and total 15 PAHs concentrations as shown in Figure 6.2, 6.3 and 6.4. Time series plots show

an increasing trend of PM_{10} during the dry season started in November 2013 and reached the highest concentration in January 2014 at all sampling sites. PM_{10}-bound PAHs major components were 4-ring, 5-ring and 6-ring PAHs. BP and IP, 6-ring PAHs, were dominant species found in PM_{10}.

The highest total PAHs concentrations were found in the rainy season at all sites whereas PM_{10} concentrations were highest in the dry-cool winter. Trends of total PAHs concentration closely follow PM_{10} concentrations at the industrial site as shown in Figure 6.2. Temporal variations of PM_{10} and PAHs concentrations exhibited the closest variation pattern at the industrial site indicating consistent emission sources. This supported the high similarity between PM_{10} and total PAHs observed in the industrial site dendrogram in Chapter 5 Section 5.3.2. In contrast, daily PM_{10} and PAHs concentrations were inconsistent at roadside and urban background sites which implied that they were originated from mix emission sources. Furthermore, the roadside and urban background PAHs may be distributed in the fine particle size range as indicated in the size segregation study (Thongsanit *et al.,* 2003).

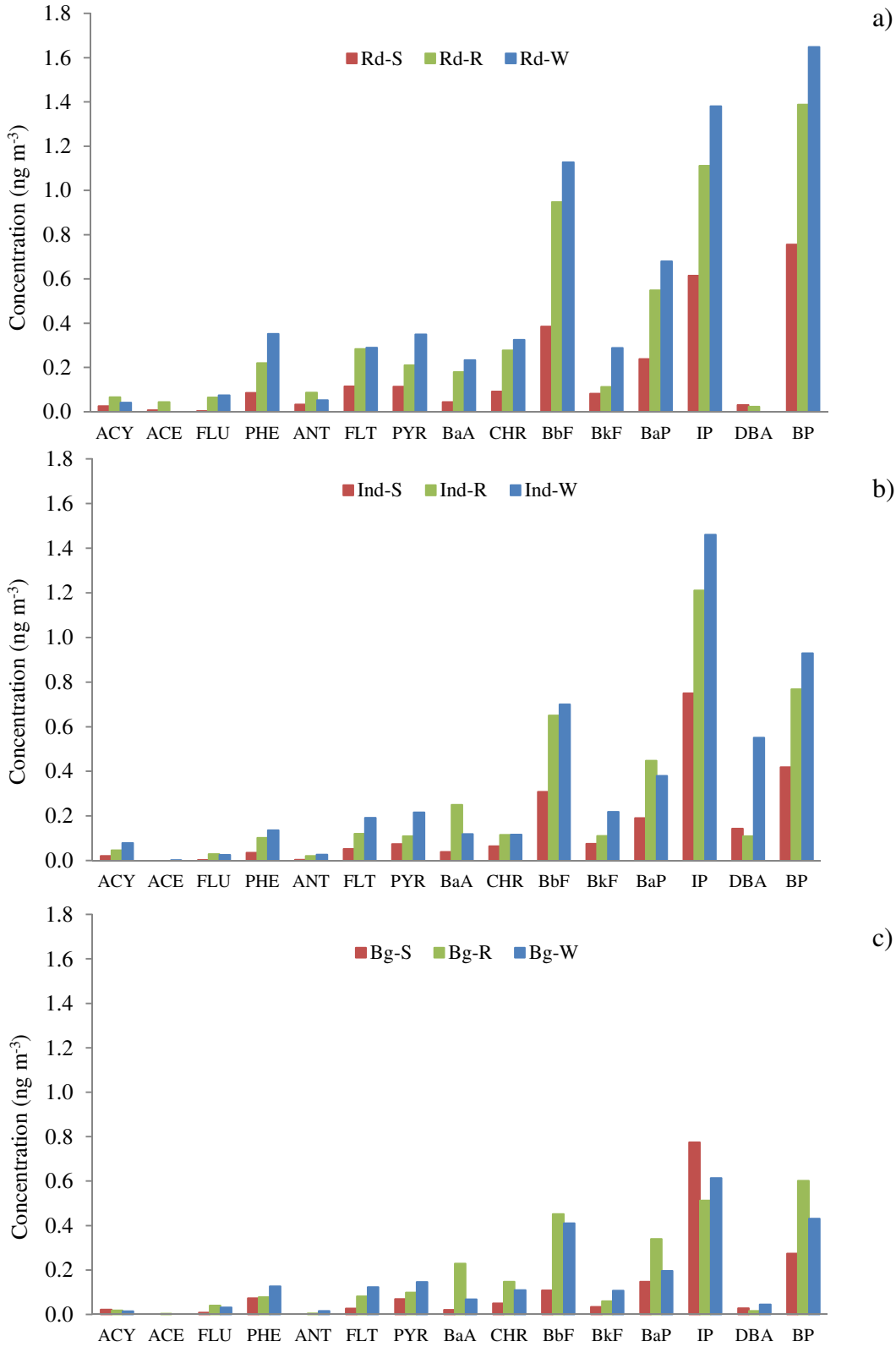

Figure 6.1 Seasonal mean PAHs concentrations at a) roadside b) industrial and c) urban background sites (S: summer-hot/humid, R: rainy season, W: winter-dry/cool).

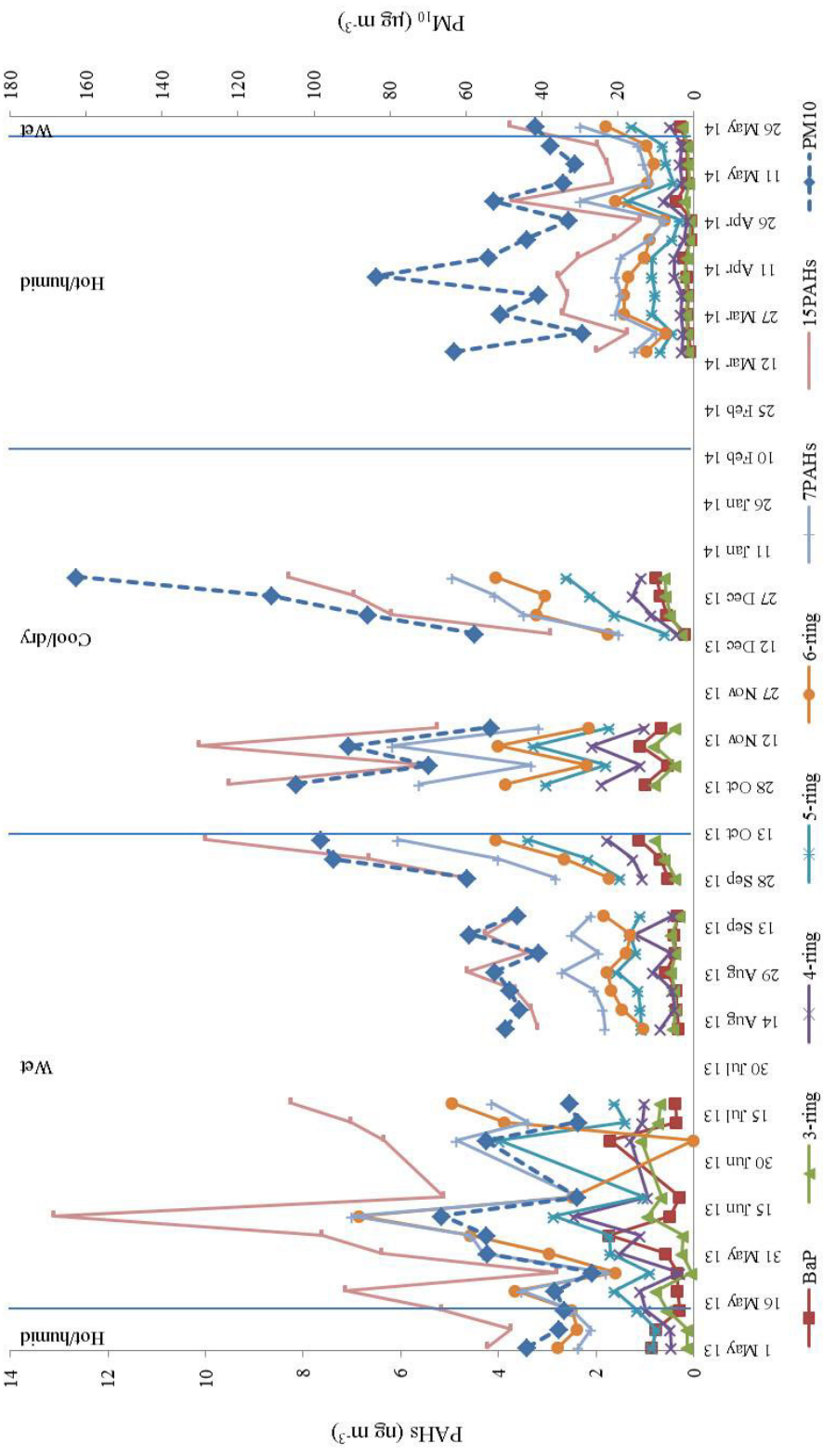

Figure 6.2 Time series plot of daily mean PM_{10} (µg m^{-3}) and PAHs (ng m^{-3}) concentrations at the roadside site. (Missing data indicted sampling failures where PM_{10} filters were not collected.)

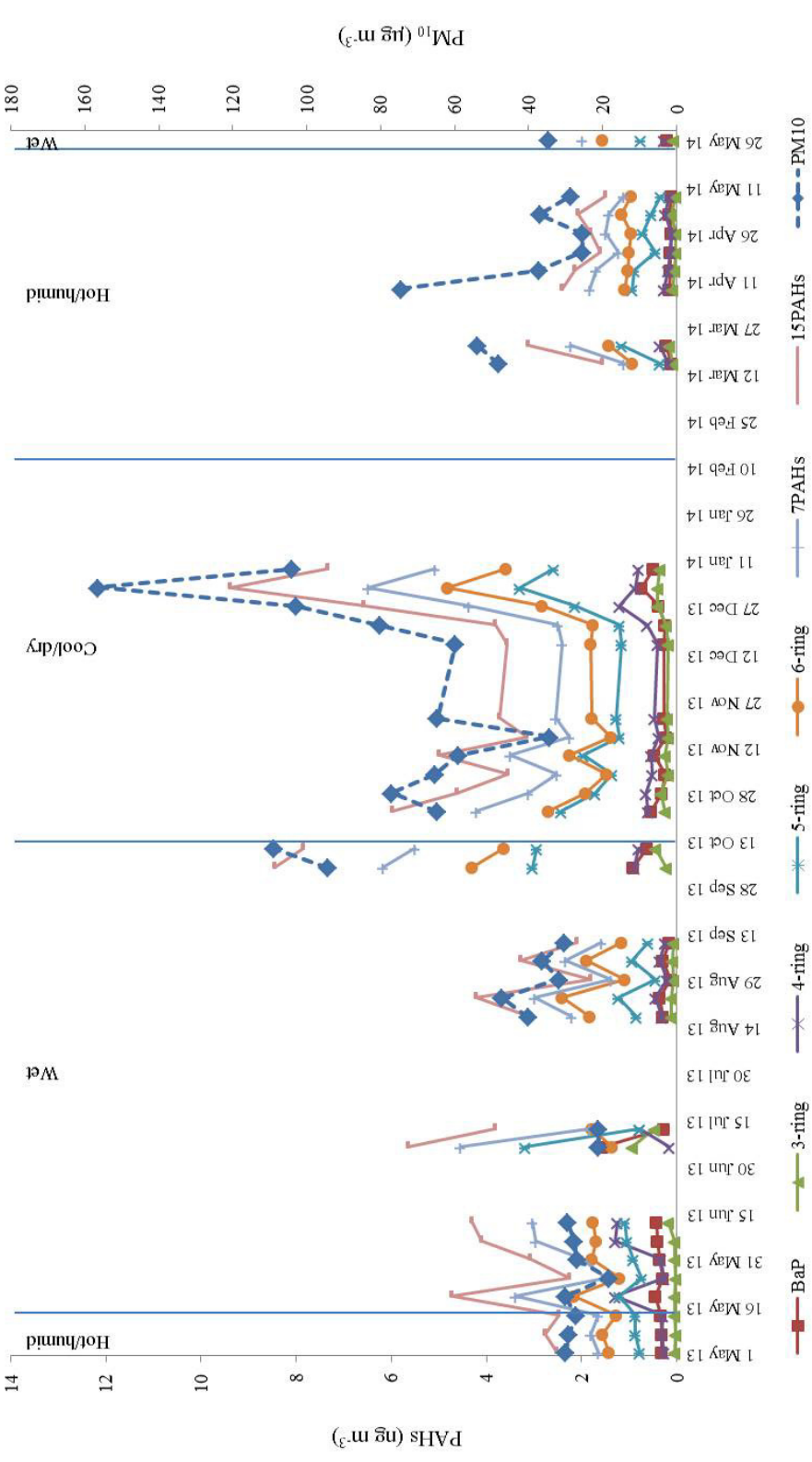

Figure 6.3 Time series plot of daily mean PM_{10} (µg m^{-3}) and PAHs (ng m^{-3}) concentrations at the industrial site. (Missing data indicted sampling failures where PM_{10} filters were not collected.)

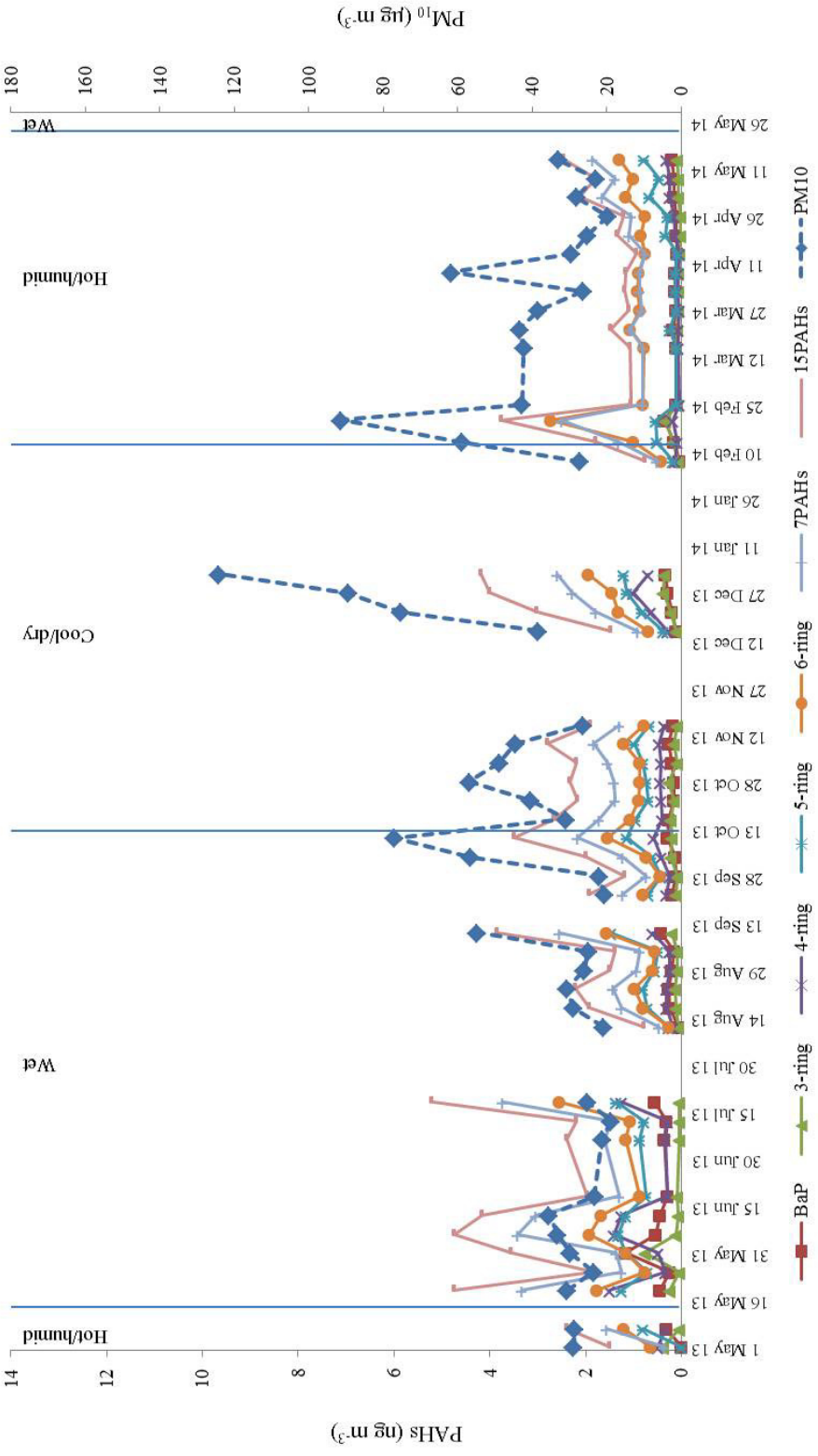

Figure 6.4 Time series plot of daily mean PM_{10} (µg m^{-3}) and PAHs (ng m^{-3}) concentrations at the urban background site. (Missing data indicted sampling failures where PM_{10} filters were not collected.)

Concentrations of PAHs are shown in log scale in Figure 6.5 to clearly illustrate trends of BaP, total PAHs, carcinogenic PAHs and PM_{10}. The variation of carcinogenic PAHs and most of the BaP daily mean concentrations were consistent with total 15 PAHs at all sites. At the industrial site, the highest PM_{10} and total PAHs concentrations were observed in the winter. While PM_{10} concentrations were highest in the winter at roadside and urban background sites, total PAHs were found to be higher during the rainy season of 2013. PM_{10} concentrations were not consistent with carcinogenic PAHs concentrations. The close correlation between carcinogenic PAHs and total PAHs concentrations affirmed that they were major constituents of total PAHs. The lack of consistency in PM_{10} and carcinogenic PAHs concentrations also implied the distribution of carcinogenic PAHs in association with smaller particle size ranges. Thongsanit *et al.* (2003) found that very fine particles <0.95 µm comprised approximately 48% of the total roadside PM weight.

BaP and carcinogenic PAHs exhibited occasional inconsistency at all sampling sites indicating the variation in carcinogenicity of pPAHs. BaP alone may not be adequate to represent carcinogenic pPAHs. The speciation of pPAHs and long-term trends observed in this study revealed a drawback from using BaP as a single marker for a PAHs mixture. Carcinogenicity of individual PAH is often explained in terms of toxicity with reference to BaP or BaP toxic equivalency factors (BaP-TEFs). BaP toxic equivalency factors can be applied to multiple PAHs in order to calculate the health risk of the exposure to a PAHs mixture. Furthermore, some PAHs have not been classified as human carcinogens but have been included when calculating the cancer risk from the exposure to a PAH mixture using BaP-TEFs. Chemical characterisation of pPAHs will give rise to a better estimation of health risks which is essential in establishing a benchmark for carcinogenic PAHs.

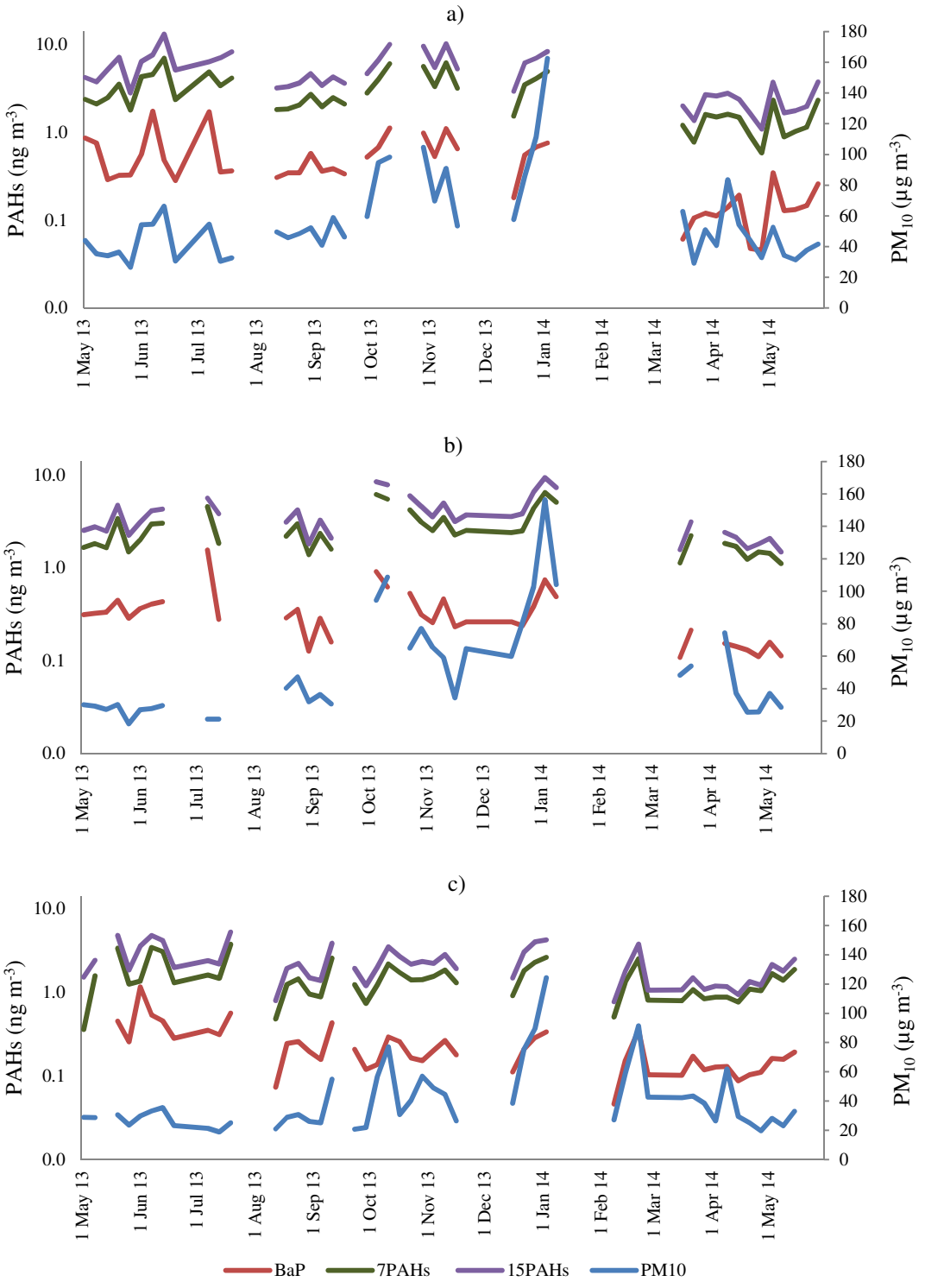

Figure 6.5 Daily concentrations of PM_{10} (µg m^{-3}) and PAHs concentrations (ng m^{-3}) shown in log-scale for BaP, carcinogenic PAHs and total PAHs at a) roadside site, b) industrial site and c) urban background site.

Figure 6.6 illustrates the linear correlation between PM_{10} and total PAHs and between carcinogenic PAHs and total PAHs of all year samples at each site. A good positive correlation between PM_{10} and total PAHs was observed at the industrial site (r^2 = 0.61) while poor correlations were observed at the roadside and urban background sites. PM_{10} at the industrial site was the major contributor of carcinogenic pPAHs. Very high positive correlations (r^2 > 0.90) were found between carcinogenic PAHs and total PAHs at all sites. A high PM_{10} concentration does not necessarily relate to high carcinogenic PAHs while high total pPAHs does.

Relationships between PM_{10} and pPAHs under different climate conditions were also determined using linear correlation plots. Despite small sample numbers in each season, positive correlations were more noticeable during the dry and cool period of winter. Positive correlations between PM_{10} and total PAHs found at the industrial site were clearly observed in the winter (r^2 = 0.62) and rainy season (r^2 = 0.80) as shown in Figure 6.7. Correlation plots were shown in the rainy season (wet) and winter (dry/cool) where relatively high correlations were observed at the industrial and urban background sites. Under hot and humid summer conditions, concentrations of PM_{10} and PAHs were significantly lower than in other seasons. No correlations between PM_{10} and PAHs were observed in the summer where r^2 were 0.01, 0.09 and 0.27 for roadside, industrial and urban background sites, respectively.

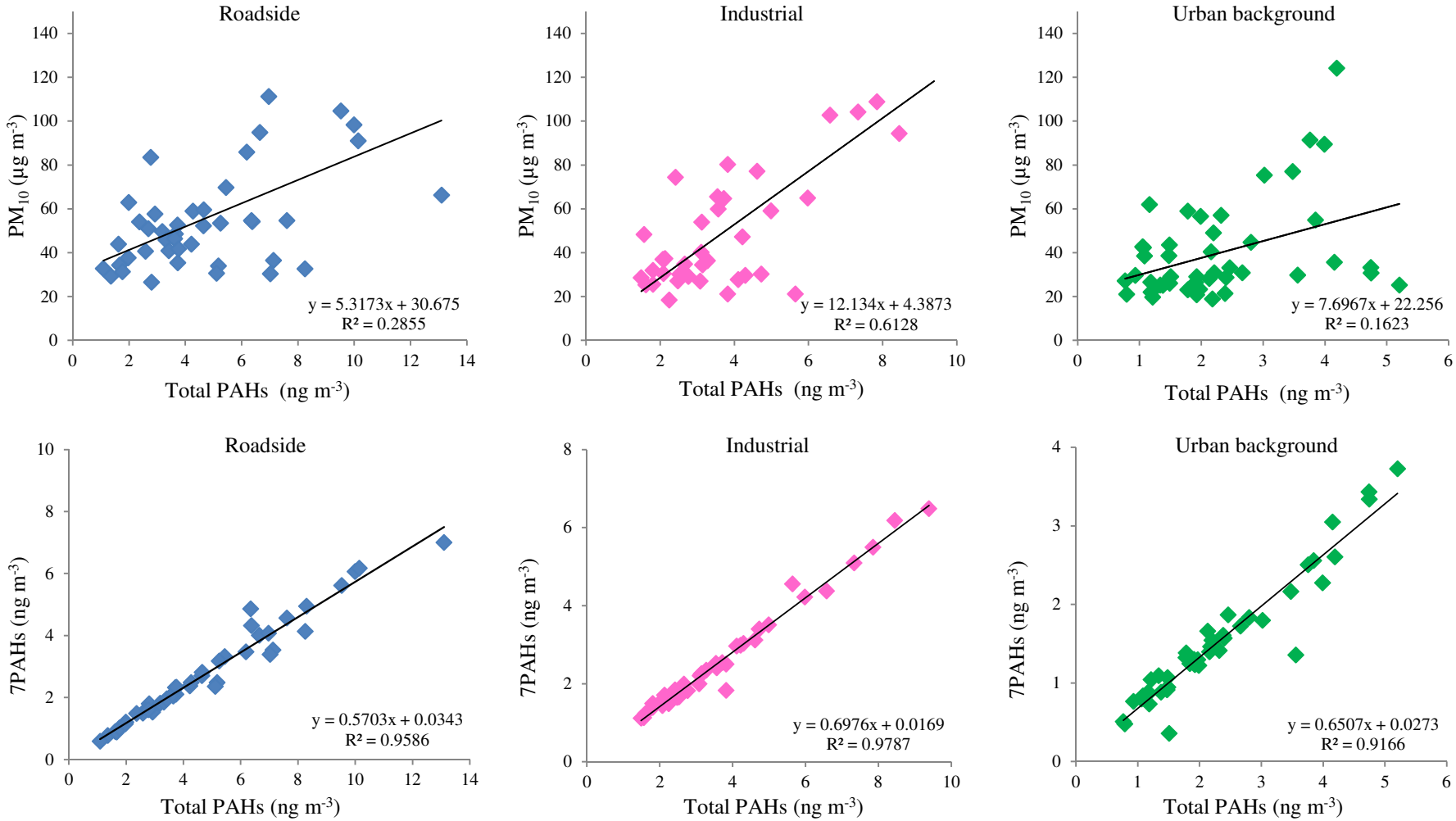

Figure 6.6 Linear correlation plots between PM_{10} vs. total PAHs and 7 carcinogenic PAHs vs. total PAHs from whole year data.

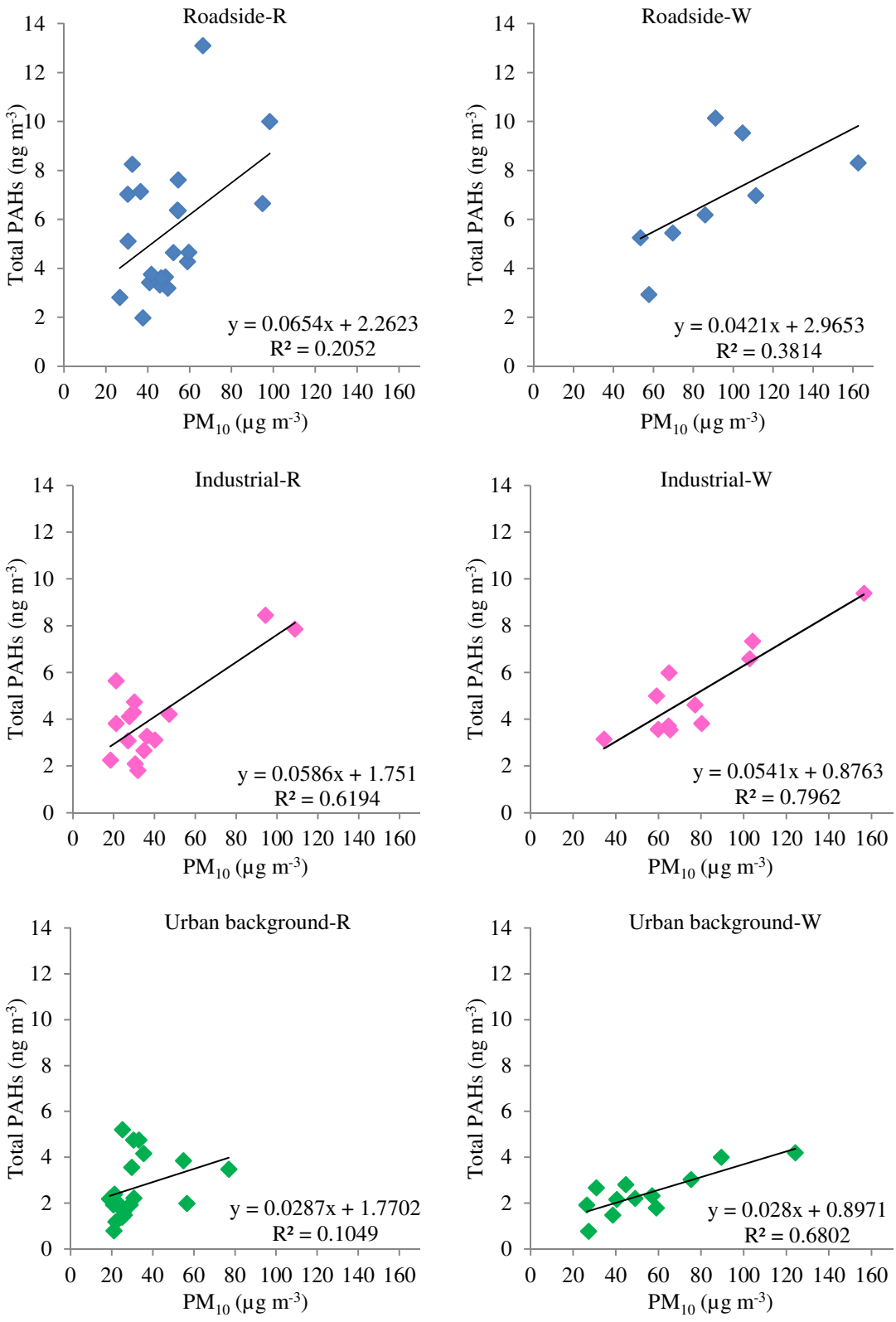

Figure 6.7 Seasonal correlation plots between PM_{10} and total PAHs concentrations in the wet season (R) and cool-dry season (W) at three sampling sites.

Seasonal high PM_{10} concentrations were clearly observed in the winter particularly at the roadside and industrial sites where PM_{10} mean concentrations were double those in other seasons. Seasonal wind directions at each site are shown in Figure 6.8. Prevailing winds blew from the south and southwest in the summer (hot and humid) and the rainy season. During cool and dry winter conditions, prevailing winds at the roadside and industrial sites were from the north to northeast while southeasterly wind directions were observed at the urban background site. Total PAHs showed different patterns and less distinct variations compared with PM_{10}, supporting the evidence that pPAHs were associated with fine particles emitted in the vicinity of each sampling site. Elevated PM_{10} concentrations during cool-dry weather conditions suggested long-range transportation of particles from the direction north to northeast of the roadside and industrial sites.

Fine particles are usually emitted from high temperature combustion sources. A previous study on size distribution of PM in Bangkok suggested that more than 97% of PAHs were found in the very-fine particle <0.95 μm which contributed to approximately 48% of total PM weight (Thongsanit *et al.,* 2003). This implied that pPAHs found at the roadside and urban background sites in this study were likely distributed in the smaller particle size range that PM_{10}. On the contrary, coarse particles were a major contributor of pPAHs at the industrial site. A good correlation of PM_{10} and pPAHs observed at the urban background site in the winter implied a better conservation of PAHs compositions after dispersal from sources. In addition to the winter (dry/cool) weather conditions that promote the suspension of particulate matter, the cool climate and less solar radiation may disfavour the photochemical degradation of pPAHs compared to other seasons.

Figure 6.8 Wind rose plots showing prevailing winds in each season (Rd: roadside; Ind: industrial; Bg: urban background).

BaP concentrations were compared at 3 sampling sites during the summer (mid-February to mid-May), rainy season (mid-May to mid-October) and winter (mid-October to mid-February) using boxplots of mean BaP concentrations shown in Figure 6.9. Seasonal mean BaP concentrations were significantly higher at the roadside than other sites in the winter (0.68 ± 0.28 ng m^{-3}) and rainy season (0.55 ± 0.44 ng m^{-3}). Seasonal variations of BaP showed the highest mean concentration at the roadside site in the winter at 0.68 ± 0.28 ng m^{-3} together with the highest mean

PM_{10} concentration of 92.03 ± 35.27 µg m^{-3}. Seasonal mean BaP concentrations were lowest in the summer and no significant mean difference was found at all sites.

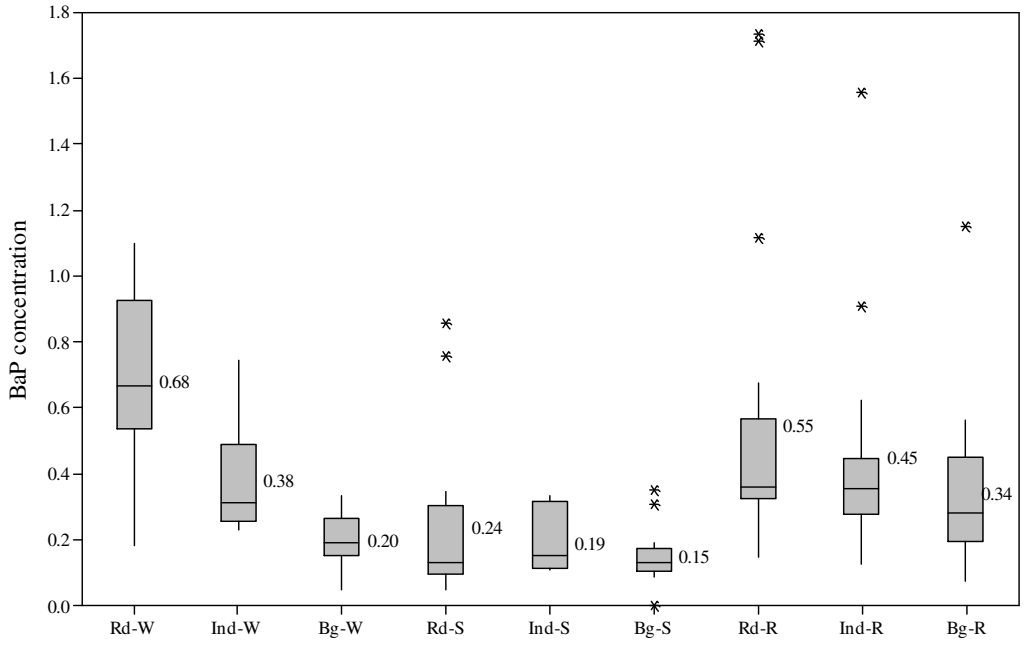

Figure 6.9 Comparison of seasonal mean BaP concentrations (ng m^{-3}) at different sampling sites (Rd: roadside; Ind: industrial; Bg: urban background; W: winter-cool/dry; S: summer-hot/humid; R: rainy season-wet).

At the roadside site, mean BaP concentration was significantly lower in hot and humid summer period (0.24 ± 0.25 ng m^{-3}, p = 0.015) than in other seasons. At the industrial site, mean BaP concentration was significantly lower in summer (0.19 ± 0.09 ng m^{-3}, p = 0.047) than in rainy season (0.45 ± 0.36 ng m^{-3}). Similarly, at the urban background site, mean BaP concentration was significantly lower in summer (0.15 ± 0.09 ng m^{-3}, p = 0.005) than in rainy season (0.34 ± 0.24 ng m^{-3}). Higher temperatures and solar radiation in the summer could favour the loss of PAHs from photochemical reactions resulting in the lowest mean BaP concentration in the summer. There was no significant difference between BaP concentrations observed in the rainy season and winter at all sampling sites. However, the fluctuation of winter BaP concentrations was less than those found in the rainy season. Highest BaP concentrations occurred in the rainy season at all sites.

Box plots of seasonal BaP, total PAHs and PM_{10} concentrations separated by sampling sites are shown in Figure 6.10. Higher mean PM_{10} concentrations were clearly observed during the dry and cool period whereas seasonal differences in total PAHs means were not significant. It can be seen that seasonal variations of pPAHs concentrations were not consistent with PM_{10} concentrations. Total PAHs concentrations were significantly higher in the winter than in the summer. Higher humidity and precipitation in the rainy season could result in the wash out of atmospheric particles, thus lowering ambient PAHs levels. This implied that climate conditions could favour the loss of pPAHs under hot and humid conditions and preserve pPAHs under dry and cool conditions.

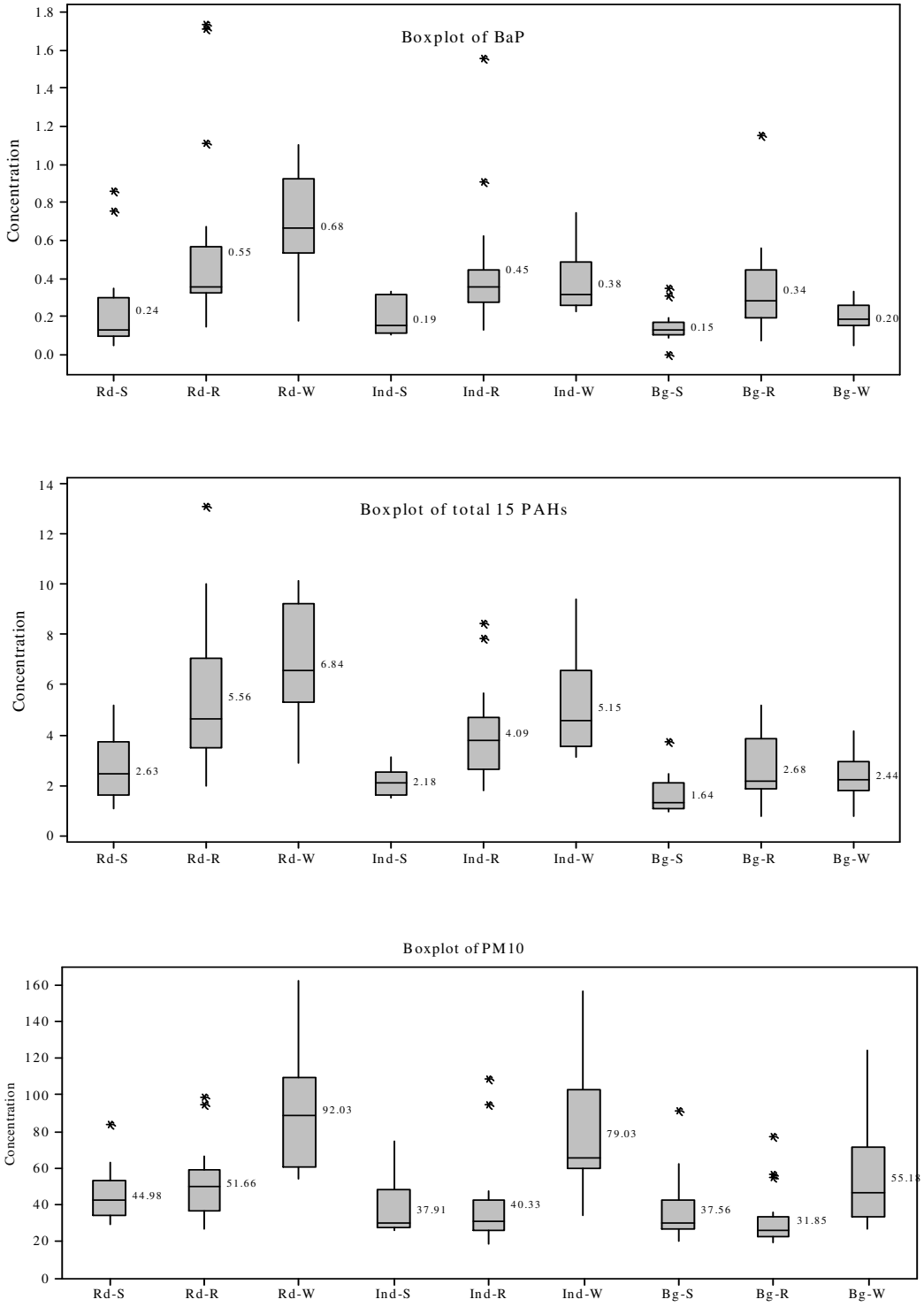

Figure 6.10 Concentrations of BaP (ng m^{-3}), 15 PAHs (ng m^{-3}) and PM_{10} (µg m^{-3}) in the summer (S: hot/humid), rainy season (R: wet) and winter (W: cool/dry) at each sampling site (Rd: roadside site, Ind: industrial site, Bg: urban background site).

Daily concentrations of BaP are compared with the annual mean EC guideline value at 1 ng m^{-3} and the UK target value at 0.25 ng m^{-3} in Figure 6.11 (EC, 2004; DEFRA, 2007). At the roadside site, 24-hour average BaP concentration exceeded the EC guideline three times in the rainy season and once in the winter. The industrial site BaP concentration exceeded the guideline once in the rainy season. At the urban background site, BaP concentrations were less fluctuating and mostly distributed below half of the EC guideline value throughout the measurement duration. Despite occasional high BaP concentrations found at the roadside site, annual average concentrations at all sites in this study were within the EC guideline value. However, annual mean concentrations of BaP at all sampling sites breached the UK guideline which sets the target annual mean BaP concentration at 0.25 ng m^{-3}.

Significantly higher concentrations of BaP and most pPAHs observed in the winter at all sampling sites indicated that more attention should be paid to acute health effects as a consequence of high exposure to particulate matter. High concentrations of carcinogenic pPAHs may result in further aggravation of cancer risks from chronic exposure.

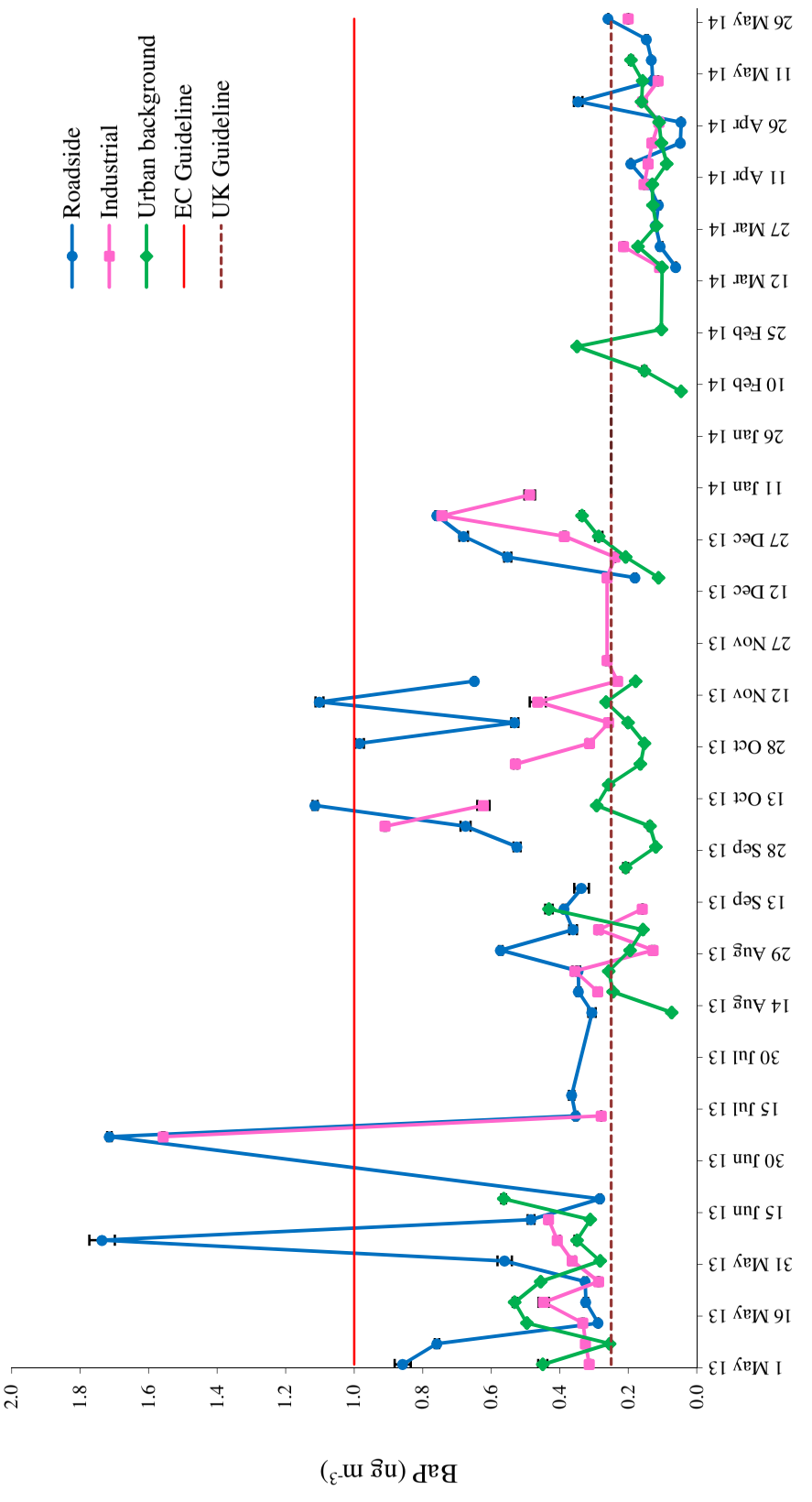

Figure 6.11 Daily mean concentrations of BaP (ng m^{-3}) at the roadside, industrial and urban background sites compared with the EC (1 ng m^{-3}) and UK (0.25 ng m^{-3}) annual average guidelines.

Carcinogenic risk from pPAHs exposure can be estimated from BaP concentration as a single marker or combined carcinogenicity of PAHs expressed as toxicity equivalent to BaP namely BaP-TEQ. To evaluate the variation of pPAH carcinogenicity over a period of time, daily BaP and BaP-TEQ were compared at the three sampling sites. Products of 13 pPAHs and BaP toxic equivalency factors (BaP-TEF) were calculated (Nisbet and LaGoy, 1992). The total sum of BaP-TEQ represented the sum of pPAHs concentrations after converted to the BaP concentration. Figure 6.12 showed trends of BaP, BaP-TEQ and PM_{10} daily mean concentrations at each site. Daily concentration patterns at the industrial site were clearly different from other sites. BaP and BaP-TEQ concentrations appeared to fluctuate in a similar manner at the roadside and urban background sites with more frequent peak concentrations at the roadside site. The highest carcinogenicities of pPAHs shown as BaP-TEQ concentrations and the highest daily BaP concentrations were found in the rainy season at both sites. At the industrial site, the highest BaP-TEQ concentration was observed in the winter whereas the highest BaP concentration was found in the rainy season.

The industrial site samples showed the highest fluctuation in daily mean BaP and BaP-TEQ concentrations among the three sites. Daily BaP-TEQ concentrations found during the dry-cool period were significantly higher than concentrations in other periods of the year. Daily BaP-TEQ concentrations were slightly higher than BaP concentrations in most roadside and urban background samples. Averaged BaP-TEQ to BaP concentration ratios were 1.7, 1.8 and 2.6 at the urban background, roadside and industrial sites, respectively. The highest proportion of BaP-TEQ/BaP ratio was found at 3.4 at the industrial site in the winter emphasising the necessity of using BaP-TEQ concentration to assess the lung cancer risk. It can be inferred that pPAHs composition plays a vital role in carcinogenic risk assessment.

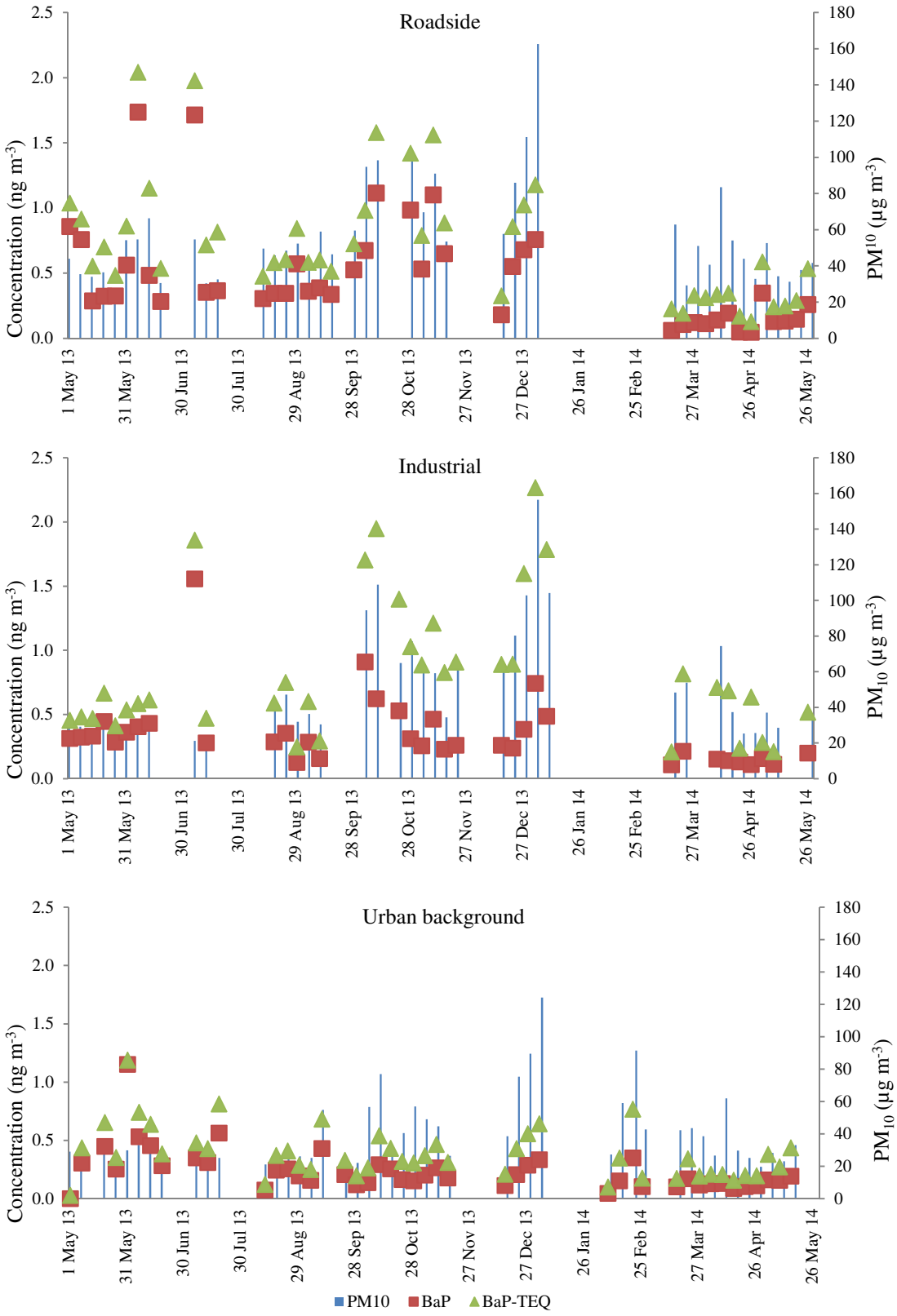

Figure 6.12 Time series data of pPAHs carcinogenicity shown as BaP and BaP-TEQ concentrations at the roadside, industrial and urban background sites in the BMA.

Seasonal variations of BaP-TEQ/BaP ratios and BaP-TEQ concentrations are summarised in Table 6.3. Higher concentrations of carcinogenic PAHs were found at the roadside site with the exception of IP and DBA which were higher at the industrial site in all seasons. The BaP-TEQ concentrations were approximately 2 – 3 times higher than BaP annual mean concentrations indicating a significant difference in the risk estimation. The adjustment of toxicity values, i.e. cancer slope factor, inhalation unit risk, etc., may apply to compensate for the lower exposure concentration of BaP used in the risk calculation.

Table 6.3 Ratios of BaP-TEQ to BaP and BaP-TEQ concentrations in different seasons and annual averages at each sampling site.

Season	BaP-TEQ/BaP ratio			BaP-TEQ concentration (ng m^{-3})		
	Roadside	Industrial	Background	Roadside	Industrial	Background
Summer	2.2	2.8	1.8	0.40	0.47	0.28
Rainy	1.7	1.9	1.5	0.84	0.79	0.48
Winter	1.5	3.4	1.9	1.00	1.24	0.37
Annual	1.8 ± 0.6	2.6 ± 1.1	1.7 ± 0.3	0.73 ± 0.46	0.83 ± 0.54	0.39 ± 0.22

An attempt to identify sources of pPAHs in ambient PM_{10} using diagnostic ratios of frequently found 4-ring and 6-ring PAHs in samples is shown in Figure 6.13. Due to the tendency to underestimate 3-ring PAHs in PM_{10} found during the method development, higher molecular weight PAHs were considered to better reflect diagnostic ratios. Ratios of IP/(IP+BP) were plotted against ratios of FLT/(FLT+PYR) in order to determine plausible emission sources of pPAHs (Yunker *et al.,* 2002; Tobiszewski and Namieśnik, 2012). These ratios were used in the identification of PAHs sources in arable soils of Poland (Maliszewska-Kordybach *et al.,* 2008). Both IP/(IP+BP) and FLT/(FLT+PYR) ratios > 0.5 suggested PAHs originate from coal/wood/grass combustion sources. The FLT/(FLT+PYR) between 0.4 – 0.5 are related to liquid fossil fuel emissions from vehicles and crude oil. Fuel combustions were major sources of pPAHs in the BMA.

pPAHs at the industrial site and urban background site showed contributions from mixed sources, whereas pPAHs at the roadside site were almost entirely products of fuel combustion.

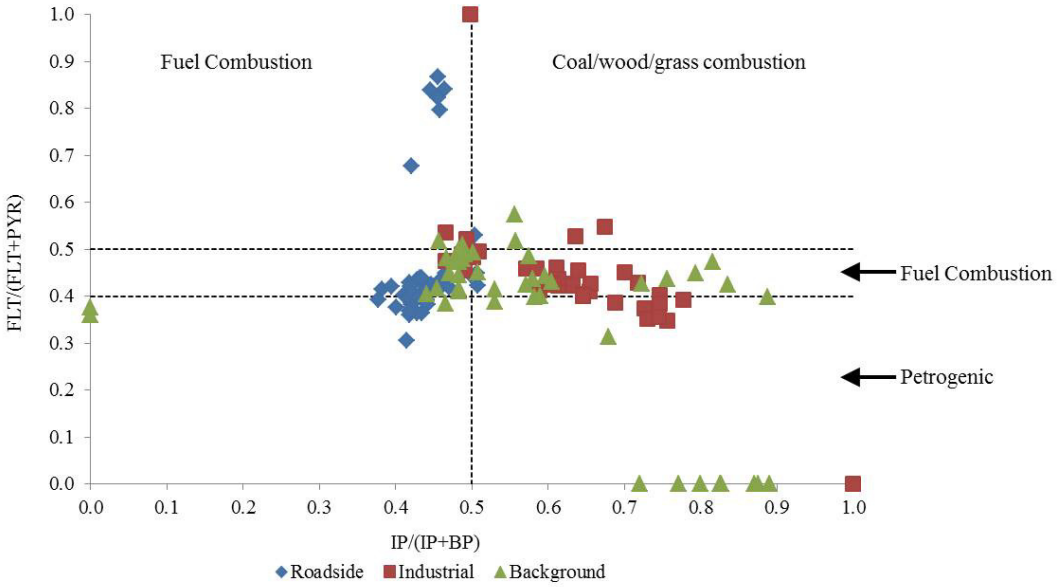

Figure 6.13 Two-dimensional plot of diagnostic ratios between FLT/(FLT+PYR) and IP/(IP+BP) showing sources contribution of pPAHs found at roadside, industrial and urban background sites in the BMA.

To further investigate emission sources in different seasons, cross plots of diagnostic ratios are illustrated in Figure 6.14. Overall seasonal distribution patterns showed that roadside pPAHs were clearly separated from industrial pPAHs and urban background pPAHs particularly during the dry period (winter and summer). Diagnostic ratios between FLT/(FLT+PYR) and IP/(IP+BP) showed different distribution patterns in the winter. Assuming that pollutant ratios were better conserved under winter climate conditions, source identification could be most appropriately assigned. Samples from each sampling site closely clustered together except a few samples at the industrial site which fell in the petrogenic sources region. Most industrial pPAHs clustered in the range of coal/wood/grass combustion. Roadside pPAHs and urban background pPAHs originated from combustion of different fuel types. Urban background pPAHs were associated with coal/wood/grass

combustion while roadside pPAHs were solely from combustion of petroleum fuels. Combustion of petroleum and biomass fuels were the most likely sources of urban background pPAH as the use of coal was not common in the study area. Small scale open burnings of biomass such as garden refuse might be one of the urban background emission sources while burning of agricultural residues may contribute to long-range transport of PM_{10} in the dry season. The shifts in FLT/(FLT+PYR) ratios to lower levels at all sites were observed in the summer. The decreases in FLT and PYR concentrations might be more rapid when compared with IP and BP owing to their volatilities. Interestingly, sources of industrial pPAHs emissions seemed to be different in all seasons. Sources of PM_{10} and pPAH in the vicinity of the industrial site should be further investigated in order to reduce toxic pPAHs emissions.

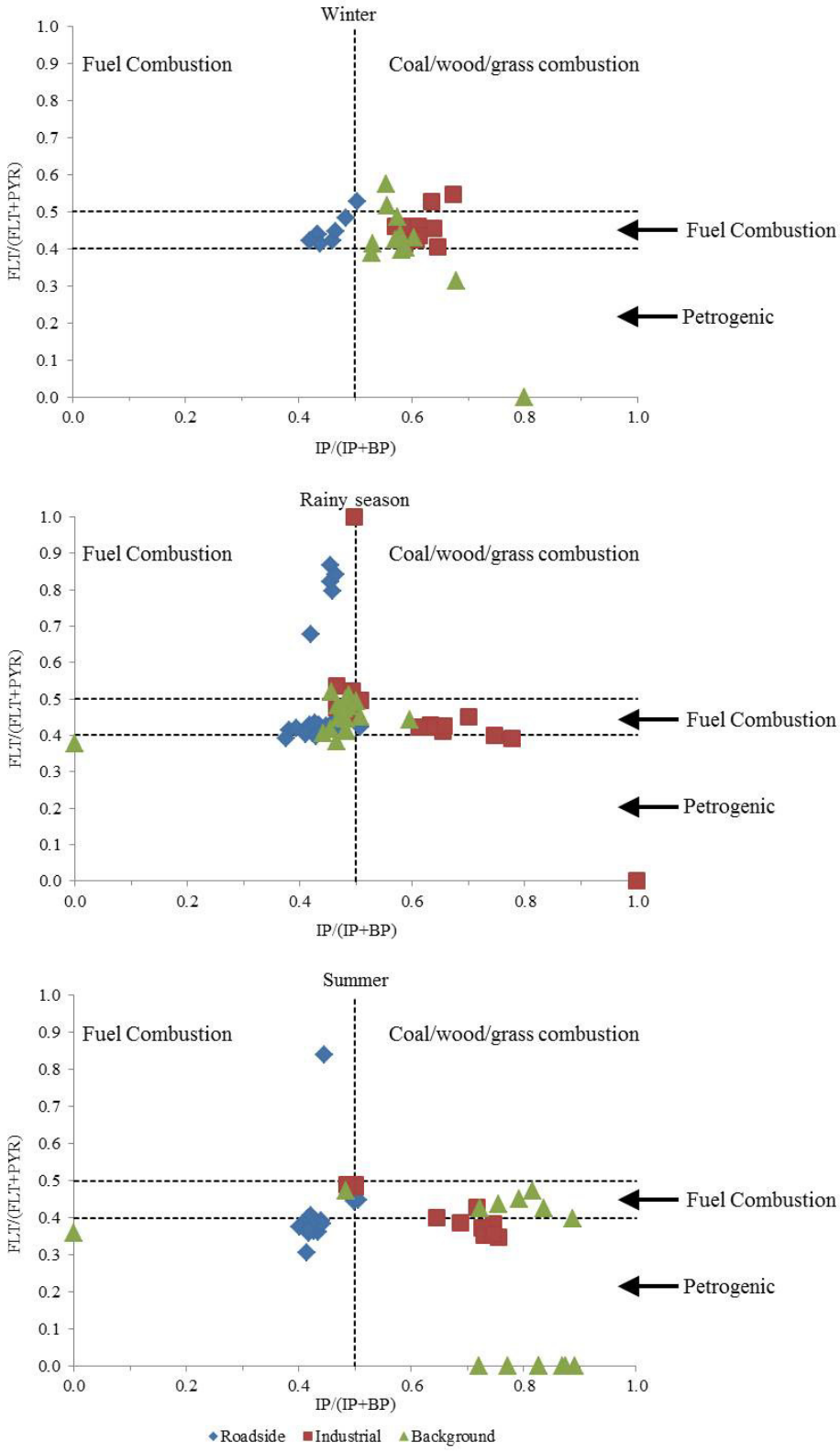

Figure 6.14 Two-dimensional plot of diagnostic ratios between FLT/(FLT+PYR) and IP/(IP+BP) of roadside, industrial and urban background sites by seasons.

6.4 Conclusion

PM_{10} samples were collected every 6 days from three sampling sites in the Bangkok Metropolitan Administration representing roadside, urban background and industrial areas. Seasonal variations showed significant difference between PM_{10} and pPAHs concentrations. Even though PM_{10} concentrations were significantly higher in the winter than other seasons at all sites, seasonal variations of pPAHs were less noticeable. This implied that urban and roadside pPAHs were associated with the fine particle fraction and emitted from local sources. PM_{10} and total PAHs at the industrial site showed strong seasonal correlations particularly in the winter and rainy season. The strong relationship between PM_{10} and total PAHs at the industrial site suggested that PM_{10} was the major source of industrial pPAHs. A strong local source influence on air pollutant concentrations can be observed at all sites.

The long-term pPAHs measurement revealed high concentrations of most PAHs in the dry-cool winter period. In contrast, PM_{10} and most pPAHs concentrations in the hot and humid summer period were significantly lower than in other seasons. Climate conditions strongly influenced the fate of pPAHs which result in noticeable seasonal variations particularly in the dry-cool period. Despite relatively small temperature differences among three seasons in the central part of Thailand, cool and dry weather conditions strongly facilitate the particle suspension and preservation of pPAHs. On the contrary, relatively high temperature and available solar insolation in hot and humid conditions may favour the photochemical degradation and thus significantly increase the removal of atmospheric pPAHs.

The highest seasonal mean BaP concentration was found in the winter at the roadside site similar to PM_{10} and total pPAHs concentrations. The lowest BaP concentrations were found during the summer at all sites and at the background site in winter. Mean BaP concentrations at all sites were not significantly different in the rainy season. However, exceptionally high BaP concentrations in samples from all sites were detected during the rainy season. While daily mean BaP concentrations did not strongly correlate with total PAHs, sum of 7 carcinogenic PAHs concentrations were

highly correlated with total PAHs. Since pPAHs major components were toxic carcinogenic PAHs, their potential health effects need to be further investigated.

This study showed that the highest exposure to elevated levels of carcinogenicity of pPAHs occurred in the rainy season and winter particularly near roadside and industrial areas. Not only high pPAHs that may lead to long-term adverse health effects, but also health threatening high PM_{10} concentrations in the dry-cool period should be mitigated. The reduction of PM_{10} concentration will eventually result in the reduction of pPAHs as fine particles that substantially constitute PM_{10} will be diminished.

6.5 Summary

This chapter summarised temporal variations of PM_{10}-bound PAHs observed in the BMA from the hot and humid season of 2013 to the rainy season of 2014. We tested the hypothesis that temporal distribution of pPAHs appeared in the central part of Thailand owing to the climate conditions despite the lack of seasonal sources in the urban area. High PM_{10} and total PAHs concentrations were found in the dry-cool period at all sites. The cool dry weather conditions and less seasonal rainfall in the winter promoted suspension of particles and preservation of pPAHs. Hot and humid conditions may favour the photochemical degradation of pPAHs resulting in significantly lower concentration in the summer than in other seasons.

A strong linear relationship between PM_{10} and total PAHs was found at the industrial site indicating a strong influence of local emission sources. At the roadside site, inconsistency of PM_{10} and pPAHs concentrations implied that pPAHs were associated with particles of smaller size range. Source identification from diagnostic ratios between FLT/(FLT+PYR) and IP/(IP+BP) indicated that pPAH at the roadside site were products of fuel combustion which tend to produce fine particle from high temperature combustion. At the urban background site where there was no prominent emission sources in the vicinity, low to moderate pPAH concentrations were found throughout the year. Fuel combustion and biomass burning were potential sources of urban background pPAH in this study.

The temporal variation of pPAHs carcinogenicity was identified in this study through the daily BaP-TEQ concentrations. Long-term monitoring data of speciated pPAHs revealed the significance of PAHs compositions on the carcinogenicity of PM_{10}-bound PAHs. Industrial site data showed a particularly high toxicity from carcinogenic pPAHs in the dry-cool period. The exposure to carcinogenic pPAHs was lowest in the hot and humid period at all sites. It is important to emphasise that BaP alone cannot adequately represent a mixture of carcinogenic PAHs. The findings in spatial and temporal variations of carcinogenic pPAHs led to the development of a health risk assessment. Lung cancer risks associated with the inhalation exposure to pPAHs will be demonstrated in the next chapter.

Chapter 7

Carcinogenic Risk Assessment of the Exposure to PM_{10}-bound PAHs in the Bangkok Metropolitan Administration

7.1 Background

7.1.1 Carcinogenicity of PAHs

Variations of PM_{10}-bound PAHs carcinogenicity were demonstrated in Chapter 6. This chapter focused on the long-term adverse health effects of exposure to pPAHs in terms of the lung cancer risk. Particulate matter has been the most concerning air pollution abatement challenge worldwide as it is associated with lung cancer and cardiopulmonary diseases. Carcinogenic and mutagenic PAHs can be found in particulate matter including benzo[a]pyrene and probable carcinogens including dibenz[a,h]anthracene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene (IARC, 2010). PAHs from anthropogenic activities appear in both outdoor and indoor air, thus people are daily exposed to PAHs via dermal, respiratory and oral routes. Exposure studies of BaP in animals demonstrated the strong evidence that tumours and cancer were developed in all exposure routes (Collins *et al.*, 1991 and Heinrich *et al.*, 1994).

The exposure to high molecular weight PAHs poses a health risk concern owing to their higher carcinogenicity and mutagenicity than low molecular weight ones. Carcinogenic PAHs have low volatility and high molecular weight and are predominantly adsorbed onto particles. In Chapter 5, measurement results showed that major components of pPAHs in the BMA study areas were 60 – 70% carcinogenic PAHs. Chronic exposure to carcinogenic and mutagenic PAHs can lead to significant adverse health outcomes and thus concentrations and sources of atmospheric PAHs in urban areas were investigated in several countries (Alves *et al.,*

2014; Belis *et al.,* 2011; Callén *et al.,* 2013; Cvetković *et al.,* 2015). The exposure to atmospheric BaP via inhalation caused the development of tumours in the pharynx and larynx in exposed hamsters (Thyssen *et al.*, 1981). A recent study confirmed that the DNA damaged in Chinese hamster lung fibroblasts was associated with higher molecular weight PAHs (Teixeira *et al.*, 2012). Published studies on particulate-bound PAHs evaluated the health risk of a PAHs mixture relative to the toxicity of BaP that is one of the most potent carcinogenic PAHs (Callén *et al.*, 2011; Wickramasinghe *et al.*, 2011; Norramit *et al.*, 2005). BaP toxicity has been well characterised and thus it is often used as a marker for PAHs carcinogenicity.

People may be exposed to toxic substances via different routes including oral, dermal and inhalation. For semi-volatile PAHs, the primary route of exposure is via the inhalation of particulate matter. The intake of chemical concentrations from inhalation exposure may not be equal to the uptake concentration at the lung owing to the size distribution of particles. After being exposed to a potential dose of a chemical, the internal dose is then metabolised and may cause adverse effect at the target organ as illustrated in Figure 7.1. Potential adverse health effects of the exposure to a carcinogen or mutagen can be investigated by the measurement of the biomarker of exposure or DNA damage in the exposure study subject.

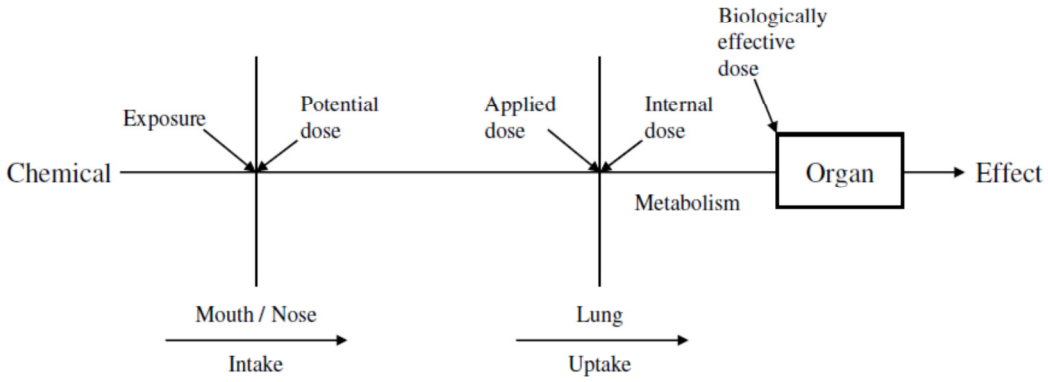

Figure 7.1 Schematic diagram of dose and exposure via respiratory route (US EPA, 1992).

PAHs entering a human body undergo metabolic transformations in order to be removed from the body. The metabolic pathway of BaP can lead to the formation of active metabolites that can bind with DNA causing oxidative damage. Figure 7.2 illustrates the metabolic transformation of BaP to the most tumourigenic form of benzo[a]pyrene 7,8-dihydrodiol 9,10-epoxide (BPDE) isomers, (+)-anti-BPDE (Gräslund and Jernström, 1989). Firstly, BaP undergoes epoxidation and hydrolysis at the 7,8-position by cytochrome P-450 (Cyt. P-450) and epoxide hydrolase and then the second expoxidation catalysed by Cyt. P-450 occurs at the 9,10-position yielding benzo[a]pyrene 7,8-dihydrodiol 9,10-epoxide isomers. Stereoisomers of BPDE are shown in Figure 7.3. Study on DNA binding indicated that (+)-anti-BPDE is highly selective to the covalent binding with the exocyclic nitrogen of deoxyguanosine (dG) forming a relatively stable DNA adduct that cannot be rapidly removed. Marker of exposure, 1-hydroxypyrene, and DNA oxidative products including 8-hydroxydeoxyguanosine (8-OH-dG), DNA strand breakage and malondialdehyde (MDA) were used to assess the oxidative damage causes by PAHs exposure in foundry workers (Liu *et al.,* 2010).

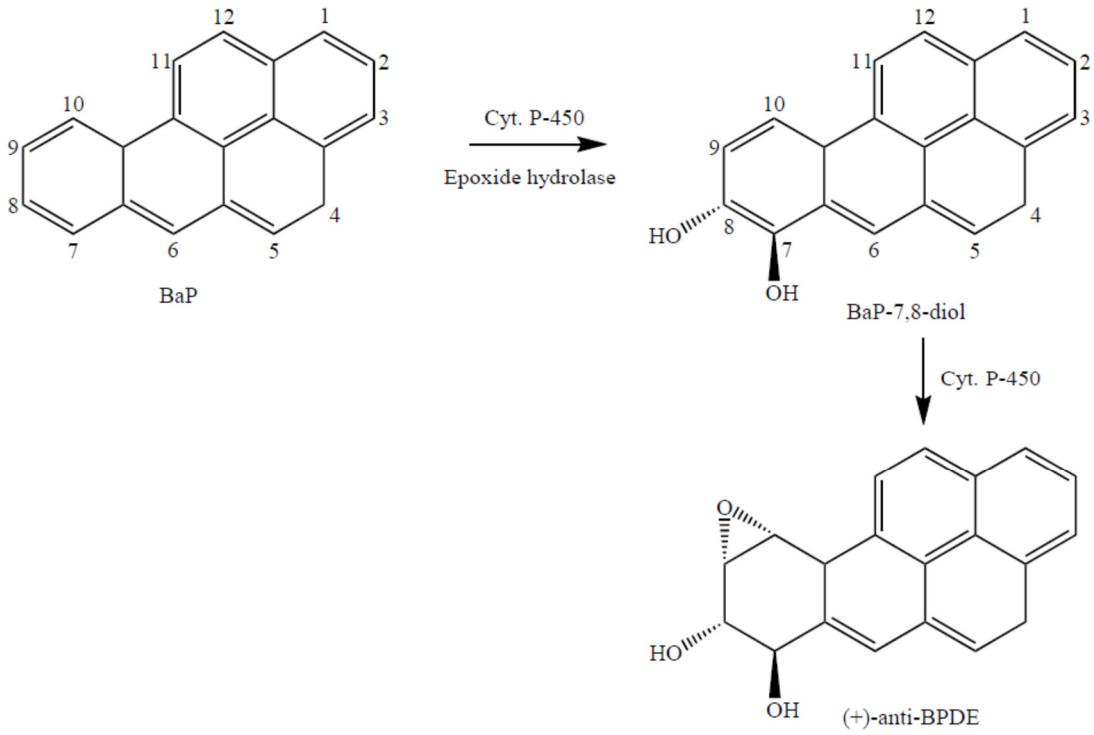

Figure 7.2 Metabolic transformation of BaP to (+)-anti-BPDE (adapted from Gräslund and Jernström, 1989).

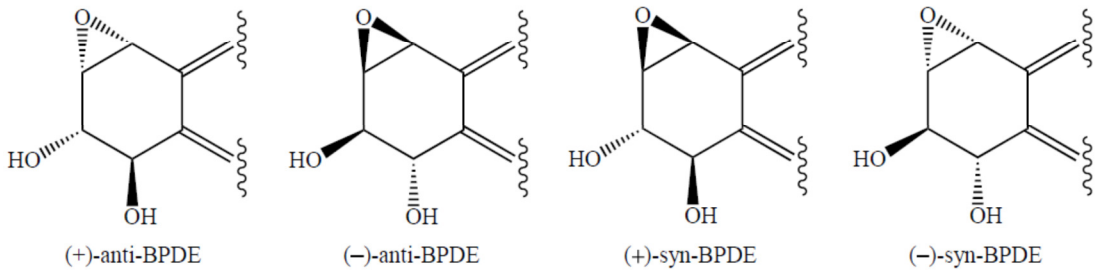

Figure 7.3 Stereoisomers of benzo[a]pyrene 7,8-dihydrodiol 9,10-epoxides.

BaP is used as representative or surrogate for the group of various PAHs to determine health risk assessment as it simplifies the risk estimation. Although BaP existence is widespread, there are limitations in using BaP as a surrogate single marker for a mixture of PAHs. PAHs in environmental samples always occur as mixtures mostly from pyrogenic sources as a result of which their compositions may vary between different emission sources. Under normal circumstances, a person can

be exposed to various PAHs via multiple routes at the same time. The determination of cancer risk from individual PAH may not be feasible. Therefore, BaP is used as the benchmark for calculating the individual PAH carcinogenicity and is assigned the toxic equivalency factor of 1. Toxic equivalency factors (TEFs) of PAHs relative to toxicity of BaP were proposed for various PAHs. A TEF value higher than 1 indicates higher carcinogenicity when compared with BaP.

Different values for the toxic equivalency factors (TEFs) of individual PAH were proposed by previous studies as shown in Table 7.1 (Nisbet and LaGoy, 1992; Petry *et al.,* 1996; Larsen and Larsen, 1998). In order to assess health risk of exposure to PM_{10}-bound PAHs, exposure via inhalation is the primary route of concern. TEFs proposed by Larsen and Larsen were selected in this study as the measure for PM_{10}-bound PAHs in filter samples encompassing 15 PAHs excluding naphthalene, the most volatile PAH, that is found in the gas phase.

Table 7.1 Toxic equivalency factors for individual PAHs.

PAH	EPA (1984)	Nisbet and LaGoy (1992)	Larsen and Larsen (1998)	MDH (2016)
naphthalene	0	0.001		
acenaphthylene	0	0.001		
acenaphthene	0	0.001		
fluorene	0	0.001	0.0005	
phenanthrene	0	0.001	0.0005	
anthracene	0	0.01	0.0005	
fluoranthene	0	0.001	0.05	0.08
pyrene	0	0.001	0.001	
benz[a]anthracene	1	0.1	0.005	0.2
chrysene	1	0.01	0.03	0.1
benzo[b]fluoranthene	1	0.1	0.1	0.8
benzo[k]fluoranthene	1	0.1	0.05	0.03

PAH	EPA (1984)	Nisbet and LaGoy (1992)	Larsen and Larsen (1998)	MDH (2016)
benzo[a]pyrene	1	1	1	1
dibenz[a,h]anthracene	1	5	1.1	10
indeno[1,2,3-cd]pyrene	1	0.1	0.1	0.07
benzo[g,h,i]perylene	0	0.01	0.02	0.009

7.1.2 Health risk assessment

Carcinogenicity from atmospheric PAHs exposure has been a health risk concern in urban areas where vehicles and industries are major emission sources. Among US EPA 16 priority PAHs, 7 PAHs including BaA, CHR, BbF, BkF, BaP, DBA and IP are classified in Group 1, Group 2A and Group 2B (IARC, 2010). Low molecular weight PAHs such as ACE, FLU, PHE, ANT, FLT and PYR are classified in Group 3 which are not classifiable as to their carcinogenicities to humans (IARC, 2010). Measurement of PM_{10}-bound PAHs gave rise to a better understanding of the carcinogenic PAHs situation as well as the estimation of lung cancer risk in study areas. Annual PAH concentrations in terms of benzo[a]pyrene toxic equivalency factors were used to estimate the lung cancer risk from the inhalation exposure to pPAHs (US EPA, 1992).

Carcinogenic risk assessment of atmospheric PAHs exposure can be estimated from the exposure concentration and the cancer slope factor (CSF). Chronic exposure to pPAHs may give rise to a risk of contracting lung cancer particularly in a susceptible population. For example, children and adults exposed to the similar concentration of a carcinogen may experience different internal doses due to their metabolism, absorption rates or intake rates. Use of age-specific values where available are recommended for the quantitative estimation of cancer risk due to the difference in exposure dose from children to adults. Epidemiological studies are often conducted in adults that may underestimate the effect of early-life exposure. Animal studies also demonstrate more potent results from early-life exposure to carcinogenic PAHs,

therefore the use of age-dependent exposure scenario for evaluating the cancer potency of a PAHs mixture is recommended. The cancer slope factor or unit risk in children and adults can be adjusted when the early-life exposure is taken into account (MDH, 2016).

Potency adjustment factors (AFs) are recommended for 3 age groups: 1) from 0 to < 2 years old, AF = 10; 2) from 2 to < 16 years old, AF = 3 and 3) from 16 to 70 years old, AF = 1(MDH, 2010). The age-dependent adjustment is to apply to both cancer slope factor and unit risk when determining a life-time cancer risk. No adjustment is required after the age of 16 when an adult unit risk is applied. Adjustments for 70-year lifetime exposure of adult cancer slope factor and unit risk are calculated as shown in the following equations. These toxicity adjustments shall reduce the underestimation of early-life exposure in the cancer risk assessment.

$$CSF_{adj\text{-}70} = CSF * (2\ y * 10 + 14\ y * 3 + 54\ y * 1) / 70\ y \qquad \text{Equation 7.1}$$

$$UR_{adj\text{-}70} = UR * (2\ y * 10 + 14\ y * 3 + 54\ y * 1) / 70\ y \qquad \text{Equation 7.2}$$

Where:

CSF = adult cancer slope factor $(mg\ kg^{-1}\ day^{-1})^{-1}$

UR = adult unit risk $(\mu g\ m^{-3})^{-1}$

An important limitation of cancer risk estimation is that toxicity of substances expressed as CSF and UR may not be available for all pollutants. For ambient PM_{10}-bound PAHs, several PAHs were measured in most air samples. Estimation of cancer risk of individual carcinogenic PAH can be troublesome. The exposure concentration of a PAHs mixture is generally expressed using the concentration equivalent to BaP by which individual PAH concentration is converted to BaP concentration. Concentration of a PAH multiplied by corresponding BaP toxic equivalency factor (BaP-TEF) giving its BaP toxic equivalent (BaP-TEQ) concentration uses for risk estimation in terms of BaP toxicity. The cancer risk estimated from the BaP toxic equivalent concentration considers contributions from both non-carcinogenic and carcinogenic PAHs found in PM_{10}. With similar PAHs concentrations, estimation using TEFs proposed by Larsen and Larsen (1998) resulted in a lower value of

cancer risk compared to TEFs proposed by Nisbet and LaGoy (1992). The Minnesota Department of Health proposed TEFs for 19 PAHs, 9 of which were in the US EPA priority pollutants list (MDH, 2016).

An exposure concentration (EC) of a PAHs mixture needs to be estimated for the cancer risk assessment from the chronic exposure to pPAHs. This can be done using time-weighted average measurement concentrations associate with exposure scenarios of subjects. Measured PAHs concentrations can be converted to BaP-TEQ concentrations using corresponding BaP-TEFs. The sum total of BaP-TEQ concentrations is the contaminant concentration (CA) expressed as ambient BaP concentration that is used to calculate EC. Chronic exposure EC can be estimated from the equation 7.3 (US EPA, 2009).

$$EC = (CA \times ET \times EF \times ED)/AT \qquad \text{Equation 7.3}$$

Where:

EC = exposure concentration (mg m^{-3})

CA = contaminant concentration in air (mg m^{-3})

ET = exposure time (hours day^{-1})

EF = exposure frequency (days $year^{-1}$)

ED = exposure duration (years)

AT = averaging time (ED in years x 365 days $year^{-1}$ x 24 hours day^{-1})

This study aimed to evaluate chronic lifetime exposure to ambient pPAHs at three study sites in the Bangkok Metropolitan Administration. Cancer risks were estimated in residents and outdoor workers exposed to pPAHs throughout a lifetime of 70 years. Exposure scenarios were determined according to recommended default exposure factors for residential child, residential adult and worker from birth to 70 years of age (US EPA, 2011; US EPA, 2014). Parameters used for risk assessment of inhalation exposure are listed in Table 7.2.

Table 7.2 Age specific exposure factors for risk calculation.

Receptor	BW (kg)	IR (m^3 d^{-1})	ET (h d^{-1})	EF (d y^{-1})	ED (y)	AT (h)
Resident (child)						
1 to < 2 years	11.4[a]	5.4[a]	24	350	2	17520
2 to < 3 years	13.8[a]	8.9[a]	24	350	3	26280
3 to < 6 years	18.6[a]	10.1[a]	24	350	6	52560
6 to <11 years	31.8[a]	12.0[a]	24	350	11	96360
11 to <16 years	56.8[a]	15.2[a]	24	350	16	140160
Adult (16 to 70 years)	70[b]	16.0[a]	24	350	54	473040
Worker (16 to 70 years)	70[b]	16.0[a]	8	250	54	473040

[a] US EPA, 2011

[b] US EPA, 2014

The carcinogenicity of an air pollutant is characterised by its inhalation unit risk (IUR) which is the upper-bound excess lifetime cancer risk estimated from continuous exposure to a chemical at the concentration of 1 µg m^{-3} in air. BaP-TEQ concentration is widely used in the risk calculation of PAHs exposure owing to availability of established toxicity values. However, BaP inhalation unit risks vary between different agencies. For example, WHO recommended IUR value is 8.7 x 10^{-5} per ng m^{-3} BaP based on epidemiological studies on coke-oven workers which corresponds to the lifetime exposure concentration of 0.012 ng m^{-3} to produce the cancer risk of 1/1,000,000 (WHO, 2000). Whereas OEHHA recommended IUR value is 1.1 x 10^{-6} per ng m^{-3} (OEHHA, 2009). Risk characterised by inhalation unit risk can be estimated from IUR and EC using the following equation.

$$\text{Risk} = \text{IUR} \times \text{EC} \qquad \text{Equation 7.4}$$

Where:

IUR = inhalation unit risk $(\mu g\ m^{-3})^{-1}$

EC = exposure concentration $(\mu g\ m^{-3})$

The cancer risk causes by inhalation exposure to ambient PAHs can be calculated to reflect the potential carcinogenic effect. The estimation of lung cancer risk associated with inhaled pPAHs can be estimated from the exposure concentration of BaP or BaP-TEQ concentration. The carcinogenicity of BaP is used as benchmark for carcinogenicity of a PAHs mixture. Risk assessment can be undertaken using BaP as a surrogate or combining toxicity of individual PAH corresponds to its BaP toxicity equivalent factor (Wickramasinghe *et al.*, 2012; Larsen and Larsen, 1998). In this study, both BaP surrogate and BaP-TEQ approaches were used to evaluate carcinogenicity of ambient pPAHs. Incremental life time lung cancer risks were estimated in 7 population groups given in Table 7.2.

Another concept of cancer risk assessment is to determine a lifetime average daily dose (LADD) of an exposed carcinogen and then estimate the cancer risk from its cancer slope factor. LADD is time-weighted average dose rate usually normalised to body weight of the exposed subject and used to estimate risk from chronic exposure. Potential dose is the integration of the chemical intake rate over exposure time as shown in the equation 7.5. For the inhalation exposure, the potential dose can be calculated from the concentration of a chemical in ambient air and the inhalation rate over a period of exposure time from t_1 to t_2 resulting in the dose of a chemical intake into a human body.

$$D_{pot} = \int_{t_1}^{t_2} C(t) IR(t)\, dt \qquad \text{Equation 7.5}$$

Where:

D_{pot} = potential dose

C(t) = concentration of a chemical in the air

IR(t) = inhalation rate

The exposure over a period of time can be determined from average values of concentration and intake rate. Intake rates for child (0 to <6 years) and adult were taken from recommended long-term exposure factors for male and female combined (US EPA, 2011). The exposure duration (ED) is the sum of the exposure of all events assuming that C and IR are nearly constant, as a consequence the potential dose can be determined from the equation 7.6 (US EPA, 1992). When estimating a cancer risk, a potential dose is averaged over a period of time and body weight to express the average daily dose. The calculation of a lifetime average daily dose of a chemical is shown in the equation 7.7.

$$D_{pot} = C \cdot IR \cdot ED \qquad \text{Equation 7.6}$$

$$LADD = \frac{C \cdot IR \cdot ED}{BW \cdot LT} \qquad \text{Equation 7.7}$$

Where:

LADD = lifetime average daily dose (mg kg^{-1} day^{-1})

C = arithmetic mean of chemical concentration (mg m^{-3})

IR = inhalation rate (m^3 day^{-1})

ED = exposure duration (years)

BW = body weight (kg)

LT = lifetime (years)

Incremental lifetime cancer risk (ILCR) estimated from LADD can be calculated from the following equation.

$$ILCR = LADD \times CSF \qquad \text{Equation 7.8}$$

Where:

CSF = cancer slope factor (mg kg^{-1} day^{-1}) $^{-1}$

Table 7.3 Carcinogenicity of PAHs, unit risks and cancer slope factors for inhalation exposure.

Compound	Class [a]	Slope factor [b] $(mg\ kg^{-1}\ d^{-1})^{-1}$	Unit risk [b] $(\mu g\ m^{-3})^{-1}$
Acenaphthene	Group 3		
Fluorene	Group 3		
Phenanthrene	Group 3		
Anthracene	Group 3		
Fluoranthene	Group 3		
Pyrene	Group 3		
Benz[a]anthracene	Group 2B	3.9E-01	1.1E-04
Chrysene	Group 2B	3.9E-02	1.1E-05
Benzo[b]fluoranthene	Group 2B	3.9E-01	1.1E-04
Benzo[k]fluoranthene	Group 2B	3.9E-01	1.1E-04
Benzo[a]pyrene	Group 1	3.9E+00	1.1E-03
Dibenz[a,h]anthracene	Group 2A	4.1E+00	1.2E-03
Indeno[1,2,3-cd]pyrene	Group 2B	3.9E-01	1.1E-04

[a] IARC Monographs on the Evaluation of Carcinogenic Risks to Humans (IARC, 2010). Group 1: carcinogenic to humans; Group 2A: probably carcinogenic to humans; Group 2B: possibly carcinogenic to humans, Group 3: not classifiable as to their carcinogenicity to humans.

[b] OEHHA, 2009

The cancer slope factor and inhalation unit risk for BaP vary between literatures. BaP inhalation unit risk of 0.0011 $(\mu g\ m^{-3})^{-1}$ recommended by WHO and cancer slope factor value of 3.9 $(mg\ kg^{-1}\ day^{-1})^{-1}$ recommended by OEHHA were selected for the risk calculation in this study.

7.2 Methodology

7.2.1 Determination of exposure concentration

Annual mean concentrations of individual PAH were measured at the 3 sampling sites representing roadside, urban background and industrial environments in the Bangkok Metropolitan Administration area. PM_{10} filter samples were collected from the roadside site and the industrial site during 2nd May 2013 to 27th May 2014 and from the urban background site during 2nd May 2013 to 15th May 2014. Details characteristic of sampling sites were given in Chapter 5. The targeted 16 PAHs were quantified in 43 samples from the roadside site, 46 samples from the urban background site and 37 samples from the industrial site. Locations of sampling sites are shown in Figure 7.4.

Contaminant concentrations in air including FLU, PHE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, BaP, DBA, IP and BP were multiplied by corresponding TEFs resulting in BaP-TEQ concentrations. BaP-TEFs were taken from Larsen and Larsen (1998) owing to measured PAH profiles that distributed in PM_{10}. Most PAHs found in the BMA were dominated by 4-ring to 6-ring that possess TEFs proposed by Larsen and Larsen (1998). Concentration in air (CA) can be calculated by combining the products of individual PAH concentration and the corresponding toxic equivalency factor given in Table 7.1. The total sum BaP-TEQ of 13 PAHs, CA, at each site is then converted to the exposure concentration (EC) according to specified exposure scenarios given in Table 7.2. CA and EC were calculated employing the following equations.

$$CA = 0.0005*FLU + 0.0005*PHE + 0.0005*ANT + 0.05*FLT + 0.001*PYR + 0.005*BaA + 0.03*CHR + 0.1*BbF + 0.05*BkF + 1*BaP + 1.1*DBA + 0.1*IP + 0.02*BP \quad \text{Equation 7.8}$$

$$EC = (CA \times ET \times EF \times ED)/AT \quad \text{Equation 7.9}$$

Where:

CA = contaminant concentration in air as BaP-TEQ concentration (mg m^{-3})

EC = exposure concentration (mg m^{-3})

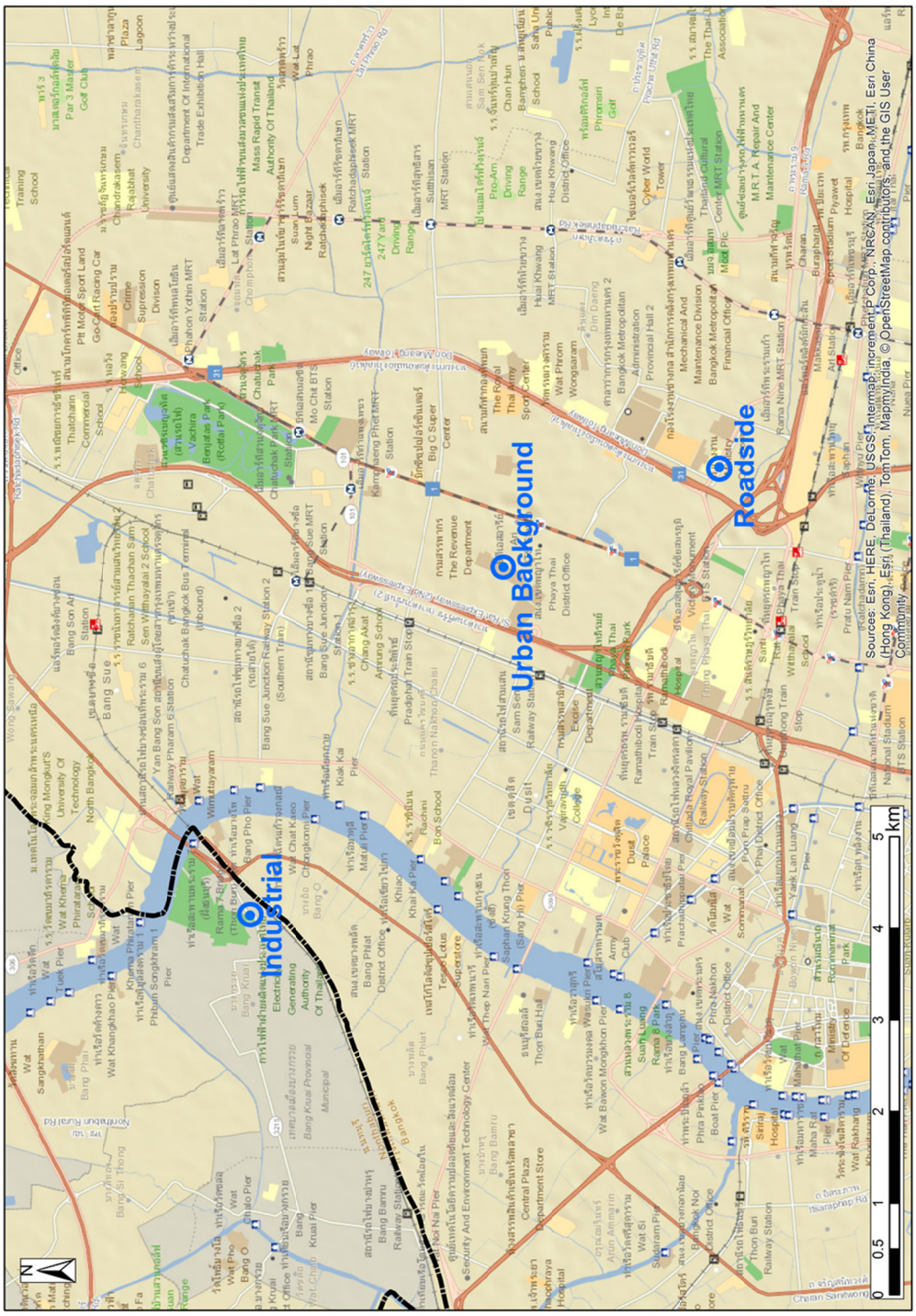

Figure 7.4 Administrative area map of PM_{10} sampling sites in the Bangkok Metropolitan Administration.

7.2.2 Estimation of incremental lifetime cancer risk (ILCR)

Exposure concentration to PAHs via inhalation of PM_{10} for each receptor can be estimated as a time-weighted average concentration from measured PAHs concentration represented by BaP-TEQ concentration. The carcinogenicity of PAHs is characterised by the inhalation unit risk (IUR) or cancer slope factor (CSF) of BaP. When EC is used to assess cancer risk characterised by IUR, the contaminant concentration in air, exposure duration and frequency are taken into account. To evaluate cancer risk, residents and workers were selected for the long-term exposure assessment. The resident group were subdivided by age to reflect the difference in receptor exposure parameters, i.e. body weight, inhalation rate, exposure duration, etc. EC is then converted to the lifetime average daily dose (LADD) for receptors at the roadside, urban background and industrial sites over a lifespan of 70 years. The incremental lifetime cancer risk to PM_{10}-bound exposure is the product of LADD and the inhalation slope factor of BaP.

As BaP is determined to cause cancer by a mutagenic mode of action, it is likely to represent a higher risk during early-life exposure. Thus age-dependent adjustment factors (ADAF) are applied in the risk calculation (US EPA, 2005). The age specific adjustment is recommended for the cancer slope factor; as such the inhalation slope factor of BaP is adjusted with ADAFs for recommended three time periods as follow:

- ADAF = 10 during 0 to 2 years of life;
- ADAF = 3 during 2 to 16 years of life; and
- ADAF = 1 from 16 to 70 years.

Using the lifetime exposure of 70 years, ADAFs were applied on the OEHHA recommended BaP inhalation slope factor value of 3.9 (mg kg^{-1} $day^{-1})^{-1}$ to the given 7 receptor groups. Adjustment factors and corresponding slope factors calculated for exposure scenarios specified in Table 7.2 were used when estimating carcinogenic risk in terms of ILCR according to the following equation.

$$ILCR = LADD \times CSF_{Adj\text{-}70} \qquad \text{Equation 7.10}$$

When risk is estimated from IUR according to the equation 7.4 and ADAFs are applied and risk can be calculated as follows.

$$\text{Risk} = (\text{IUR} \times EC_{<2} \times ADAF_{<2}) + (\text{IUR} \times EC_{<16} \times ADAF_{<16}) + (\text{IUR} \times EC_{>16}) \quad \text{Equation 7.11}$$

The adjustment is recommended when chemical-specific data on susceptibility from early-life exposures are not available. ADAFs are not applied when CSFs are derived from early-life exposure data.

7.3 Results and Discussion

Annual mean concentrations of PAHs in the BMA were determined from PM_{10} samples collected during May 2013 – May 2014. Due to the limitation in sampling and analysis methods, naphthalene was not reliably quantified in PM_{10} collected on a quartz fibre. Total PAHs concentrations were combined 15 PAHs, thus toxicity equivalency factors (TEF) of 13 PAHs proposed by Larsen and Larsen (1998) were selected for the calculation of BaP-TEQ concentrations from PM_{10}-bound PAHs. Annual mean concentrations of 13 PAHs and total BaP-TEQ concentrations at the three sampling sites are summarised in Table 7.4. Despite the highest BaP and total PAHs concentrations at the roadside site, the highest BaP-TEQ concentration was found at the industrial site emphasising the importance of carcinogenic PAHs compositions. DBA having a higher TEF than BaP played an important role in the total carcinogenicity of PM_{10}-bound PAHs at the industrial site. Therefore speciation of PAHs is essential in evaluating the cancer risk posed by long-term exposure to particulate-bound PAHs. Total BaP-TEQ concentrations were 0.83, 0.72 and 0.39 ng m^{-3} at the industrial, roadside and urban background sites, respectively. Levels of BaP-TEQ in the BMA were comparable with BaP-TEQ in metropolitan area of Curitiba, Brazil which ranged between 0.45 – 0.69 ng m^{-3} (Froehner *et al.*, 2011). Froehner (2011) employed the CSF value of 3.14 (kg mg^{-1} d^{-1}) $^{-1}$ which resulted in estimated risks between 8.16 x 10^{-9} to 1.38 x 10^{-8}.

Table 7.4 Annual mean concentration of 13 PAHs included in risk calculation, BaP-TEQ and total BaP-TEQ concentrations.

PAH	TEF	Roadside			Industrial			Urban Background		
		Ambient (ng m^{-3})	BaP-TEQ (ng m^{-3})	BaP-TEQ (%)	Ambient (ng m^{-3})	BaP-TEQ (ng m^{-3})	BaP-TEQ (%)	Ambient (ng m^{-3})	BaP-TEQ (ng m^{-3})	BaP-TEQ (%)
FLU	0.0005	0.05	0.000025	0.003	0.02	0.00001	0.001	0.03	0.000015	0.004
PHE	0.0005	0.20	0.0001	0.014	0.09	0.000045	0.005	0.09	0.000045	0.012
ANT	0.0005	0.06	0.00003	0.004	0.02	0.00001	0.001	0.01	0.000005	0.001
FLT	0.05	0.23	0.0115	1.590	0.12	0.006	0.726	0.07	0.0035	0.903
PYR	0.001	0.20	0.0002	0.028	0.13	0.00013	0.016	0.10	0.0001	0.026
BaA	0.005	0.15	0.00075	0.104	0.15	0.00075	0.091	0.12	0.0006	0.155
CHR	0.03	0.23	0.0069	0.954	0.10	0.003	0.363	0.11	0.0033	0.851
BbF	0.1	0.80	0.08	11.063	0.56	0.056	6.774	0.33	0.033	8.515
BkF	0.05	0.14	0.007	0.968	0.13	0.0065	0.786	0.06	0.003	0.774
BaP	1	0.47	0.47	64.997	0.35	0.35	42.340	0.24	0.24	61.925
IP	0.1	1.00	0.1	13.829	1.15	0.115	13.912	0.62	0.062	15.997
DBA	1.1	0.02	0.022	3.042	0.25	0.275	33.267	0.03	0.033	8.515
BP	0.02	1.23	0.0246	3.402	0.71	0.0142	1.718	0.45	0.009	2.322
Total		4.78	0.72		3.78	0.83		2.26	0.39	

Human health risk assessment of PM_{10}-bound PAHs exposure concerned the inhalation route of exposure. Cancer risk of total PAHs is usually expressed by the BaP toxic equivalent. Thus the carcinogenicity of BaP is applied when performing risk calculation. It is shown that BaP were accounted for approximately 65% and 62% total risk at roadside and urban background sites, respectively. At the industrial sites, BaP was accounted for approximately 40% of total risk calculated from BaP-TEQ. This implied that the composition of carcinogenic PAHs at the industrial site differed from those of roadside and urban background sites where BaP dominated the total pPAH carcinogenicity.

Using a BaP inhalation slope factor of 3.9 $(mg\ kg^{-1}\ day^{-1})^{-1}$ adjusted according to age groups up to 16 years of age, LADD and ILCR were calculated for resident child, resident adult and worker at 3 sampling sites (OEHHA, 2009). In the same way, risks characterised by BaP inhalation unit risk were estimated using the IUR value of 0.0011 $(\mu g\ m^{-3})^{-1}$ (OEHHA, 2009). Results of LADD and ILCR at each sampling site were calculated from the BaP concentration alone in comparison with the BaP-TEQ concentration as shown in Table 7.5. Cancer risks were calculated from the inhalation unit risk of BaP adjusted with age specific factors as shown in Table 7.6. Risks calculated from EC and IUR were slightly higher than ILCR estimated from LADD.

Table 7.5 Cancer risk assessment of age specific population group expressed as incremental lifetime cancer risks characterised by the BaP cancer slope factor of 3.9 (mg kg^{-1} day^{-1}) $^{-1}$.

Receptor	BaP			BaP-TEQ		
	Roadside	Industrial	Urban BG	Roadside	Industrial	Urban BG
LADD (mg kg^{-1} d^{-1})						
Resident (child)						
1 to < 2 years	6.1E-09	4.5E-09	3.1E-09	9.4E-09	1.1E-08	5.0E-09
2 to < 3 years	1.2E-08	9.3E-09	6.4E-09	1.9E-08	2.2E-08	1.0E-08
3 to < 6 years	2.1E-08	1.6E-08	1.1E-08	3.2E-08	3.7E-08	1.7E-08
6 to <11 years	2.7E-08	2.0E-08	1.4E-08	4.1E-08	4.7E-08	2.2E-08
11 to <16 years	2.8E-08	2.1E-08	1.4E-08	4.2E-08	4.8E-08	2.3E-08
Resident (adult)	7.9E-08	5.9E-08	4.1E-08	1.2E-07	1.4E-07	6.6E-08
Worker	1.9E-08	1.4E-08	9.7E-09	2.9E-08	3.3E-08	1.6E-08

Receptor	BaP			BaP-TEQ		
	Roadside	Industrial	Urban BG	Roadside	Industrial	Urban BG
Risk characterised by CSF						
Resident (child)						
1 to < 2 years	6.8E-09	5.1E-09	3.5E-09	1.0E-08	1.2E-08	5.6E-09
2 to < 3 years	1.6E-08	1.2E-08	8.2E-09	2.5E-08	2.8E-08	1.3E-08
3 to < 6 years	3.7E-08	2.8E-08	1.9E-08	5.8E-08	6.6E-08	3.1E-08
6 to <11 years	7.0E-08	5.2E-08	3.6E-08	1.1E-07	1.2E-07	5.8E-08
11 to <16 years	9.5E-08	7.1E-08	4.9E-08	1.5E-07	1.7E-07	7.9E-08
Resident (adult)	2.4E-07	1.8E-07	1.2E-07	3.7E-07	4.2E-07	2.0E-07
Total risk (70 years exposure)	4.6E-07	3.5E-07	2.4E-07	7.1E-07	8.2E-07	3.8E-07
Worker	5.7E-08	4.2E-08	2.9E-08	8.8E-08	1.0E-07	4.7E-08

Table 7.6 Incremental lifetime cancer risks of age specific population group estimated from the BaP inhalation unit risk of 0.0011 $(\mu g\, m^{-3})^{-1}$.

Receptor	BaP			BaP-TEQ		
	Roadside	Industrial	Urban BG	Roadside	Industrial	Urban BG
Risk characterised by IUR						
Resident (child)						
1 to < 2 years	1.4E-07	1.1E-07	7.2E-08	2.2E-07	2.5E-07	1.2E-07
2 to < 3 years	1.6E-07	1.2E-07	8.3E-08	2.5E-07	2.9E-07	1.3E-07
3 to < 6 years	2.3E-07	1.7E-07	1.2E-07	3.5E-07	4.0E-07	1.9E-07
6 to <11 years	3.3E-07	2.5E-07	1.7E-07	5.1E-07	5.9E-07	2.7E-07
11 to <16 years	4.4E-07	3.3E-07	2.2E-07	6.8E-07	7.7E-07	3.6E-07
Resident (adult)	3.8E-07	2.8E-07	2.0E-07	5.9E-07	6.7E-07	3.2E-07
Total risk (70 years exposure)	1.7E-06	1.3E-06	8.6E-07	2.6E-06	3.0E-06	1.4E-06
Worker	9.1E-08	6.8E-08	4.6E-08	1.4E-07	1.6E-07	7.5E-08

Incremental lifetime cancer risks estimated from BaP-TEQ concentrations and CSF ranged between 5.6×10^{-9} and 4.2×10^{-7}. The highest ILCR of 4.2×10^{-7} was estimated in the resident adult at the industrial site owing to its highest total BaP-TEQ concentration. It is demonstrated that the longer the exposure, the higher the risk estimated were observed among the resident group. Total risks were combined for 70 years exposure of resident resulting in cancer risks of 8.2×10^{-7}, 7.1×10^{-7} and 3.8×10^{-7} at the industrial site, roadside site and urban background site.

ILCRs characterised by IUR gave a slightly higher values. ILCR of all age groups ranged between 1.2×10^{-7} and 2.6×10^{-6}. The use of IUR and EC did not allow for the consideration of body weights and inhalation rates. Taken that the inhaled concentrations were similar in children and adults, the dose rate was not considered.

Although lifetime cancer risks estimated at all sampling sites were within 1 in a million population threshold, the discrepancy between ILCRs estimated from CSF and IUR should be brought to attention. Since there is no safe threshold for the exposure to carcinogenic or mutagenic substances, the highest estimated risk might be considered as a precautionary measure to protect public health. Risks estimated in this study implied that carcinogenicity of PM_{10}-bound PAHs was within acceptable range. Seasonal high PM_{10} and PAHs occurred during cool and dry weather conditions. Therefore, the general public may avoid exposing to high particulate matter in order to reduce the personal risk.

In addition, when only BaP data is available for cancer risk assessment, a higher value of carcinogenicity might be employed to compensate for the deficiency of other PAHs. BaP has been used as a single marker for the PAH mixture and is one of the most potent carcinogens among 16 PAHs listed by the US EPA. The BaP surrogate approach to assess cancer risk related to indoor air PAHs can be estimated using the WHO recommended IUR value of 8.7×10^{-5} $(ng\ m^{-3})^{-1}$ (WHO, 2010). This IUR value resulted in the corresponding BaP concentration of 0.012 ng m^{-3} to produce the excess cancer risk of 1/1,000,000 for a lifetime exposure. Comparing with OEHHA recommended inhalation unit risk, BaP surrogate approach using WHO recommended IUR will result in 79 folds higher risk than that of IUR

recommended by OEHHA. This may raise the concern of health impact as the cancer risk level increases from the order of 1/10,000,000 to 1/100,000.

7.4 Conclusion

The concept of health risk assessment of particulate-bound PAHs exposure focuses on the inhalation route of exposure. It is crucial to obtain a long-term measurement data of PAHs concentrations in air in order to estimate a reasonable risk. In most cases, the long-term data is the limitation owing to the high investment cost of the air sampling. Health risk assessment is often conducted on a high exposure population. However, this research is intended to evaluate the health risk to the general public caused by the exposure to PM_{10}-bound PAHs in urban areas of the Bangkok Metropolitan Administration. Due to the limitation in long-term air sampling, three sampling sites in this research were located in urban areas where a large of population is potentially affected.

The use of BaP toxic equivalent to evaluate human health risk is a suitable technique for explaining the risk posed by exposure to the ambient pPAHs mixture as most PAHs measured are incorporated into the toxicity estimation. Although BaP is the most studied PAHs in terms of carcinogenicity, previous studies showed different toxicity values implying uncertainties associated with the risk assessment (Heinrich *et al.*, 1994; Collins *et al.*, 1999). Incremental lifetime cancer risks of ambient PM_{10}-bound PAHs exposure calculated from BaP cancer slope factor at all sampling sites ranging between 10^{-7} to 10^{-9} were well below the 1/1,000,000 threshold. However, the result of BaP surrogate approach suggests that PM_{10}-bound PAHs may pose significant health risk in the long-term at the industrial site where total risk was estimated at 1.3×10^{-6}. This can be considered as precautionary grounds for a further investigation of the health risk from pPAHs exposure in other problematic areas.

7.5 Summary

Evaluation of carcinogenic risk of exposure to PM_{10}-bound PAHs in 3 urban areas of the Bangkok Metropolitan Administration is described in this chapter. Incremental

lifetime cancer risks estimated at all study sites fall in the acceptable range of the US EPA guideline of 1/1,000,000. It is unlikely that pPAHs exposure alone will pose a significant health risk to the general public in the study areas except at the industrial site where the total risk estimated by IUR of BaP surrogate was at 1.3×10^{-6}. Taking this value as the minimum requirement to meet a safe threshold, the fluctuation of pPAHs concentrations might result in a higher risk. The further monitoring of PM_{10}-bound PAHs in this area might be required to ensure that pPAHs concentrations are not posing a significant risk in the long run.

Previous studies have pointed out the evidence of significant health risk in highly exposed groups including school children and roadside outdoor workers in Bangkok (Tuntawiroon *et al.*, 2006; Ruchirawat *et al.*, 2007; Pongpiachan *et al.*, 2013). Furthermore, early-life exposure is an important factor that may represent a higher risk in children. Proactive measures should be developed for maintaining acceptable levels of risk experienced by the general public while progressing towards health protection for the susceptible population.

Chapter 8

Comprehensive Two-dimensional Gas Chromatography for Non-targeted Screening of Particulate Matter

8.1 Background

The chemical characterisation of particulate-bound PAHs and their carcinogenic risks were demonstrated in Chapter 5 – Chapter 7. Significant differences between composition of PAHs at roadside and industrial sites were revealed. Fluctuations of pPAHs carcinogenicity owing to the change in composition could be greater than the concentration. Therefore, speciated PAHs should be incorporated when estimating the cancer risk. In this chapter, the attempt to further explore organic air pollutants in PM_{10} was carried out using a state-of-the-art two-dimensional chromatographic technique. The better identification of carcinogenic PAHs and other toxic pollutants could raise the awareness on the threat of PM_{10} exposure.

Chemical analysis of organic air pollutants has been dramatically improved as a result of the enhancement to the instrumentation sensitivity and selectivity particularly for trace analysis. Limitations such as small sample amount, difficulties in extraction and clean-up methods. causing the loss and contamination of sample had prevented exploration of organic air pollutants. During the past decade, the development of gas chromatography namely comprehensive two-dimensional gas chromatography (GCxGC) has resolved both sample preparation and chromatographic separation issues. GCxGC has been widely utilised for maximising chromatographic information of samples particularly the identification of unknown or non-targeted compounds in various matrices including food, marine species, water and environmental samples (Skoczyńska *et al.*, 2008; Hashimoto *et al.*, 2011; Ochiai *et al.*, 2011; Myers *et al.*, 2014; Costa *et al.*, 2015).

The comprehensive two-dimensional gas chromatography separates the sample mixture in two dimensions using 2 capillary columns with different properties. Column temperature programmes are controlled with separate column ovens where a modulator is installed in between to trap and focus the sample from the primary column (C1) before being injected into the second column (C2). The modulator uses cryogenic cooling such as liquid nitrogen or liquid carbon dioxide to trap a small amount of sample eluted from C1 and refocus before transferring to C2 by heating up the trapped effluent. A portion of the sample trapped by the modulator is further separated on the second dimension, hence the two-dimensional GC. The diagram of a GCxGC instrument is illustrated in Figure 8.1. The trapping feature of a GCxGC enables the separation of the sample in 2 dimensions resulting in high resolution chromatographic information when coupled with an appropriate detector. A mass spectrometer is the detector of choice for the identification of unknown compounds. As GCxGC instrumentation requires a fast detector, it is usually coupled with a time-of-flight mass spectrometer (TOFMS) which can scan from 1 to 2000 amu in a few microseconds (Herbert and Johnstone, 2003).

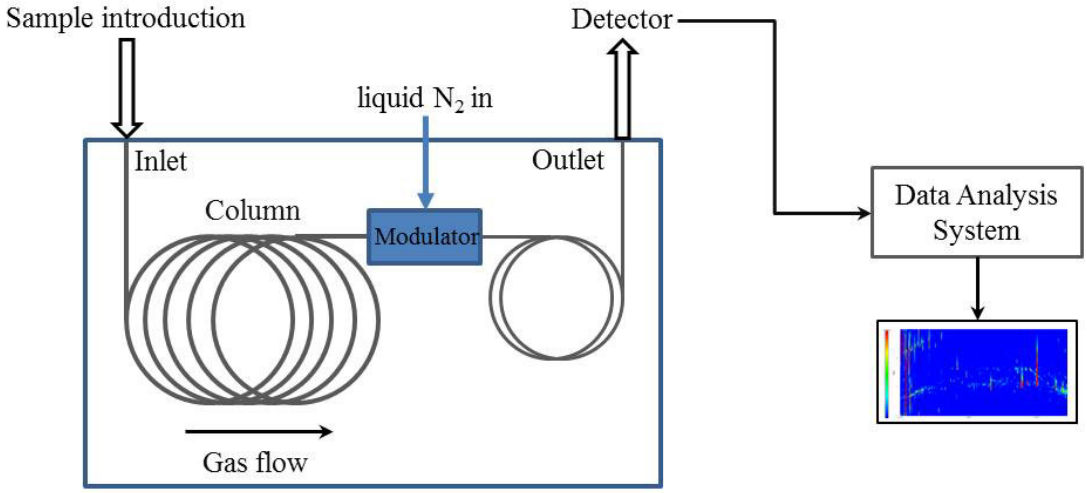

Figure 8.1 Schematic diagram of a two-dimensional gas chromatograph system with a liquid nitrogen cryogenic modulator.

A mixture of compounds that mostly appear as a big hump at the end of a chromatogram known as unresolved complex mixtures (UCM) contains large amount of information in a semi-volatile range which cannot be resolved by one-dimensional

GC (1D-GC). Some target compounds in UCM may be analysed according to their specific masses and fragment ions, however, most unknown components cannot be identified causing problems in sample characterisation. Utilising advantages of GCxGC, these problems are solved by chromatographic separation of UCM according to carbon numbers on the x-axis (first dimension) while classification of compounds are separated along the y-axis (second dimension). This technique was used to separate PAHs and alkyl-PAHs with similar carbon skeletons in highly polluted sediment samples (Skoczyńska *et al.,* 2008).

GCxGC has been applied for the analysis of unknown in atmospheric samples ranging from volatile to semi-volatile compounds. A GCxGC coupled with a flame ionisation detector (FID) was used in the analysis of urban aerosols; however, the confirmation of tentative identified compounds was performed by a GCxGC-QMS (Kallio *et al.,* 2003). Kallio *et al.* (2003) reported the identification and quantification of PAHs and oxy-PAHs in urban aerosols collected at the University of Helsinki using a GCxGC-QMS in combination with a GCxGC-FID. The automated library search result of GCxGC-QMS found approximately 1,500 peaks including alkylated-PAH i.e., trimethylnaphthalene, methylfluorene and methylchrysene. GCxGC-QMS was applied for the analysis of ambient volatile organic compounds showing that peak detection and compound identification can be improved by maximising QMS data acquisition (Wang *et al.,* 2014). The study showed that quantification by a GCxGC-FID can complement the drawback of QMS. It is also suggested that GCxGC-QMS is adequate for the qualitative analysis of volatile organic compounds (VOCs) with molecular weights below 300 amu and can be a less expensive alternative of the TOFMS for VOCs application. The MS detector plays a vital role for compound identification and a fast sampling rate is preferred for maximising GCxGC efficiency when a variety of unknown compounds is of concern.

Furthermore, GCxGC is widely used in qualitative analysis particularly for complex matrix samples. Methods and search criteria of GCxGC TOFMS data were developed for non-targeted screening of household dust and airborne particulate matter (Hilton, Jones, and Sjödin, 2010). It is illustrated that the conventional GC

technique could only identify approximately 15% of total semi-volatile organic compounds (SVOC) in urban fine particulate matter ($PM_{2.5}$) while the complex mixture contributed to about 70% of SVOC mass in $PM_{2.5}$ left unresolved (Welthagen, Schnelle-Kreis and Zimmermann, 2003). GCxGC TOFMS is one of the most powerful techniques for the analysis of UCM with a unique advantage in minimal sample preparation.

Comprehensive two-dimensional GC coupled with a mass selective detector is an attractive tool for the investigation of unknown air pollutants owing to high sensitivity and high separation power in two dimensions. In contrast to the conventional GC that may separate a maximum number of a few hundred peaks, thousands of peaks can be found when using a GCxGC. The identification of an unknown mass spectrum is done by comparing unknown with known mass spectrum compiled in the database e.g. the NIST Mass Spectral Database. Some customised search criteria were developed to differentiate compounds with similar fragment patterns (Welthagen, Schnelle-Kreis and Zimmermann, 2003; Vogt, Gröger and Zimmermann, 2007) When isomers exist, compounds with the same molecular formula but different chemical structures cannot be identified using only mass spectra, thus a group of compounds may be assigned to represent isomeric compounds. GCxGC TOFMS is a suitable tool for the screening of unknown pollutants in ambient particulate matter. We aimed to explore a wider range of unknown air pollutants in PM_{10} utilising the sensitivity of the GCxGC TOFMS to identify trace pollutants that occurred beyond the capacity of 1D-GC. A procedure for the non-targeted screening of unknown pollutants in PM_{10} extract is shown in Figure 8.2.

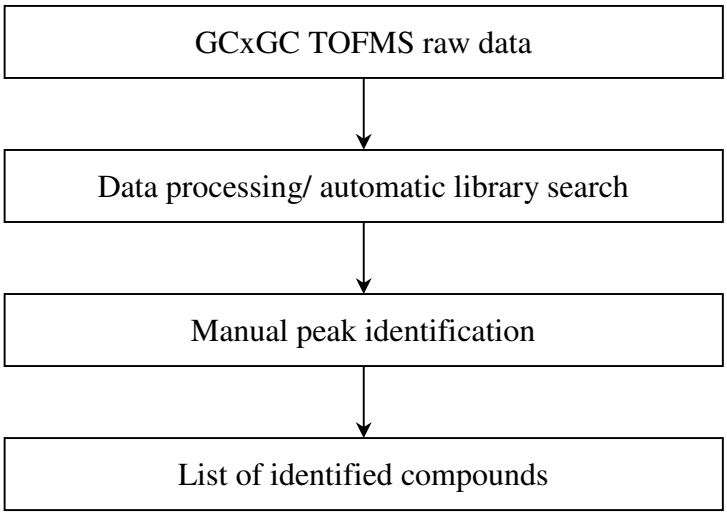

Figure 8.2 Non-targeted screening of air pollutants in PM_{10} extract.

While GCxGC techniques have been widely used for the identification and classification of unknown substances, their application in quantitative analysis is still limited. Due to the data acquisition technique of a 2D-GC, a peak separated in the first column will produce a set of peaks after the modulation process as illustrated in Figure 8.3. These modulated peaks are summed to give a total peak area of a compound. The criteria for the integration of modulated peaks can influence the quantification accuracy. As it is not certain that 100% of total modulated peak response can be measured, the use of relative response ratios between sample and an internal standard were recommended (Amador-Muñoz and Marriott, 2008). Amador-Muñoz *et al.* (2008) demonstrated the use of two or three most intense modulated peaks and peaks of deuterated internal standard in PAHs quantification resulted in <6% of bias when compared with the total modulated peak area sum. A satisfactory quantitative analysis result could be achieved with 2D-GC despite a complication of the data analysis process.

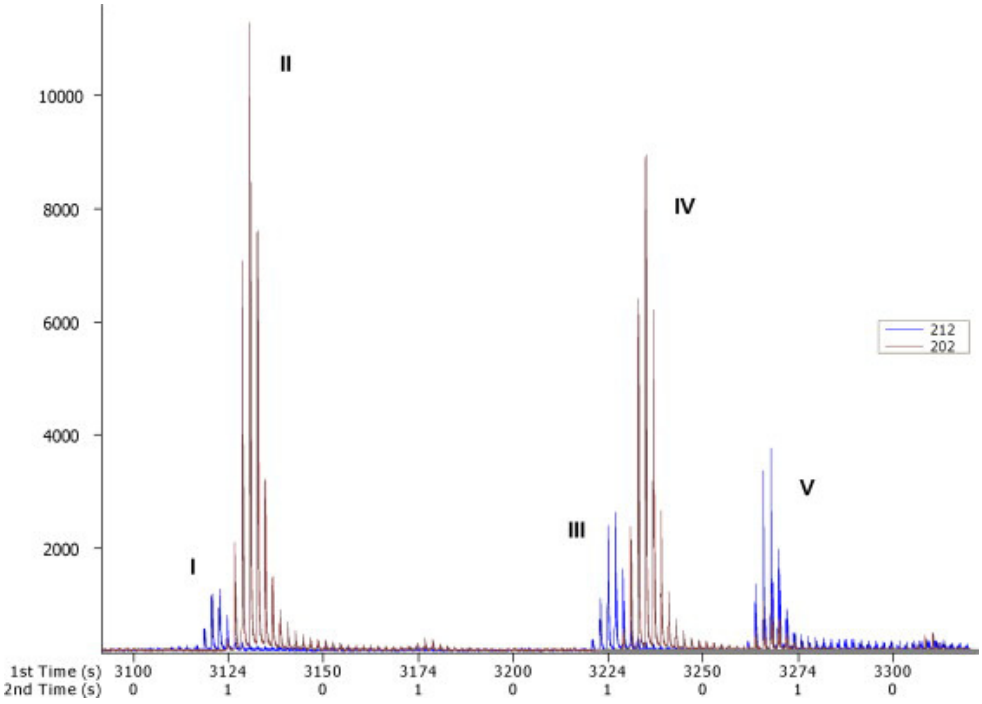

Figure 8.3 Modulated peaks of PAHs with m/z 202 (II and IV), internal standard peaks with m/z 212 (I and III) and an unknown compound with m/z 212 (V) and other trace compounds correspond to mass 202 and 212 appeared in low intensity peaks (Reprinted from Amador-Muñoz *et al.* (2008) Copyright (2008) with permission from Elsevier).

Quantification by GCxGC can be problematic as it results in a set of modulated peaks that need to be summed up or selectively integrated. Several methods were employed for the integration depending upon the type of detector used i.e. sum of modulated peak areas, peak volumes, peak areas (Murray, 2012). It is suggested that automatic integration may result in significant underestimation of low level contaminations, thus manual integration is recommended for a better quantification of GCxGC data (Amador-Muñoz *et al.,* 2008). In this research, the quantification of 15 PAHs in particulate matter was carried out by the GC-QMS using a fast analysis method suitable for a routine quantitative analysis. In order to explore information contained in ambient particulate samples, the GCxGC TOFMS was utilised for the screening of non-targeted air pollutants.

Previous studies show that comprehensive two-dimensional gas chromatography is a versatile tool for analysis of complex samples ranging from benzene and its derivatives, PAHs and heteroatom-containing compounds/heterocyclic aromatic compounds (von Muhlen *et al.,* 2006). GC x GC coupled with a mass spectrometer is a powerful tool that enables a high sensitivity quantification of alkylated PAHs and other POPs (McGregor *et al.,* 2011). The aim of this study was to solve the problem on trace analysis of a complex mixture PAHs and other semi-volatile air pollutants utilising the sensitivity and resolution power of a GCxGC TOFMS.

8.2 Experimental

8.2.1 Sample preparation

The extraction of PM_{10} filter samples was performed by an accelerated solvent extraction system ASE350 (Dionex Ltd, Camberley, UK). Packing agents including Silica gel 60, anhydrous sodium sulphate (Sigma-Aldrich Company Ltd., Dorset, UK) and diatomaceous earth (Dionex Ltd., Camberley, UK) were baked at 450°C for 8 hours prior to use. Silica gel 60 was deactivated with 10% (w/w) deionised water.

A quartz fibre filter was cut into small pieces and packed into a 100 mL stainless steel extraction cell together with in-cell clean-up agents. Approximately 3 g of Silica gel and 3 g of anhydrous sodium sulphate were used per filter (a filter sample weighed between 4.2 – 4.4 g containing approximately 0.1 g of particulate matter). Each sample was extracted in 3 cycles at 110°C with 6 minutes static time using a 4:1 ratio toluene/hexane flushing at 30% of the cell volume. Combined extracts were dried with anhydrous sodium sulphate (if required) before solvent removal by a Syncore® Analyst parallel concentration system (Buchi UK Ltd., Oldham, UK). The final volume of each sample was adjusted to 1.5 mL and preserved at -80°C until analysis.

8.2.2 GCxGC TOFMS analysis

After quantification of ambient PAHs using a GC-QMS, the analytical method for non-targeted contaminants in particulate samples is developed using GCxGC

TOFMS. A comprehensive method aimed to extend the analytical range for trace level air contaminants developed using an Agilent 7890A gas chromatograph coupled with a LECO Pegasus 4D time-of-flight mass spectrometer.

The non-targeted screening of PM_{10} sample extracts was performed by a GCxGC TOFMS (LECO Corporation, St. Joseph, Michigan, USA). Reverse phase column conditions were used with a primary column TR-50MS (28 m x 0.25 mm i.d. x 0.25 µm df) and a secondary column Rxi-5Sil MS (1.5 m x 0.25 mm i.d. x 0.25 µm df) connected via a Restek Press-tight® glass connector (Thames Restek UK Ltd., Saunderton, UK). The primary column stationary phase was mid-polarity 50% phenyl polysilphenylene-siloxane while the secondary column was low-polarity Crossbond® 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane.

The oven temperature programme initial temperature was 60°C with 2 min isothermal then ramped at 10°C min^{-1} to 110°C, then at 3°C min^{-1} to 210°C and then at 8°C min^{-1} to 310°C with 15 min isothermal. The secondary oven temperature offset was at 10°C above the primary oven temperature. The modulator temperature offset was set at 20°C relative to the primary oven temperature with the modulation period of 6 seconds. The hot pulse time and cool time of the modulator were 1.30 and 1.70 s. The transfer line temperature was set at 300°C. A 1 µL of sample was injected under splitless mode using a Gerstel-Twister MPS2 Autosampler (Gerstel, MD, USA). The injector temperature was set at 250°C. Helium carrier gas flow rate was held constant at 1 mL min^{-1} throughout the run.

Samples were scanned at 200 spectra per second with the mass range between 45 and 550 amu. Ion source temperature was set at 200°C. The acquisition voltage and electron ionisation voltage were set at 1700 V and 70 eV. GCxGC data processing was done using the ChromaTOF® software (Version 4.50, LECO Corporation). Peak detection was set at the signal to noise ratio of 60:1 (S/N 60:1) with the maximum number of 10,000 peaks to be detected. Mass spectra of samples were compared with the reference mass spectra of the NIST mass spectral database (Gaitherburg, MD, USA) provided by the National Institute of Standard and Technology (NIST). A list

of hit compounds tentatively identified by the automatic search of the software gave 10 hit compounds per spectrum. Thus manual interpretation is required when identifying peaks from library search results.

8.3 Results and Discussion

Due to the low concentration of compounds in the PM_{10} extract, the attempt to identify unknown pollutants from GC-QMS scan results was not successful. The library search of unknown compounds in these samples was hindered by low intensity signals that often appeared as mixture at the same time. The complexity of the mass spectrum failed the library search and therefore the screening of unknown compounds was beyond the capability of the GC-QMS used in this study.

In order to further investigate information contained in the ambient PM_{10} obtained from Thailand, the GCxGC TOFMS was utilised for the screening of unknown pollutants. The analysis of PM_{10} extract by the GCxGC TOFMS revealed several groups of semi-volatile organic compounds that can be classified according to molecular structures and functional groups appearing in different regions of a chromatogram. Samples from roadside, industrial and urban background sites were screened for air contaminants. The TOFMS scanned the mass range from 45 to 550 amu and the mass spectra of peaks identified were compared with standard mass spectrum of the NIST mass spectral database. Chromatograms of a split sample analysed by GC-MS and GCxGC TOFMS were compared in Figure 8.4.

The GCxGC result showed that hundreds of peaks can be found in the ambient PM_{10} sample extract owing to the high sensitivity of the TOFMS. The distribution of peaks in the second dimension indicated the coelution in 1D-GC which obstructed the identification of unknown compounds as a result of peak purity issue. The chromatographic separation power of the GCxGC resolved peaks coelution while the sensitivity of the TOFMS enabled the detection of substances below picogramme level. In addition to the quantification of 16 US EPA priority PAHs using a GC-QMS, the identification of trace air contaminants in particulate matter can be done by the GCxGC TOFMS.

Another advantage of a GCxGC is that the column configuration can be arranged in order of increasing polarity from column 1 to column 2 (normal phase) or decreasing polarity (reverse phase). The column configuration can alter the order of elution of compounds from low to high polarity in normal phase and vice versa. In order to separate semi-volatile compounds with higher polarities and boiling points, the reverse phase column conditions were selected to allow the faster elution of polar compounds than non-polar compounds. The analytical conditions resulted in the separation of 16 US EPA priority PAHs relatively fast on the second dimension as they appeared in the bottom half of the chromatogram shown in Figure 8.5(a). The sample chromatogram, Figure 8.5(b), revealed separated bands of potential homologous series in different regions. It is shown that most peaks are distributed in the bottom half of the plot indicating compounds with relatively high polarity.

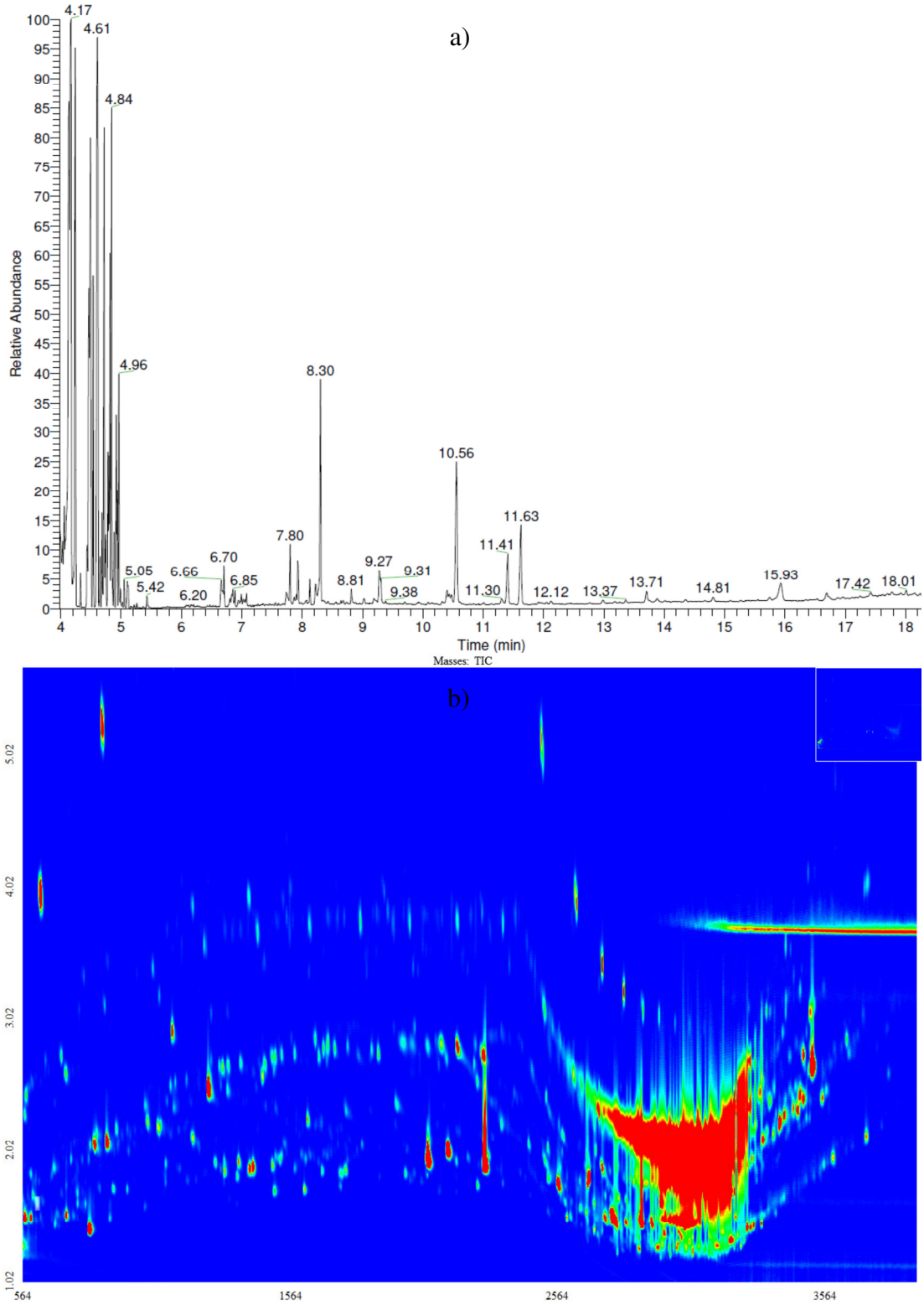

Figure 8.4 Total ion chromatograms of a sample collected from the industrial site on 5th October 2013 split into 2 halves and analysed by a) GC-QMS and b) GCxGC TOFMS.

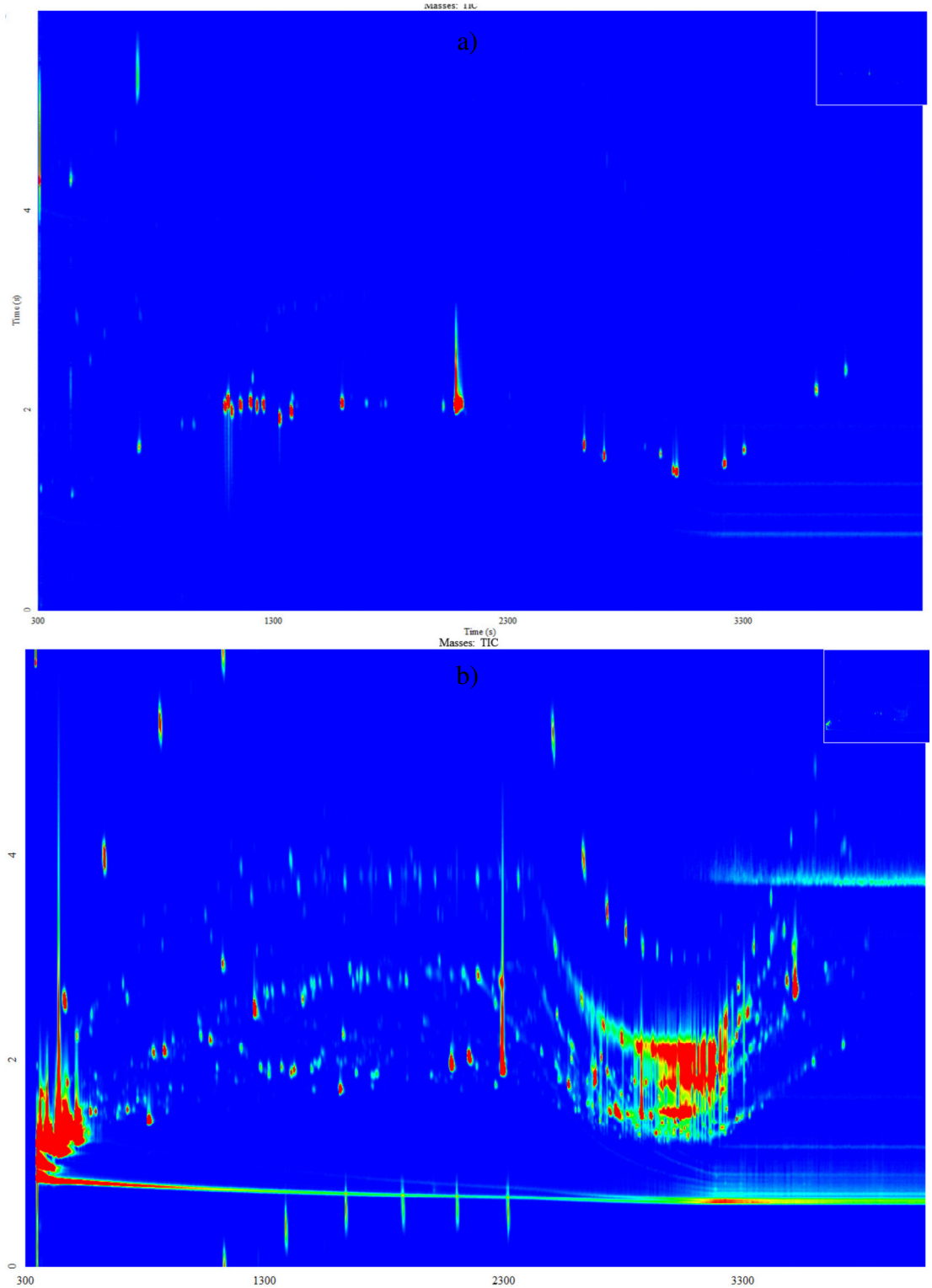

Figure 8.5 GCxGC TOFMS contour plots of a) standard solution of the US EPA 16 PAHs and b) PM_{10} sample extract from urban background site collected on 3rd January 2014.

GCxGC data were processed using the ChromaTOF® software returning a peak table of 10,000 peaks specified in the processing setup. Each peak contained a list of 10 hit compounds, tentatively identified compounds, selected from the match between sample and reference mass spectra in terms of similarity (forward search) or reverse (reverse search). Mass spectra of sample peaks were reviewed in order to identify unknown air pollutants. Series of compounds possessing similar properties were found clustering together, hence classification of unknowns in groups. Figure 8.6, 8.7 and 8.8 illustrated the classification of substances identified in samples from industrial, roadside and urban background sites, respectively. Samples from industrial and roadside sites were collected on 5th October 2013. The urban background sample was collected on 3rd January 2014.

Several groups of organic air pollutants were found in PM_{10} samples. The reverse phase columns setup facilitated faster separation of more polarity compounds. This can be seen clearly in the second dimension. PAHs and alkylated PAHs eluted faster and appeared from 1 to 2 s while low polarity straight chain and branched alkanes were distributed from 2 to 4 s. Low molecular weight compounds eluted faster in the first dimension as they were separated according to the increasing carbon number. In other words, separation of the first dimension is the property of 1D-GC. The second dimension separated peaks those would have been coeluted in 1D-GC and thus sample peaks were chromatographically purified by the GCxGC separation.

Compounds identified in all samples were classified into groups including straight-chain and branched alkanes; alkanes with a phenyl group; substituted naphthalene including methyl naphthalene (C1-naphthalene), dimethyl/ethyl naphthalene (C2-naphthalene), trimethyl/ethyl-methyl naphthalene (C3-naphthalene); biphenyl derivatives and PAHs with different ring numbers. Various compounds were not classified in major groups but also found in samples such as alcohols, diols, aldehydes, ketones, esters, organic acids, etc. The results of this study showed very diverse particulate phase air pollutants those occurred at trace amounts. Furthermore, high molecular weight PAHs ranging from 4-ring to 6-ring other than 16 US EPA

priority PAHs were found in all samples. Particulate matter is a complex matrix that contains a variety of semi-volatile air pollutants.

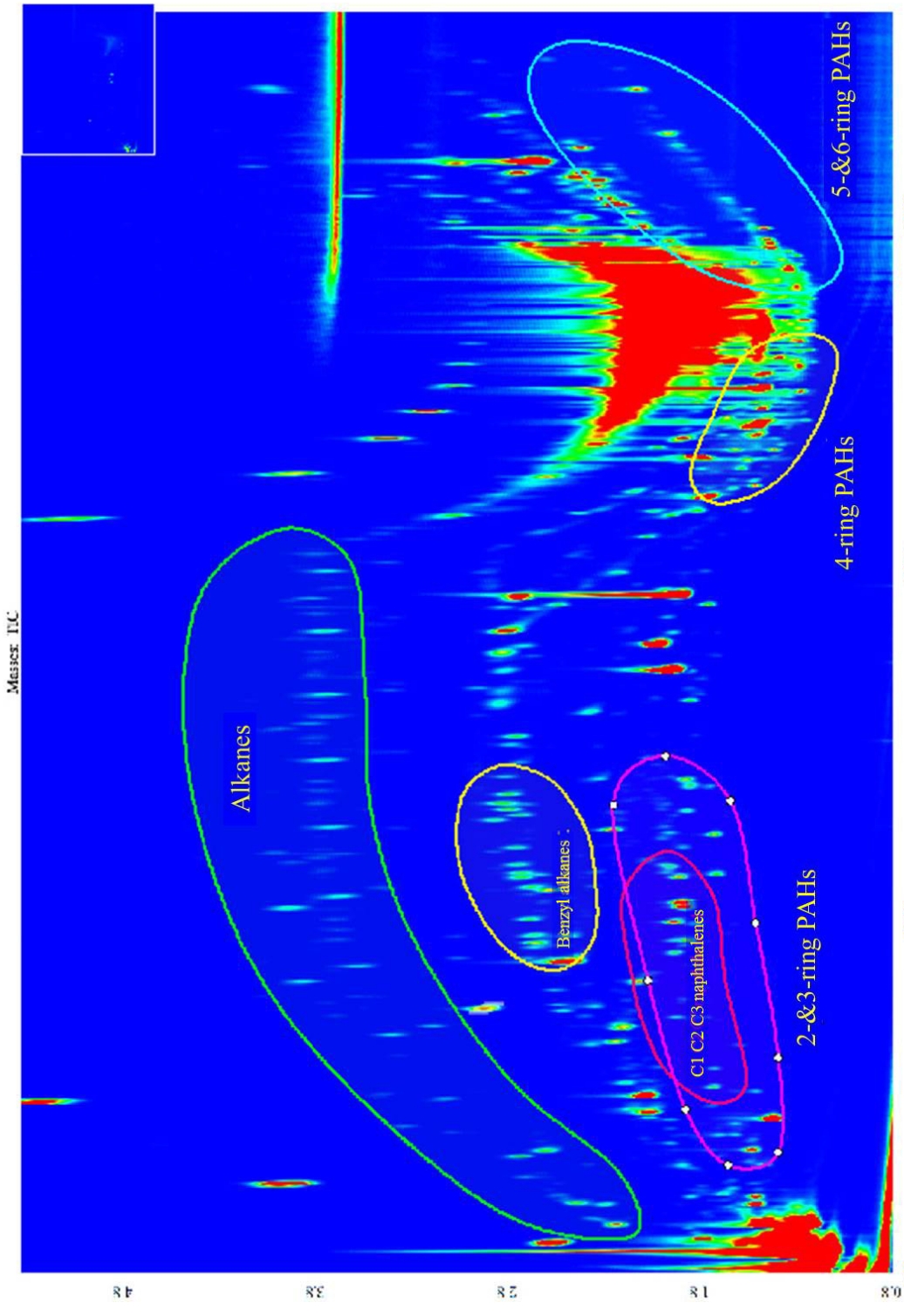

Figure 8.6 Classification of compounds in the PM_{10} sample extract collected from the industrial site on 5th October 2013.

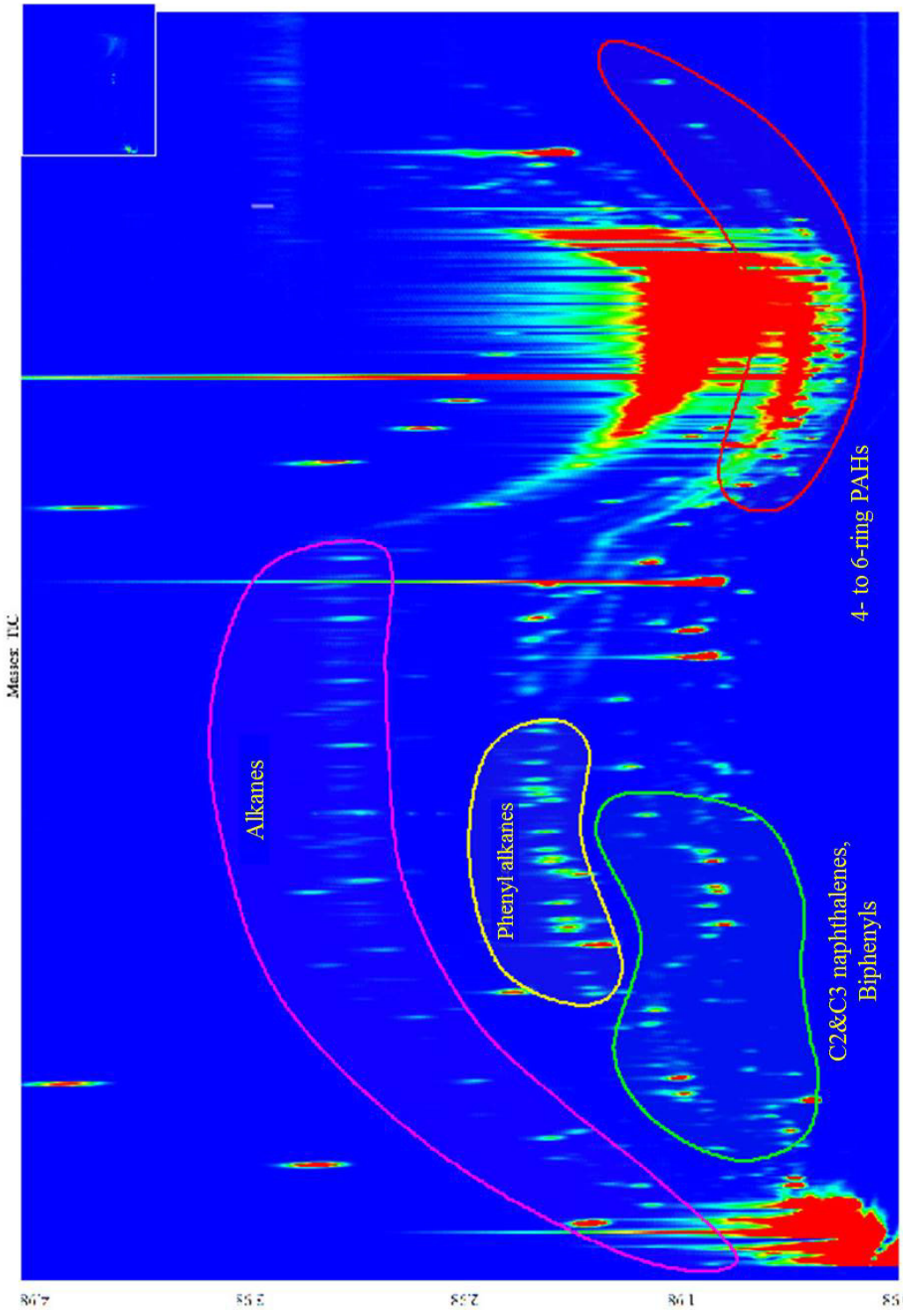

Figure 8.7 Classification of compounds in the PM_{10} sample extract collected from the roadside site on 5th October 2013.

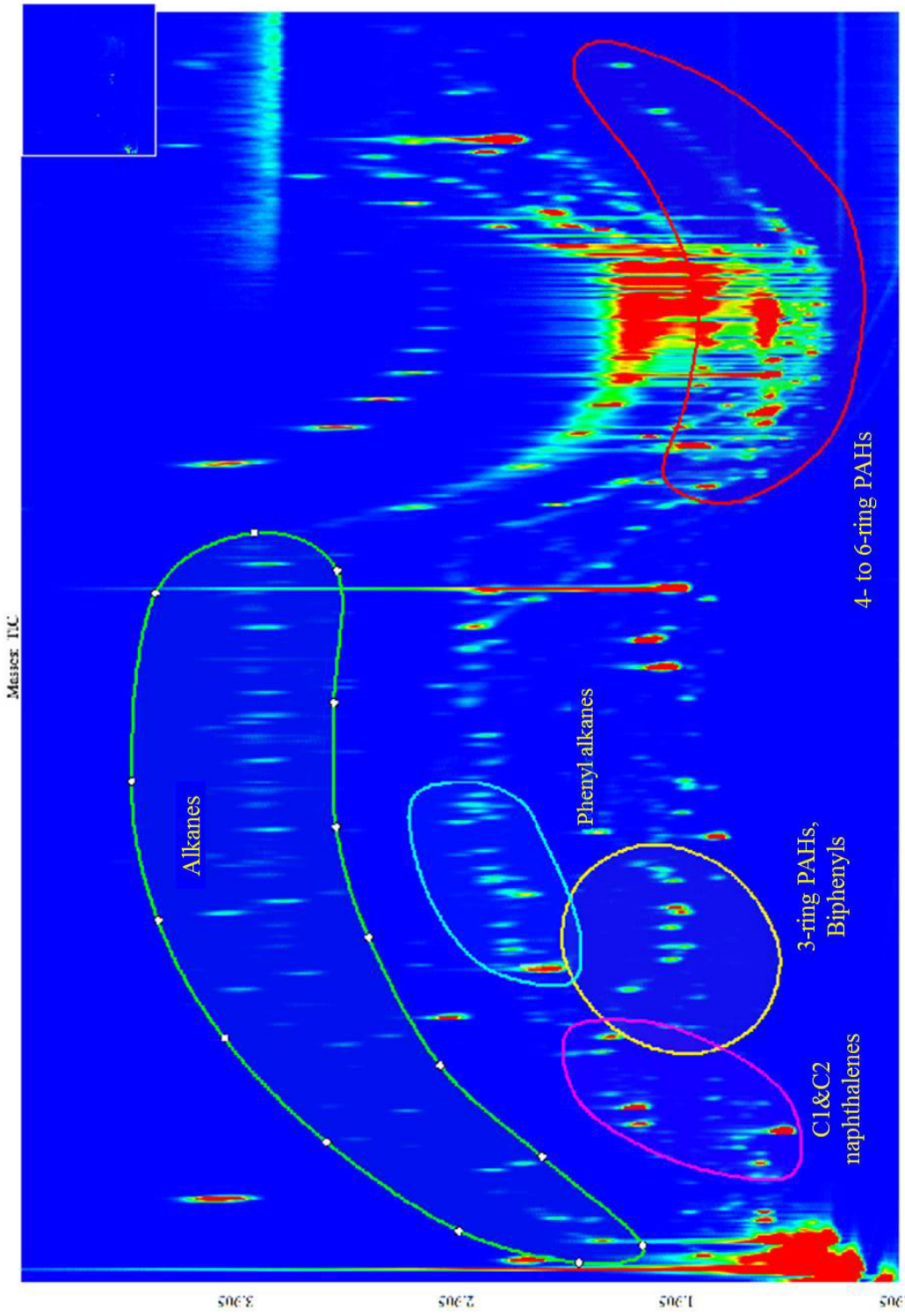

Figure 8.8 Classification of compounds in the PM_{10} sample extract collected from the urban background site on 3rd January 2014.

Data acquired by a GCxGC required intensive manual interpretation. Among thousands of peaks found, some can be identified by matching with spectra available in the software database. Library search results of a sample were compiled in a peak table containing peak specific information including retention times (first and second dimensions), similarity, probability, peak area, formula, etc. After reviewing data, particularly the sample mass spectrum and the hit compound(s), pollutants found in PM_{10} sample extracts were manually verified and shown in Table 8.1.

Extracts of PM_{10} samples collected from industrial, roadside and background sites in the Bangkok Metropolitan Administration were scanned from mass 45 to 550 amu. The data processing method was programmed to find 10,000 peaks in each sample. Found peaks and library search hit compounds (10 compounds per peak) were reviewed manually. Approximately a hundred compounds were tentatively identified in each sample. After manual reviewing automatic library search results, 248 compounds were identified in 3 extracts. Toxicity of chemicals found in samples including irritation to eyes, skin, mucous membrane and respiratory system. Benzo[j]fluoranthene found in all sample is identified as IARC group 2B which is possible carcinogenic to humans. Several peaks were isomers of high molecular weight PAHs found in the region of 4-ring to 6-ring PAHs. Classification of PAHs according to numbers of ring can be seen in chromatograms; however, identification of these unknown PAHs was not possible without PAHs standard. These PAHs may pose additional health risk in terms of carcinogenicity and mutagenicity of PM_{10} estimated in previous chapter.

Table 8.1 Non-targeted screening of PM_{10} samples from the industrial site (Ind), roadside site (Rd) and urban background site (Bg).

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
1	Undecane	$C_{11}H_{24}$	156	378	1.560	923		x		x
2	2,9-dimethyldecane	$C_{12}H_{26}$	170	516	2.235	856	x			
3	3-Nitro-4-phenyl-2-butanol	$C_{10}H_{13}O_3$	195	516	1.515	680			x	
4	4,6-Dimethyldodecane	$C_{14}H_{30}$	198	516	2.240	842			x	
5	2-Methylundecane	$C_{12}H_{26}$	170	516	2.125	839		x		
6	1-Methyl-4-isopropylbenzene	$C_{10}H_{14}$	134	522	1.465	865			x	x
7	1,4-Diethyl-2-methylbenzene	$C_{11}H_{16}$	148	528	1.510	743			x	
8	2,4,6-Trimethyloctane	$C_{11}H_{24}$	156	528	2.320	814			x	
9	1,2,4-Trimethylbenzene	C_9H_{12}	120	534	1.125	663			x	x
10	1-Isopropenyl-4-methyl-1,3-cyclohexadiene	$C_{10}H_{14}$	134	534	1.320	518			x	
11	C5 benzene	$C_{11}H_{16}$	148	558	1.580	754			x	
12	Acetophenone	C_8H_8O	120	564	1.290	869			x	x
13	Benzyl formate	C_8H_8O	136	564	1.350	818			x	
14	2,6,8-Trimethyldecane	$C_{13}H_{28}$	184	570	2.305	823	x			

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
15	1-Methylindane	$C_{10}H_{12}$	132	570	1.505	768			x	
16	$C_{13}H_{28}$ (alkane)	$C_{13}H_{28}$	184	570	2.175	913		x		
17	Tridecane	$C_{13}H_{28}$	184	576	2.450	861	x		x	x
18	2,6,8-Trimethyldecane	$C_{13}H_{28}$	184	576	2.285	841			x	
19	3,7-Dimethylundecane	$C_{11}H_{24}$	184	576	2.320	857		x		
20	1-(1-Ethylpropyl)-4-methylbenzene	$C_{12}H_{18}$	162	582	1.680	756			x	
21	Benzyl alcohol	C_7H_8O	108	606	1.225	820			x	x
22	Ethylphenylacetylene	$C_{10}H_{10}$	130	612	1.500	832			x	
23	1,2-Dimethylindane	$C_{11}H_{14}$	146	618	1.625	830			x	
24	1H-3-Methylindene	$C_{10}H_{10}$	130	630	1.505	820			x	
25	Tetrahydronaphthalene	$C_{10}H_{12}$	132	630	1.535	827			x	
26	1,1-Dimethylindane	$C_{11}H_{14}$	146	642	1.640	794			x	
27	4,7-Dimethylundecane	$C_{13}H_{28}$	184	648	2.555	872		x		
28	Benzyl acetate	$C_9H_{10}O_2$	150	684	1.455	745			x	x
29	$C_{14}H_{30}$ (alkane)	$C_{14}H_{30}$	184	708	2.735	878	x			

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
30	2-Ethylindane	$C_{11}H_{14}$	146	708	1.695	729			x	
31	2,5,9-Trimethyldecane	$C_{13}H_{28}$	184	708	2.740	819			x	
32	Tetradecane	$C_{14}H_{30}$	198	708	2.580	921		x		x
33	5-Tetradecene	$C_{14}H_{28}$	196	726	2.600	881	x			
34	Dimethylindane isomer	$C_{11}H_{14}$	146	726	1.755	754			x	
35	3-Dodecene	$C_{12}H_{24}$	168	726	2.600	880			x	
36	3-Tetradecene	$C_{14}H_{28}$	196	726	2.455	875		x		
37	Naphthalene	$C_{10}H_{8}$	128	726	1.475	927	x	x	x	x
38	Dimethylindane isomer	$C_{11}H_{14}$	146	750	1.780	820	x			
39	p-Nitrotoluene	$C_{7}H_{7}NO_{2}$	137	750	1.485	851		x		x
40	1-Methyl-3-nitrobenzene	$C_{7}H_{7}NO_{2}$	137	756	1.525	812	x			x
41	2-Methyl-1-undecanol	$C_{12}H_{16}O$	186	756	2.085	740	x			
42	2-Benzothiophene	$C_{8}H_{6}S$	134	768	1.510	694	x			
43	di-N-Butylnitrosamine	$C_{8}H_{18}N_{2}O$	158	768	1.695	825	x			
44	2,6-Dimethylbenzaldehyde	$C_{9}H_{10}O$	134	780	1.595	669	x			

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
45	1-Ethoxy-4-ethylbenzene	$C_{10}H_{14}O$	150	786	1.715	645	x			
46	4,7-Dimethylindane	$C_{11}H_{14}$	146	798	1.790	751	x			
47	3,4-Dihydro-1-naphthalenylacetic acid	$C_{12}H_{12}O_2$	188	816	2.065	589	x	x		
48	Dimethylindane isomer	$C_{11}H_{12}$	144	822	1.955	516		x		
49	1-(2-Hydroxy-1-methylethyl)-2,2-dimethylpropyl 2-methylpropanoate	$C_{12}H_{24}O_3$	216	834	2.075	861		x	x	
50	1-Undecanol	$C_{11}H_{24}O$	172	840	2.145	857	x			x
51	p-tert-Butylphenol	$C_{10}H_{14}O$	150	852	1.735	789	x			
52	Pentadecane	$C_{15}H_{32}$	212	870	2.930	865	x	x		x
53	3-Hydroxy-2,4,4-trimethylpentyl-2-methylpropanoate	$C_{12}H_{24}O_3$	216	876	2.090	855	x			
54	Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	$C_{12}H_{24}O_3$	216	876	2.100	843			x	
55	3-Hydroxy-2,4,4-trimethylpentyl 2-methylpropanoate	$C_{12}H_{24}O_3$	216	876	2.000	849		x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
56	Benzotriazole	C_7H_5NS	135	888	1.455	896	x	x		
57	2-Methylnaphthalene	$C_{11}H_{10}$	142	900	1.735	886	x		x	x
58	Benzocycloheptatriene	$C_{11}H_{10}$	142	900	1.670	876		x		
59	1-Methylnaphthalene	$C_{11}H_{10}$	142	954	1.730	870	x		x	x
60	p-tert-Butylstyrene	$C_{12}H_{16}$	160	1014	1.985	682	x			
61	1-Nonanol	$C_9H_{20}O$	144	1020	2.370	883	x			x
62	2,6-Dimethyl-4-octene	$C_{10}H_{20}$	140	1020	2.260	776		x		
63	2(3H)-Benzofuranone, 3a,4,5,6-tetrahydro-3a,6,6,-trimethyl	$C_{11}H_{16}O_2$	180	1032	2.265	555			x	
64	Hexadecane	$C_{16}H_{34}$	226	1050	3.200	890	x	x		x
65	n-Tridecanol	$C_{13}H_{28}O$	200	1074	3.195	865	x			x
66	5,10-Pentadecadiyno-1-ol	$C_{15}H_{24}O$	220	1074	2.090	356		x		
67	Dipropyl hexanedioate	$C_{12}H_{22}O_4$	230	1080	2.020	785	x			
68	2-Ethylnaphthalene	$C_{12}H_{12}$	156	1086	1.875	832	x			
69	1,1-Diphenylethane	$C_{14}H_{14}$	182	1093	1.935	740	x			

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
70	1-Ethylnaphthalene	$C_{12}H_{12}$	156	1098	1.915	583	x			
71	Biphenyl	$C_{12}H_{10}$	154	1098	1.715	900		x		x
72	C2 naphthalene	$C_{12}H_{12}$	156	1098	1.835			x		
73	C2 naphthalene	$C_{12}H_{12}$	156	1104	1.895	654	x			
74	2-Undecen-1-ol	$C_{11}H_{22}O$	170	1104	2.400	870	x			
75	5-Phenyldecane	$C_{16}H_{26}$	218	1116	2.390	877	x	x		
76	Oxalic acid, decyl propyl ester	$C_{15}H_{28}O_4$	272	1128	2.355	614	x			
77	4-Phenyldecane	$C_{16}H_{26}$	218	1134	2.405	860		x		
78	2,3-Dimethylnaphthalene	$C_{12}H_{12}$	156	1152	1.885	862	x			
79	C2 naphthalene	$C_{12}H_{12}$	156	1152	1.815			x	x	
80	C2 naphthalene	$C_{12}H_{12}$	156	1194	1.915				x	
81	2,6,10-Trimethyldodecane	$C_{15}H_{32}$	212	1200	3.870	862			x	
82	2,3,5,8-Tetramethyldecane	$C_{14}H_{30}$	198	1200	3.620	836		x		
83	C21H44 (branched alkane)	$C_{21}H_{44}$	296	1200	3.620	848		x		
84	1-Naphthylaldehyde	$C_{11}H_8O$	156	1206	1.805	434		x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
85	C2 naphthalene	$C_{12}H_{12}$	156	1218	1.880	628	x			
86	Heptadecane	$C_{17}H_{36}$	240	1242	3.585	899	x			
87	C2 naphthalene	$C_{12}H_{12}$	156	1248	1.885	764	x		x	
88	Propionic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	$C_{16}H_{30}O_4$	286	1254	2.510	886			x	
89	Propanoic acid, 2-methyl-, 1-(1,1-dimethyl)-2-methyl-1,3-propanediyl ester	$C_{17}H_{30}O_4$	286	1254	2.365	909		x		
90	Acenaphthene	$C_{12}H_{10}$	154	1262	1.830	884	x			x
91	2-Phenyldecane	$C_{16}H_{26}$	218	1266	2.575	856			x	
92	2,4a-Dihydrofluorene	$C_{13}H_{12}$	168	1278	1.965	544			x	
93	2-Ethylbiphenyl	$C_{14}H_{14}$	182	1284	1.850	809		x		
94	6-Phenylundecane	$C_{17}H_{28}$	232	1296	2.675	851		x	x	
95	4-Methylbiphenyl	$C_{13}H_{12}$	168	1302	1.820	874		x		x
96	5-Phenylundecane	$C_{17}H_{28}$	232	1308	2.655	866		x	x	

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
97	1-Phenylethyl benzene	$C_{14}H_{14}$	182	1314	1.870	780	x			
98	Acenaphthylene	$C_{12}H_{8}$	152	1314	1.780	702			x	x
99	1,1-Diphenylethane	$C_{14}H_{14}$	182	1314	1.790	798		x		
100	4-Phenylundecane	$C_{17}H_{28}$	232	1332	2.665	856			x	
101	C3 naphthalene	$C_{13}H_{14}$	170	1344	1.915			x		
102	C3 naphthalene	$C_{13}H_{14}$	170	1350	2.035	748	x			
103	Acenaphthene	$C_{12}H_{10}$	154	1362	1.830	820		x	x	x
104	Benzyl sulfone	$C_{14}H_{14}O_2S$	246	1368	1.940	866			x	
105	3-Phenylundecane	$C_{17}H_{28}$	232	1374	2.705	818			x	
106	Phenylundecane	$C_{17}H_{28}$	232	1374	2.550	840		x		
107	C3 naphthalene	$C_{13}H_{14}$	170	1398	1.945			x		
108	1-Benzyl-3-methylbenzene	$C_{14}H_{14}$	182	1410	1.885	826	x			
109	p-Benzyltoluene	$C_{14}H_{14}$	182	1410	1.890	875		x	x	
110	2-Methyldodecane	$C_{13}H_{28}$	184	1410	3.690	827		x		
111	2,2'-Dimethylbiphenyl	$C_{14}H_{14}$	182	1422	1.905	776	x	x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
112	1-Benzyl-3-methylbenzene	$C_{14}H_{14}$	182	1422	1.915	851			x	
113	1,1-Diphenylethane	$C_{14}H_{14}$	182	1428	1.825	780		x		
114	3-Methyltridecane	$C_{14}H_{30}$	198	1440	3.680	857	x			
115	C3 naphthalene	$C_{13}H_{14}$	170	1452	2.015	664	x			
116	Dodecyl acrylate	$C_{15}H_{28}O_2$	240	1458	2.595	895		x	x	
117	2-Phenylundecane	$C_{17}H_{28}$	232	1464	2.685	846	x		x	
118	4,4'-Dimethylphenylmethane	$C_{15}H_{16}$	196	1494	1.915	824	x			
119	2,2-Diphenylpropane	$C_{15}H_{16}$	296	1494	1.925	846			x	
120	6-Phenylundecane	$C_{18}H_{30}$	246	1494	2.750	829			x	
121	Di-p-tolylmethane	$C_{15}H_{16}$	196	1494	1.840	822		x		
122	Dimethylbiphenyl	$C_{14}H_{14}$	182	1506	1.985	749	x			
123	5-Phenyldodecane	$C_{18}H_{30}$	246	1506	2.730	843	x		x	
124	2-Naphthalenecarboxaldehyde	$C_{11}H_8O$	156	1506	1.700	792		x		
125	Bis-p-tolylmethane	$C_{15}H_{16}$	196	1524	1.955	813			x	
126	2,2'-Diphenylpropane	$C_{15}H_{16}$	196	1524	1.870	820		x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
127	4-Phenyldodecane	$C_{18}H_{30}$	246	1530	2.745	822	x			
128	4,4'-Dimethylbiphenyl	$C_{14}H_{14}$	182	1530	2.005	882			x	
129	4-Phenyldodecane	$C_{18}H_{30}$	246	1530	2.765	873		x	x	
130	3-Phenyldodecane	$C_{18}H_{30}$	246	1578	2.750	861	x			
131	3-Phenylundecane	$C_{17}H_{28}$	246	1578	2.785	768			x	
132	Fluorene	$C_{13}H_{10}$	166	1578	1.815	835	x	x		x
133	C6 naphthalene	$C_{16}H_{20}$	212	1608	2.060	726		x		
134	Isopropyl myristate	$C_{17}H_{34}O_2$	270	1656	2.865	805	x		x	x
135	2-Phenyldodecane	$C_{18}H_{30}$	246	1668	2.740	860	x			
136	(2-Phenoxyethyl)benzene	$C_{14}H_{14}O$	198	1680	1.810	901		x		
137	C6 naphthalene	$C_{16}H_{20}$	212	1680	2.150	771		x		
138	6-Phenyltridecane	$C_{19}H_{32}$	260	1686	2.795	796	x		x	
139	2,2',5,5'-Tetramethyl-1,1'-biphenyl	$C_{16}H_{18}$	210	1686	1.915	739		x		
140	Methyl-9H-fluorene	$C_{14}H_{12}$	180	1698	1.905	570		x		
141	2-Methylhexadecanal	$C_{17}H_{34}O$	254	1704	2.845	803	x			

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
142	9,9-Dimethylxantene	$C_{15}H_{14}O$	210	1716	1.980	632	x			
143	4-Phenyltridecane	$C_{19}H_{32}$	260	1728	2.650	766		x		
144	1-Methyl-2-(phenylmethoxy)-benzene	$C_{14}H_{14}O$	198	1746	1.785	814		x		
145	1-Phenyl-1-phenoxyethane	$C_{14}H_{14}O$	198	1752	1.780	623		x		x
146	Benzophenone	$C_{13}H_{10}O$	182	1752	1.685	883		x		
147	(2-Phenoxyethyl)benzene	$C_{14}H_{14}O$	198	1770	1.800	854		x		
148	Methyl-9H-fluorene	$C_{14}H_{12}$	180	1776	1.875	509		x		
149	$C_{14}H_{14}O$	$C_{14}H_{14}O$	260	1776	2.700	645		x		
150	1-Methylfluorene	$C_{14}H_{12}$	180	1800	1.970	662			x	
151	Acenaphthylene	$C_{12}H_{8}$	152	1814	1.705	752		x		x
152	1-Dodecanol	$C_{12}H_{26}O$	186	1818	2.755	872			x	x
153	Nonadecane	$C_{19}H_{40}$	268	1824	3.745	898	x	x		
154	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	$C_{15}H_{22}O_{2}$	234	1830	1.985	719		x		
155	(1-Bromoethyl)benzene	$C_{8}H_{9}Br$	184	1866	2.810	855			x	x
156	2-Phenyltridecane	$C_{19}H_{32}$	260	1866	2.650	818		x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
157	Methyl undacanoate	$C_{12}H_{24}O_2$	200	1890	2.770	788	x			
158	Dipropyleneglycol	$C_6H_{14}O_3$	134	1986	2.830	785	x			x
159	Phenanthrene	$C_{14}H_{10}$	178	2076	1.845	914	x	x	x	x
160	Dipropyleneglycol	$C_6H_{14}O_3$	134	2130	2.820	802	x	x		
161	7,9-Di-tert-butyl-1-oxospiro(4,5)deca-6,9-diene-2,8-dione	$C_{17}H_{24}O_3$	276	2154	2.035	917		x	x	
162	8-Dodecenol	$C_{12}H_{24}O$	184	2178	2.355	571		x		
163	1-Hexadecanol	$C_{17}H_{34}O$	242	2190	2.800	920	x	x		x
164	Tridecanol	$C_{13}H_{28}O$	200	2190	2.820	907			x	x
165	Benzil dimethylketal	$C_{16}H_{16}O_3$	256	2262	1.690	881		x		
166	$C_6H_{14}O_3$	$C_6H_{14}O_3$	134	2286	2.745	770	x		x	
167	Triethyleneglycol	$C_6H_{14}O_4$	150	2352	2.245	604		x	x	x
168	4,5-Dihydropyrene	$C_{16}H_{12}$	204	2442	1.815	681	x			
169	Phenylnaphthalene	$C_{16}H_{12}$	204	2442	1.820	703			x	
170	4-Hydroxyundecanoic acid lactone	$C_{11}H_{20}O_2$	184	2454	2.090	847		x	x	

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
171	Ethyl cyclohexyl ketone	$C_9H_{16}O$	140	2520	2.320	488		x		
172	Ethylhexylcinnamate	$C_{13}H_{26}O_3$	290	2592	1.625	841	x			
173	2-Ethylhexyl methoxycinnamate	$C_{18}H_{26}O_3$	290	2592	1.570	815		x		
174	Dibenzyl disulfide	$C_{14}H_{14}S_2$	246	2598	1.465	850		x		
175	Fluoranthene	$C_{16}H_{10}$	202	2610	1.525	855	x	x	x	x
176	Cyclopenta[d,e,f]phenanthrenone	$C_{15}H_8O$	204	2622	1.465	651	x			
177	1-Iodotetradecane	$C_{14}H_{29}I$	324	2622	2.615	801			x	
178	4-ring PAH	$C_{16}H_{10}$	202	2652	1.425	743		x		
179	4-ring PAH	$C_{16}H_{10}$	202	2652	1.460	826	x			
180	4-ring PAH	$C_{16}H_{10}$	202	2652	1.475	749			x	
181	Hexanedioic acid, dioctyl ester	$C_{22}H_{42}O_4$	370	2682	1.820	895	x			
182	3,10B-Dihydrofluoranthene	$C_{16}H_{12}$	230	2682	1.450	372			x	
183	4-ring PAH	$C_{16}H_{10}$	202	2694	1.455				x	
184	Pyrene	$C_{16}H_{10}$	202	2700	1.380	873	x	x	x	x
185	4-Methoxycinnamic acid	$C_{10}H_{10}O_3$	178	2742	1.445	590		x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
186	Methyl heneicosanoate	$C_{22}H_{44}O_2$	340	2892	1.790	787			x	
187	2-Methyloctadecane	$C_{19}H_{40}$	268	2892	2.160	845			x	
188	Benzanthrone	$C_{17}H_{10}O$	230	2922	1.270	701	x	x		x
189	Cyclopenta[c,d]pyrene	$C_{18}H_{10}$	226	2952	1.275	691		x		
190	11H-Benzo[a]fluoren-11-one	$C_{17}H_{10}O$	230	2976	1.270	751	x	x	x	
191	$C_{17}H_{10}O$	$C_{17}H_{10}O$	230	2976	1.285	592			x	
192	Benz[a]anthracene	$C_{18}H_{12}$	228	2994	1.290	793	x	x	x	x
193	Cyclopenta[c,d]pyrene	$C_{18}H_{10}$	226	3006	1.275	691	x			
194	Chrysene	$C_{18}H_{12}$	228	3012	1.285	722		x	x	x
195	4-ring PAH	$C_{16}H_{10}$	202	3036	1.235	543		x		
196	N-Methyl-N-methoxybenzamide	$C_9H_{11}NO_2$	165	3042	1.265	456	x			
197	6H-Benzo[d,e]anthracen-6-one	$C_{17}H_{10}O$	230	3066	1.235	813	x	x		
198	7-Chloro-1-phenyl-1,4-dihydroquinoxaline	$C_{14}H_{11}ClN_2$	242	3090	1.265	367		x		
199	2,2'-Bynaphthalene	$C_{20}H_{14}$	254	3096	1.275	247	x			
200	Benz[a]anthracene-7,12-dione	$C_{18}H_{10}O_2$	258	3108	1.255	732	x		x	x

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
201	5,12-Naphthacenequinone	$C_{18}H_{10}O_2$	258	3108	1.230	685		x		x
202	9-Phenylanthracene	$C_{20}H_{14}$	254	3120	1.270	510	x			x
203	1,1'-Binaphthalene	$C_{20}H_{14}$	254	3120	1.280	468			x	
204	4-ring PAH	$C_{16}H_{10}$	230	3126	1.230	466	x			
205	$C_{17}H_{10}O$	$C_{17}H_{10}O$	230	3138	1.246				x	
206	2,3-Dihydrofluoranthene	$C_{16}H_{12}$	204	3168	1.245	433	x			x
207	$C_{18}H_{10}O_2$	$C_{18}H_{10}O_2$	258	3168	1.255	519			x	
208	4-ring oxy PAH	$C_{18}H_{10}O_2$	258	3168	1.235	456		x		
209	Perylene	$C_{20}H_{12}$	252	3210	1.340	810	x			x
210	Benzo[b]fluoranthene	$C_{20}H_{12}$	252	3210	1.355	803		x	x	x
211	Benzo[k]fluoranthene	$C_{20}H_{12}$	252	3234	1.375	664	x		x	x
212	Dinaphtho[1,2-b;1',2'-d]furan	$C_{20}H_{12}O$	268	3240	1.405	533			x	
213	1,3,5-Triphenylbenzene	$C_{24}H_{18}$	306	3270	1.430	786	x	x	x	x
214	Benzo[j]fluoranthene	$C_{20}H_{12}$	252	3283	1.450	818	x	x	x	x
215	Benzo[a]pyrene	$C_{20}H_{12}$	252	3294	1.450	800	x	x	x	x

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
216	5-ring PAH	$C_{22}H_{14}$	252	3300	1.460			x		
217	1,3-Diethynylanthracene	$C_{18}H_{10}$	226	3324	1.460	664	x			
218	Benzo[e]pyrene	$C_{22}H_{14}$	252	3324	1.510	708			x	x
219	Benzo[j]fluoranthene	$C_{20}H_{12}$	252	3324	1.460	668	x	x		
220	5-ring PAH	$C_{22}H_{14}$	278	3330	1.520	334			x	
221	5-ring PAH	$C_{21}H_{14}$	266	3330	1.560	572			x	
222	2,4,6-Triphenylpyridine	$C_{23}H_{11}N$	307	3336	1.545	745			x	
223	Dibenzo[a,j]anthracene	$C_{22}H_{14}$	278	3336	1.510	372		x		x
224	1,3-Diethynyl anthracene	$C_{18}H_{10}$	226	3347	1.460	664	x			
225	3-Methylperylene	$C_{21}H_{14}$	266	3396	1.670	455			x	
226	13H-Dibenzo[a,h]fluorene	$C_{21}H_{14}$	266	3396	1.615	554		x		
227	Perylene	$C_{20}H_{12}$	252	3462	1.760	453			x	
228	6-ring PAH	$C_{22}H_{12}$	267	3492	1.380				x	
229	6-ring PAH	$C_{22}H_{12}$	267	3492	1.805		x			
230	Dibenzo[cd,jk]pyrene	$C_{22}H_{12}$	276	3492	1.830	732			x	

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
231	6-ring PAH	$C_{22}H_{12}$	267	3492	1.770			x		
232	Dibenzo[a,c]fluoren-13-one	$C_{21}H_{12}O$	280	3516	1.860	590			x	
233	Pentacene	$C_{22}H_{14}$	278	3546	1.910	585			x	
234	Indeno[1,2,3-cd]fluoranthene	$C_{22}H_{12}$	276	3558	1.920	816	x	x	x	
235	5-ring PAH	$C_{22}H_{14}$	278	3582	1.980	561			x	
236	Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	3588	1.970	824	x	x	x	x
237	Dibenz[a,h]anthracene	$C_{22}H_{14}$	278	3600	2.000	474		x	x	x
238	Benzo[b]triphenylene	$C_{22}H_{14}$	278	3642	2.045	597			x	x
239	5-ring PAH	$C_{22}H_{14}$	278	3660	2.030	650	x			
240	5-ring PAH	$C_{22}H_{14}$	278	3666	2.075	588			x	
241	6-ring PAH	$C_{22}H_{12}$	276	3672	2.055		x	x		
242	Benzo[g,h,i]perylene	$C_{22}H_{12}$	276	3708	2.070	840	x	x	x	x
243	6-ring PAH	$C_{22}H_{12}$	276	3756	2.175		x			
244	6-ring PAH	$C_{22}H_{12}$	276	3768	2.240				x	
245	6-ring PAH	$C_{22}H_{12}$	276	3774	2.155			x		

No	Chemical	FW	MW	1st RT (s)	2nd RT (s)	Similarity	Ind	Rd	Bg	Toxicity [a]
246	6-ring PAH	$C_{22}H_{12}$	276	3774	2.205		x			
247	6-ring PAH	$C_{22}H_{12}$	276	3774	2.225				x	
248	4-Methylbenzo[g,h,i]perylene	$C_{23}H_{14}$	290	3948	2.550	557	x			
	Total						99	103	109	55

[a] U.S. National Library of Medicine (2016) Human health effects

8.4 Conclusion

GCxGC TOFMS is a powerful tool for the investigation of unknown air pollutants in particulate matter. Ambient PM_{10}-bound PAHs were detected in the nanogramme range with the selected ion monitoring mode of the GC-QMS. However, trace levels of pollutants in ambient particles is a hindrance to the identification of unknown compounds in the scan mode of the GC-QMS. With the high separation power and high sensitivity the GCxGC TOFMS, thousands of chromatographic peaks were revealed. The search results showed identified peaks according to the data processing setup giving a list of hit compounds with corresponding match number i.e. similarity. The higher match number implied the better similarity between the reference mass spectra and the sample mass spectra which also depended on a search algorithm. The identification is limited to the mass spectral database availability. Therefore, it can be used to support but not pinpoint the result. Compounds identified by the software need to be reviewed before reporting. Among 10,000 found peaks, a few hundreds to thousands might be confidently identified depending on the availability of mass spectral database and skills of an analyst. In this study, almost 250 compounds were identified in 3 PM_{10} samples collected from industrial, roadside and urban background sites. Approximately a hundred compounds were found in each sample with the tendency to find more unknown if a more extensive database is available. Toxicity data were identified in 55 chemicals including a range of acute and chronic health effects. For example, aliphatic hydrocarbons such as alkanes and alkenes can cause eye, skin and mucous membranes irritation (U.S. National Library of Medicine, 2016).

In the previous chapter, we estimated lung cancer risks of the exposure to PM_{10}-bound PAHs that included 13 out of 15 PAHs measured in the BaP-TEQ calculation. Results from the screening implied the lack of information that may significantly relate to adverse health effects from PM_{10}-bound PAHs exposure. Therefore, further investigation of pPAHs should be carried out for both qualitative and quantitative analysis.

8.5 Summary

This chapter highlights a state-of-the-art chromatographic technique suitable for the screening of unknown air pollutants that exist at trace levels as well as other complex mixture samples. The use of GCxGC TOFMS in PM_{10} analysis enable the identification of 248 compounds in 3 PM_{10} sample extracts. Although these results may need further in-depth research to evaluate potential adverse health effects, it is found that pPAHs in PM_{10} were more diverse than we first anticipated. From the screening of samples from 3 different environmental surroundings, more than 20 unknown isomers of high molecular weight PAHs ranging from 4-ring to 6-ring PAHs were found. In addition to parent PAHs, alkylated naphthalene derivatives were identified in all samples.

Concentrations of contaminant in ambient particulate samples were extremely low and thus prevent the identification of unknown compounds when using routine analytical techniques. A high sensitivity instrument is required to explore the ambient air sample compositions. GCxGC TOFMS is the ideal equipment for the screening of unknown substances in trace analysis and resolving a complex mixture sample with minimal sample pre-treatment required.

Chapter 9

Conclusions and Recommendations for Future Work

9.1 Summary Conclusions

The aim of this research to investigate particulate-bound polycyclic aromatic hydrocarbons and their associated health risks in the Bangkok Metropolitan Administration (Thailand) has been demonstrated. The objectives of this study were achieved as follows:

(i) Highly sensitive and fast analytical methods were developed for the quantification of 16 US EPA priority PAHs using a pressurised fluid extraction system and a quadrupole GC-MS. Chemical characterisation of particulate-bound PAHs was performed in both rural household dust and urban particulate matter samples.

(ii) The air quality situation related to PM_{10}-bound PAHs in three study areas representing roadside, industrial and urban background environments in the BMA were characterised. The highest PM_{10} and total pPAHs concentration were found at the roadside site while the highest carcinogenicity of pPAHs was found at the industrial site. Composition of PAHs clearly plays an important role in their toxicity.

(iii) Quantification of 15 PAHs in PM_{10} samples were performed for one year. Seasonal variations of pPAHs were observed particularly in the cool and dry period when the highest concentrations of PM_{10} were found at all sampling sites.

(iv) Lung cancer risks were estimated and incremental lifetime exposure risks were identified for both residents and workers in three study areas. The highest risk of 1.4×10^{-7} (1.4 cases in 10,000,000) was found in adult

residents at the industrial site as a result of the highest BaP toxic equivalent.

(v) A high sensitivity and high resolution method for the screening of non-targeted air pollutants was developed by using a comprehensive two-dimensional gas chromatograph coupled with a time-of-flight mass spectrometer. Almost 250 organic air contaminants were identified in three PM_{10} samples, of which 55 compounds were known toxic pollutants.

In conclusion, key findings of this research were:

The chemical characterisation of particulate-bound PAHs was performed in order to estimate carcinogenicity, especially lung cancer risks that are anticipated to arise from long-term exposure. Two types of samples were analysed in this study including dust samples from households in the rural area of Malawi and ambient particulate samples from three urban areas of central Thailand.

Analytical methods for the analysis of pPAHs in dust and particulate filter samples were developed. Pressurised liquid extraction conditions were optimised using an accelerated solvent extraction system instead of the conventional Soxhlet extraction. The ASE extraction time was approximately 30 minutes per sample compared to the Soxhlet method that required 18-hour reflux. An additional advantage of ASE vs. Soxhlet method was the smaller amount of toxic solvent used. The ASE extraction method using in-cell clean-up agents replaced the short column chromatography in the clean-up step which reduced loss of PAHs and contamination of samples that may occur during the solvent evaporation and transferring of the extract. The high investment cost of the ASE is offset by reduced environmental impact of the procedure: the extraction method developed in this study used a combination of hexane and toluene solvents at the volume of 80 – 100 mL, which compared to 700 mL of diethyl ether/hexane used in Soxhlet extraction are relatively low in amount and toxicity. Both hexane and toluene are not classifiable as human carcinogens (ASTDA, 1999; ASTDA, 2015). With appropriate personal protection equipment and good laboratory skills, health risks to the analyst should be negligible.

PAHs were identified and quantified using a quadrupole gas chromatograph-mass spectrometer with a run time of < 20 minutes for the analysis of 16 US EPA priority PAHs. The GC-QMS is able to quantify pg m^{-3} trace amounts of PAHs when operated in the selected ion monitoring mode.

The analysis of 16 PAHs from households in rural Malawi showed that low molecular weight 2-ring and 3-ring PAHs comprised more than 80% of total 16 PAHs weight in most dust samples. In contrast, soot samples deposited on kitchen walls had relatively higher amounts of higher molecular weight PAHs, especially 4-ring compounds suggesting that they were distributed in the smaller particle size range. High molecular weight PAHs composed of more than 4 conjugated aromatic rings possess higher toxicity than low molecular weight ones. Thus exposure to fine particles may result in adverse health effects from more variety of toxic substances.

Concentrations of semi-volatile 3-ring to 6-ring PAHs were quantified from archived PM_{10} samples collected at three sampling sites in the Bangkok Metropolitan Administration during May 2013 to May 2014. In Bangkok 15 PAHs were quantified from PM_{10} collected on quartz fibre filters. High molecular weight 4-ring to 6-ring PAHs represented >90% of total PAH mass. Differences in PAHs composition between the BMA and Malawi samples suggested different combustion mechanisms. Dust samples from Malawi were rich in low molecular weight 2-ring to 3-ring PAHs while PM_{10} samples from the BMA dominated by 4-ring to 6-ring PAHs. Relatively low temperature biomass fuel burning is anticipated to generate larger particles and low molecular weight PAHs while higher temperature combustion in traffic sources is likely to produce smaller particles and high molecular weight PAHs. The latter are more toxic and are anticipated to pose significant carcinogenic risk to people through long-term exposure.

In line with common practice, the carcinogenic health risk associated with pPAH mixtures was assessed in terms of total concentration equivalents to BaP concentration (BaP-TEQ). The life-time carcinogenic risk at the three sites in the BMA was highest at the industrial site, intermediate for the roadside, and lowest for the urban background site. Incremental lifetime cancer risks were estimated from the

lifetime daily dose of BaP. Total risks of 70 years exposure were found at 8.2 x 10^{-7}, 7.1 x 10^{-7} and 3.8 x 10^{-7} at the industrial site, roadside site and urban background site, respectively. The risks estimated in this study were within the 'acceptable' threshold of 1 in a million people (US EPA, 2005).

When employing IUR and BaP as surrogate for the risk estimation, ILCR were almost 10 times higher than the former approach. Total risks were found at 3.0 x 10^{-6}, 2.6 x 10^{-6} and 1.4 x 10^{-6} expressing the risk of contracting lung cancer over a lifetime exposure of 3, 2.6 and 1.4 cases per million people at the industrial, roadside and urban background site, respectively. The higher value estimated by BaP surrogate approach may compensate the lack of information used for risk calculation. It might be useful for the screening of contaminated areas; however, the more thorough estimation should be performed to investigate the health risk of exposed population where PAHs monitoring is available.

A GCxGC TOFMS was used for qualitative indication of unknown air pollutants in PM_{10}. Almost 250 compounds were identified from the 'library search' screening results of PM_{10} extracts from the industrial, roadside and urban background sites. In addition to 15 US EPA priority PAHs quantified by GC-QMS, 20 unknown PAHs were indicated by this method. These PAHs were high molecular weight 4-ring to 6-ring compounds that might be mutagens or carcinogens. Consequently, the risks evaluated using 13 priority US EPA pPAHs quantified in PM_{10} may be underestimated. This highlights the importance of further investigation of pPAHs in Bangkok extending beyond the 16 US EPA priority PAHs which may allow improved health risk estimation when more information is available.

9.2 Recommendations for Future Work

Due to the lack of existing long-term air sampling, PM_{10} samples were collected from 3 ambient air quality monitoring sites in Thailand. Study areas selected in this research represented urban environments, reflecting the grave concern over potential impact on a large population. Further study might be done in areas with different particulate matter profiles such as provinces in the northern part of Thailand that suffer from recurring haze episodes during the dry season. A study on emission from

wildfires in southern Europe observed significant increases in PM and organic carbon during the smouldering phase of fire and PAHs were found to be higher in coarse particles ($PM_{2.5-10}$) than in fine particles size less than 2.5 μm (Alves *et al.,* 2011). The contribution of particulate matter from biomass burning and wildfires should not be neglected.

The study of particulate-bound PAHs in Thailand should be extended to areas with high particulate matter issues in order to evaluate the health risk to local residents from long-term exposure. The most concerning adverse health effect form PAHs exposure is lung cancer which was the second most common form of cancer in Thailand during 1992-1994 (Deerasamee *et al.*, 1999). Previous studies focused on effects of short-term exposure during smoke haze periods (Phoothiwut and Junyapoon, 2013; Pongpiachan, 2015). Since the evidence of health effects from pPAH exposure were demonstrated, it is reasonable to conduct long-term monitoring in order to follow-up the situation.

Further studies may consider the characterisation of PAHs in fine particle sizes such as $PM_{2.5}$. Smaller particles are very likely to result in higher adverse health effects as they can enter deeper into the respiratory system. Apart from physical properties, they are associated with high molecular weight PAHs bearing higher carcinogenicity than low molecular weight ones. It is essential to establish a clear understanding of the environmental state of atmospheric PAHs in order to protect public health.

The application of methods developed in this research can be applied to the monitoring of pPAHs in Thailand which will provide necessary background information for policy-makers to establish cost-effective mitigation measures for environmental pollution. In addition to the long-term monitoring of pPAHs conducted in this study, high time resolved air pollutants information is invaluable in terms of air pollution management. A high time resolution study in Bangkok revealed periodic relationships between the traffic flow, vehicle exhaust odour and real-time PAHs measured by photoelectric aerosol sensors (Hoshiko *et al.,* 2011). PAHs signals were found to follow the traffic flow and vehicle exhaust odour with lag times approximately a few ten of seconds at kerbside areas implying that traffic

congestions caused accumulation and concentration of vehicle exhaust resulting in the following peak PAHs signal. Pedestrian exposure to traffic related pollutants can be reduced by avoiding rush hour travelling. Furthermore, a traffic flow management approach such as shortening traffic light intervals may result in decreasing air pollutant concentrations at roadside areas. This temporary measure might be considered while the reduction from emission sources is yet to progress.

Seasonal variation of PM_{10} and PAHs in this study showed the highest pollutant concentrations during the winter period. Dry and cool weather conditions with less solar radiation may facilitate the suspension of particulate matter as well as preserve organic pollutants from photochemical degradation. In order to significantly reduce the health risk posed by pPAHs exposure, seasonal particulate matter emission sources particularly agricultural residue burnings and forest fires should be stringently controlled, especially in the winter. The abatement of particulate-bound pollutants in the winter period could be one of the most effective measures in lowering overall adverse health effects from particulate matter exposure under current circumstances. Contributions from industrial and mobile sources can be mitigated through the use of more efficient combustion technologies and/or the reduction of particulate emissions at sources.

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Appendix A

Meteorological parameters and PAHs concentrations

Table A.1 Meteorological and pollutant data measured at the roadside site.

dd/mm/yy	Concentration (ng m^{-3})						
	PM_{10} (µg m^{-3})	**WS ($m\ s^{-1}$)**	**WD (Degree)**	**T (°C)**	**RH (%)**	**Rain (mm)**	**ACY**
02/05/13	43.90	0.6	223	34.5	57	0.0	0
08/05/13	35.40	0.4	201	33.9	60	0.0	0
14/05/13	34.00	0.3	233	33.3	60	0.1	0.154
20/05/13	36.50	0.3	196	31.4	71	0.0	0.162
26/05/13	26.60	0.4	205	31.7	65	0.3	0
01/06/13	54.20	0.4	182	31.9	62	0.0	0.137
07/06/13	54.60	0.3	173	30.8	70	0.0	0
13/06/13	66.30	0.2	105	27.8	89	0.6	0.182
19/06/13	30.60	0.4	211	31.1	70	0.5	0.154
07/07/13	54.60	0.3	156	29.8	76	0.4	0
13/07/13	30.40	0.6	244	31.8	62	0.0	0.160
19/07/13	32.60	0.6	236	30.0	65	0.0	0.161
12/08/13	49.60	0.4	136	30.9	71	0.1	0.029
18/08/13	45.80	0.3	237	30.9	63	0.0	0.027
24/08/13	48.50	0.3	228	29.8	71	0.0	0.028
30/08/13	52.30	0.5	181	29.8	73	1.2	0.036
05/09/13	40.90	0.4	204	31.6	64	0.0	0.028
11/09/13	59.00	0.5	88	29.7	73	1.7	0.034
17/09/13	46.40	0.3	228	29.7	71	0.0	0.027
29/09/13	59.60	0.4	136	29.1	78	0.1	0.039
05/10/13	94.80	0.3	63	29.3	77	0.7	0.057
11/10/13	98.30	0.2	93	31.2	68	0.0	0.077
29/10/13	104.60	0.3	147	31.3	68	0.0	0.072
04/11/13	69.70	0.7	79	31.7	46	0.0	0.031
10/11/13	91.00	0.6	107	31.3	63	0.0	0.073
16/11/13	53.50	0.6	79	28.1	75	0.3	0.028
16/12/13	57.70	0.3	221	30.8	71	0.0	0.016
22/12/13	85.90	0.8	230	25.4	53	0.0	0.031
28/12/13	111.20	0.7	121	25.5	52	0.0	0.033
03/01/14	162.60	0.3	128	29.0	54	0.0	0.042
16/03/14	62.90	0.4	189	32.4	68	0.0	0.016
22/03/14	29.30	0.4	152	29.9	77	0.6	0.014
28/03/14	51.00	0.7	208	31.8	71	0.0	0.021
03/04/14	40.70	0.7	207	32.6	67	0.0	0.020
09/04/14	83.50	0.4	211	33.1	58	0.0	0.022
15/04/14	54.10	0.4	94	31.8	67	0.1	0.018
21/04/14	43.90	0.5	210	33.5	61	0.0	0.014
27/04/14	32.80	0.6	209	33.6	62	0.0	0.009
03/05/14	52.60	0.5	160	32.5	70	1.4	0.024
09/05/14	34.30	0.6	202	33.8	64	0.0	0.016
15/05/14	31.30	0.6	235	34.8	57	0.0	0.022
21/05/14	37.70	0.6	241	33.9	58	0.0	0.021
27/05/14	41.70	0.5	189	33.4	68	0.0	0.032
Annual							
min	26.60	0.2	63	25.35	46	0.0	0.00
max	162.60	0.8	244	34.77	89	1.7	0.18
Average	56.44	0.5	176	31.16	66	0.2	0.05
SD	27.29	0.1	53	2.13	8	0.4	0.05

dd/mm/yy	Concentration (ng m^{-3})						
	ACE	**FLU**	**PHE**	**ANT**	**FLT**	**PYR**	**BaA**
02/05/13	0	0	0.132	0	0.147	0.184	0
08/05/13	0	0	0.127	0	0.151	0.186	0
14/05/13	0	0.026	0.120	0.237	0.649	0.125	0
20/05/13	0.137	0.043	0.180	0.250	0.677	0.174	0
26/05/13	0	0	0.034	0	0.061	0.068	0
01/06/13	0	0.010	0.085	0	0.106	0.136	0.976
07/06/13	0	0	0.212	0	0.245	0.334	0
13/06/13	0.137	0.046	0.281	0.285	0.810	0.385	0.690
19/06/13	0.123	0.030	0.119	0.237	0.644	0.099	0
07/07/13	0	0.375	0.702	0	0.147	0.266	0
13/07/13	0.124	0.031	0.150	0.245	0.674	0.145	0
19/07/13	0.122	0.029	0.133	0.239	0.664	0.126	0
12/08/13	0.039	0.084	0.210	0.047	0.132	0.187	0.168
18/08/13	0.036	0.082	0.177	0.048	0.108	0.143	0.076
24/08/13	0.040	0.088	0.182	0.050	0.115	0.153	0.090
30/08/13	0.041	0.080	0.240	0.062	0.175	0.241	0.208
05/09/13	0.043	0.080	0.178	0.048	0.117	0.171	0.097
11/09/13	0.038	0.081	0.240	0.060	0.209	0.323	0.283
17/09/13	0.035	0.038	0.149	0.027	0.091	0.130	0.100
29/09/13	0	0.045	0.250	0.038	0.180	0.269	0.257
05/10/13	0	0.087	0.374	0.065	0.255	0.346	0.289
11/10/13	0	0.114	0.512	0.083	0.365	0.474	0.404
29/10/13	0	0.104	0.520	0.081	0.418	0.533	0.368
04/11/13	0	0.042	0.259	0.040	0.225	0.289	0.225
10/11/13	0	0.110	0.531	0.089	0.386	0.545	0.463
16/11/13	0	0.042	0.255	0.038	0.196	0.271	0.241
16/12/13	0	0.030	0.161	0.024	0.095	0.130	0.057
22/12/13	0	0.079	0.323	0.041	0.278	0.299	0.130
28/12/13	0	0.081	0.394	0.051	0.435	0.388	0.169
03/01/14	0	0.106	0.372	0.060	0.279	0.344	0.219
16/03/14	0.010	0	0.062	0.018	0.049	0.085	0.042
22/03/14	0.013	0	0.074	0.021	0.046	0.076	0.045
28/03/14	0.015	0	0.087	0.022	0.060	0.093	0.045
03/04/14	0.015	0	0.076	0.022	0.052	0.090	0.042
09/04/14	0.034	0	0.107	0.030	0.091	0.147	0.062
15/04/14	0	0	0.083	0.023	0.071	0.115	0.078
21/04/14	0	0	0.045	0.017	0.042	0.075	0.035
27/04/14	0.010	0	0.040	0.015	0.025	0.058	0.023
03/05/14	0	0	0.124	0.032	0.116	0.176	0.143
09/05/14	0	0	0.054	0.020	0.053	0.091	0.043
15/05/14	0	0.025	0.062	0.010	0.064	0.094	0.056
21/05/14	0.010	0.025	0.066	0.010	0.061	0.092	0.042
27/05/14	0	0	0.145	0.030	0.114	0.157	0.090
Annual							
min	0.00	0.00	0.03	0.00	0.03	0.06	0.00
max	0.14	0.38	0.70	0.28	0.81	0.54	0.98
Average	0.02	0.05	0.20	0.06	0.23	0.20	0.15
SD	0.04	0.06	0.15	0.08	0.21	0.13	0.20

dd/mm/yy	Concentration (ng m^{-3})						
	CHR	**BbF**	**BkF**	**BaP**	**IP**	**DBA**	**BP**
02/05/13	0.129	0	0	0.859	1.381	0	1.388
08/05/13	0.133	0	0	0.758	1.206	0	1.175
14/05/13	0.211	0.876	0	0.288	1.108	0	1.378
20/05/13	0.249	1.288	0	0.324	1.669	0	1.977
26/05/13	0.163	0.561	0	0.326	0.743	0	0.847
01/06/13	0.281	1.139	0	0.561	1.356	0	1.591
07/06/13	0.508	0	0	1.736	2.321	0	2.254
13/06/13	0.568	2.375	0	0.484	2.881	0	3.976
19/06/13	0.191	0.751	0	0.283	1.129	0	1.350
07/07/13	0.871	2.275	0	1.714	0	0	0
13/07/13	0.230	1.035	0	0.353	1.765	0	2.111
19/07/13	0.216	1.261	0	0.365	2.291	0	2.644
12/08/13	0.190	0.582	0.142	0.306	0.395	0.034	0.638
18/08/13	0.067	0.535	0.135	0.345	0.609	0.080	0.847
24/08/13	0.087	0.551	0.154	0.346	0.728	0.083	0.949
30/08/13	0.217	0.735	0.199	0.572	0.696	0.071	1.066
05/09/13	0.102	0.582	0.164	0.361	0.586	0.064	0.797
11/09/13	0.397	0.721	0.171	0.387	0.484	0.040	0.800
17/09/13	0.086	0.597	0.164	0.336	0.814	0	1.020
29/09/13	0.340	0.778	0.206	0.524	0.707	0	1.016
05/10/13	0.362	1.175	0.318	0.675	1.184	0	1.464
11/10/13	0.527	1.850	0.434	1.114	1.730	0	2.314
29/10/13	0.559	1.656	0.381	0.984	1.665	0	2.186
04/11/13	0.346	1.020	0.248	0.531	0.952	0	1.238
10/11/13	0.673	1.749	0.426	1.101	1.753	0	2.243
16/11/13	0.295	0.884	0.202	0.649	0.903	0	1.249
16/12/13	0.065	0.329	0.089	0.180	0.804	0	0.943
22/12/13	0.177	0.821	0.238	0.552	1.555	0	1.660
28/12/13	0.249	1.120	0.323	0.680	1.533	0	1.511
03/01/14	0.240	1.442	0.397	0.758	1.882	0	2.160
16/03/14	0.066	0.454	0.111	0.061	0.421	0.049	0.550
22/03/14	0.059	0.247	0.072	0.107	0.225	0.020	0.336
28/03/14	0.059	0.546	0.138	0.120	0.627	0.056	0.797
03/04/14	0.049	0.506	0.121	0.112	0.610	0.056	0.817
09/04/14	0.089	0.547	0.128	0.140	0.588	0.048	0.743
15/04/14	0.124	0.514	0.124	0.192	0.419	0.031	0.575
21/04/14	0.044	0.303	0.062	0.048	0.378	0.033	0.526
27/04/14	0.029	0.176	0.040	0.046	0.247	0.024	0.348
03/05/14	0.179	0.741	0.191	0.346	0.662	0.054	0.929
09/05/14	0.046	0.188	0.057	0.128	0.392	0.033	0.545
15/05/14	0.066	0.302	0.098	0.132	0.342	0.027	0.470
21/05/14	0.053	0.360	0.093	0.147	0.409	0.040	0.543
27/05/14	0.118	0.762	0.187	0.258	0.843	0.069	0.950
Annual							
min	0.03	0.00	0.00	0.05	0.00	0.00	0.00
max	0.87	2.38	0.43	1.74	2.88	0.08	3.98
Average	0.23	0.80	0.14	0.47	1.00	0.02	1.23
SD	0.19	0.56	0.13	0.39	0.65	0.03	0.76

dd/mm/yy	Concentration (ng m-3)					
	3-ring	**4-ring**	**5-ring**	**6-ring**	**7PAHs**	**15PAHs**
02/05/13	0.132	0.460	0.859	2.769	2.369	4.220
08/05/13	0.127	0.469	0.758	2.381	2.098	3.736
14/05/13	0.537	0.985	1.163	2.487	2.483	5.172
20/05/13	0.772	1.099	1.611	3.646	3.529	7.129
26/05/13	0.034	0.292	0.887	1.590	1.793	2.803
01/06/13	0.232	1.499	1.700	2.947	4.313	6.378
07/06/13	0.212	1.087	1.736	4.575	4.565	7.610
13/06/13	0.931	2.453	2.859	6.857	6.998	13.100
19/06/13	0.663	0.934	1.034	2.478	2.353	5.109
07/07/13	1.077	1.283	3.990	0	4.860	6.350
13/07/13	0.710	1.048	1.388	3.876	3.383	7.022
19/07/13	0.685	1.006	1.626	4.934	4.132	8.250
12/08/13	0.411	0.676	1.064	1.033	1.817	3.184
18/08/13	0.370	0.394	1.095	1.456	1.848	3.316
24/08/13	0.388	0.445	1.135	1.678	2.040	3.645
30/08/13	0.461	0.841	1.577	1.763	2.698	4.641
05/09/13	0.377	0.487	1.171	1.382	1.956	3.418
11/09/13	0.453	1.212	1.319	1.284	2.484	4.269
17/09/13	0.276	0.407	1.097	1.834	2.098	3.615
29/09/13	0.372	1.046	1.509	1.724	2.812	4.650
05/10/13	0.583	1.252	2.168	2.649	4.003	6.651
11/10/13	0.786	1.768	3.398	4.043	6.057	9.995
29/10/13	0.777	1.879	3.022	3.851	5.614	9.528
04/11/13	0.371	1.086	1.799	2.190	3.322	5.445
10/11/13	0.803	2.067	3.276	3.995	6.165	10.141
16/11/13	0.362	1.003	1.734	2.153	3.173	5.252
16/12/13	0.231	0.347	0.598	1.747	1.524	2.923
22/12/13	0.473	0.884	1.611	3.215	3.473	6.183
28/12/13	0.559	1.240	2.124	3.044	4.075	6.967
03/01/14	0.581	1.082	2.598	4.042	4.939	8.302
16/03/14	0.106	0.241	0.675	0.971	1.204	1.993
22/03/14	0.122	0.226	0.446	0.561	0.774	1.355
28/03/14	0.145	0.256	0.859	1.424	1.590	2.684
03/04/14	0.133	0.232	0.794	1.428	1.495	2.587
09/04/14	0.193	0.389	0.863	1.330	1.602	2.775
15/04/14	0.124	0.389	0.860	0.994	1.481	2.367
21/04/14	0.077	0.196	0.445	0.904	0.903	1.622
27/04/14	0.074	0.134	0.286	0.595	0.584	1.089
03/05/14	0.181	0.614	1.333	1.591	2.318	3.719
09/05/14	0.089	0.233	0.406	0.937	0.886	1.664
15/05/14	0.118	0.280	0.559	0.811	1.022	1.768
21/05/14	0.132	0.248	0.639	0.953	1.143	1.971
27/05/14	0.207	0.479	1.277	1.793	2.328	3.756
Annual						
min	0.03	0.13	0.29	0.00	0.58	1.09
max	1.08	2.45	3.99	6.86	7.00	13.10
Average	0.38	0.81	1.43	2.23	2.80	4.85
SD	0.27	0.56	0.87	1.40	1.60	2.74

Table A.2 Meteorological and pollutant data measured at the industrial site.

dd/mm/yy	Concentration (ng m^{-3})						
	PM_{10} (µg m^{-3})	**WS ($m\ s^{-1}$)**	**WD (Degree)**	**T (°C)**	**RH (%)**	**Rain (mm)**	**ACY**
02/05/13	30.1	0.9	211	32.7	57	0.0	0
08/05/13	29.2	1.0	211	32.0	62	0.0	0
14/05/13	27.2	0.9	208	32.5	60	0.0	0
20/05/13	30.2	0.5	201	30.4	71	0.0	0
26/05/13	18.4	1.1	195	30.5	68	0.1	0
01/06/13	27.0	0.7	227	31.2	60	0.0	0
07/06/13	27.7	0.4	205	29.6	71	0.1	0
13/06/13	29.6	0.3	186	26.9	91	1.1	0.133
07/07/13	21.2	0.8	152	28.7	77	0.3	0
13/07/13	21.2	0.4	230	30.2	66	0.0	0.153
18/08/13	40.2	0.6	224	28.9	70	0.0	0.039
24/08/13	47.2	0.7	215	28.3	77	0.3	0.043
30/08/13	31.9	0.7	196	28.5	77	1.9	0.031
05/09/13	36.3	0.6	235	30.0	67	0.0	0.038
11/09/13	30.5	0.6	127	28.3	77	0.8	0.029
05/10/13	94.4	0.6	204	29.6	71	0.2	0.074
11/10/13	108.8	0.3	254	29.9	71	0.0	0.131
23/10/13	64.9	0.2	199	29.8	70	0.0	0.071
29/10/13	77.1	0.4	182	28.6	74	0.0	0.062
04/11/13	65.5	1.1	80	30.0	45	0.0	0.063
10/11/13	59.1	0.6	298	29.6	64	0.0	0.071
16/11/13	34.4	0.9	207	26.4	74	0.3	0.060
22/11/13	64.7	0.8	225	29.2	61	0.0	0.063
16/12/13	59.9	0.5	219	28.8	72	0.0	0.062
22/12/13	80.3	0.9	301	22.6	55	0.0	0.062
28/12/13	102.8	0.7	116	22.8	51	0.0	0.114
03/01/14	156.4	0.2	257	26.1	58	0.0	0.117
09/01/14	104.2	0.5	217.7	28.6	62	0.0	0.124
16/03/14	48.3	0.7	179	31.0	66	0.0	0.055
22/03/14	53.9	0.8	153	28.3	75	0.2	0.065
09/04/14	74.4	1.0	195	31.8	56	0.0	0.058
15/04/14	37.3	0.6	228	30.0	69	0.1	0
21/04/14	25.4	1.1	186	32.3	58	0.0	0
27/04/14	25.6	1.3	182	32.4	60	0.0	0
03/05/14	37.0	1.1	130	30.5	72	1.8	0.058
09/05/14	28.6	0.9	191	31.9	65	1.0	0
27/05/14	34.8	0.9	170	31.4	70	0.6	0.030
Annual							
min	18.40	0.2	80	22.56	45	0.0	0.00
max	156.40	1.3	301	32.71	91	1.9	0.15
Average	50.96	0.7	200	29.46	67	0.2	0.05
SD	31.12	0.3	44	2.33	9	0.5	0.04

dd/mm/yy	Concentration (ng m^{-3})						
	ACE	**FLU**	**PHE**	**ANT**	**FLT**	**PYR**	**BaA**
02/05/13	0	0.009	0.026	0	0.057	0.060	0
08/05/13	0	0	0.030	0	0.067	0.072	0
14/05/13	0	0.010	0.033	0	0.065	0.068	0
20/05/13	0	0	0.043	0	0.083	0.100	0.933
26/05/13	0	0.008	0.021	0	0.059	0.054	0
01/06/13	0	0.008	0.040	0	0.078	0.079	0
07/06/13	0	0.010	0.046	0	0.095	0.082	0.937
13/06/13	0	0.010	0.039	0	0.069	0.077	0.932
07/07/13	0	0.332	0.602	0	0	0.158	0
13/07/13	0	0	0.089	0.229	0.623	0	0
18/08/13	0	0	0.058	0.006	0.069	0.100	0.088
24/08/13	0	0	0.079	0	0.096	0.129	0.130
30/08/13	0	0	0.037	0.004	0.041	0.064	0.058
05/09/13	0	0	0.054	0.005	0.078	0.105	0.103
11/09/13	0	0	0.040	0.004	0.051	0.076	0.073
05/10/13	0	0	0.142	0.013	0.190	0.261	0.248
11/10/13	0	0.066	0.198	0.057	0.208	0.285	0.161
23/10/13	0	0.022	0.126	0.030	0.164	0.193	0.123
29/10/13	0.023	0.092	0.140	0.028	0.188	0.220	0.102
04/11/13	0	0	0.097	0.024	0.140	0.168	0.102
10/11/13	0	0.025	0.116	0.028	0.131	0.187	0.112
16/11/13	0	0.019	0.073	0.021	0.089	0.131	0.080
22/11/13	0	0.018	0.093	0.024	0.127	0.164	0.095
16/12/13	0	0.016	0.090	0.022	0.108	0.145	0.088
22/12/13	0	0.019	0.128	0.023	0.239	0.214	0.090
28/12/13	0	0.034	0.258	0	0.480	0.397	0.147
03/01/14	0	0.038	0.194	0.043	0.234	0.275	0.206
09/01/14	0	0	0.181	0.049	0.206	0.280	0.171
16/03/14	0	0	0.037	0	0.040	0.064	0.044
22/03/14	0	0	0.077	0.021	0.093	0.139	0.080
09/04/14	0	0	0.042	0	0.073	0.097	0.061
15/04/14	0	0.017	0.029	0	0.038	0.064	0.050
21/04/14	0	0	0.027	0	0.029	0.053	0.046
27/04/14	0	0	0.020	0	0.023	0.043	0.042
03/05/14	0	0	0.047	0.019	0.058	0.092	0.061
09/05/14	0	0	0.029	0	0.035	0.064	0.041
27/05/14	0	0	0.045	0.004	0.058	0.070	0.081
Annual							
min	0.00	0.00	0.02	0.00	0.00	0.00	0.00
max	0.02	0.33	0.60	0.23	0.62	0.40	0.94
Average	0.00	0.02	0.09	0.02	0.12	0.13	0.15
SD	0.00	0.06	0.10	0.04	0.12	0.09	0.24

dd/mm/yy	Concentration (ng m^{-3})						
	CHR	**BbF**	**BkF**	**BaP**	**IP**	**DBA**	**BP**
02/05/13	0.160	0.462	0	0.314	0.720	0	0.718
08/05/13	0.168	0.543	0	0.324	0.782	0	0.777
14/05/13	0.163	0.528	0	0.332	0.621	0	0.656
20/05/13	0.187	0.763	0	0.447	1.066	0	1.109
26/05/13	0.150	0.451	0	0.287	0.599	0	0.616
01/06/13	0.172	0.547	0	0.363	0.912	0	0.880
07/06/13	0.174	0.652	0	0.407	0.793	0	0.912
13/06/13	0.177	0.671	0	0.432	0.818	0	0.938
07/07/13	0	1.631	0	1.558	1.365	0	0
13/07/13	0.167	0.497	0	0.279	0.886	0	0.896
18/08/13	0.056	0.326	0.128	0.289	1.202	0.111	0.634
24/08/13	0.093	0.551	0.194	0.356	1.524	0.137	0.886
30/08/13	0.038	0.219	0.097	0.127	0.849	0	0.243
05/09/13	0.070	0.372	0.157	0.286	1.240	0.116	0.651
11/09/13	0.050	0.311	0.128	0.158	0.871	0	0.296
05/10/13	0.185	1.367	0.462	0.910	2.722	0.285	1.587
11/10/13	0.156	1.100	0.386	0.623	2.226	0.845	1.407
23/10/13	0.132	1.088	0.302	0.529	1.538	0.505	1.155
29/10/13	0.131	0.736	0.227	0.313	1.167	0.441	0.743
04/11/13	0.101	0.533	0.167	0.257	0.947	0.410	0.535
10/11/13	0.116	0.807	0.238	0.464	1.323	0.448	0.925
16/11/13	0.070	0.443	0.141	0.231	0.895	0.398	0.492
22/11/13	0.084	0.435	0.157	0.262	1.088	0.421	0.686
16/12/13	0.071	0.346	0.136	0.262	1.087	0.414	0.718
22/12/13	0.091	0.406	0.134	0.238	1.113	0.424	0.639
28/12/13	0.177	0.700	0.249	0.386	1.908	0.808	0.924
03/01/14	0.157	1.261	0.351	0.744	2.820	0.945	2.002
09/01/14	0.154	0.948	0.311	0.488	2.176	0.841	1.406
16/03/14	0.022	0.167	0.081	0.109	0.704	0	0.239
22/03/14	0.051	0.400	0.145	0.214	0.923	0.407	0.507
09/04/14	0.047	0.278	0.115	0.154	0.788	0.394	0.311
15/04/14	0.022	0.250	0.103	0.142	0.746	0.391	0.281
21/04/14	0.011	0.217	0.103	0.130	0.729	0	0.270
27/04/14	0.014	0.133	0.078	0.110	0.720	0.390	0.232
03/05/14	0.036	0.267	0.120	0.158	0.797	0	0.361
09/05/14	0.015	0.143	0.079	0.113	0.722	0	0.247
27/05/14	0.050	0.301	0.114	0.200	1.096	0.144	0.469
Annual							
min	0.00	0.13	0.00	0.11	0.60	0.00	0.00
max	0.19	1.63	0.46	1.56	2.82	0.95	2.00
Average	0.10	0.56	0.13	0.35	1.15	0.25	0.71
SD	0.06	0.36	0.12	0.27	0.56	0.28	0.42

dd/mm/yy	Concentration (ng m-3)					
	3-ring	**4-ring**	**5-ring**	**6-ring**	**7PAHs**	**15PAHs**
02/05/13	0.035	0.277	0.775	1.437	1.655	2.525
08/05/13	0.030	0.307	0.868	1.559	1.817	2.764
14/05/13	0.044	0.296	0.860	1.277	1.644	2.476
20/05/13	0.043	1.302	1.210	2.175	3.395	4.729
26/05/13	0.029	0.263	0.738	1.215	1.486	2.245
01/06/13	0.048	0.330	0.910	1.792	1.994	3.080
07/06/13	0.056	1.288	1.059	1.704	2.962	4.108
13/06/13	0.181	1.255	1.103	1.756	3.030	4.295
07/07/13	0.933	0.158	3.188	1.365	4.553	5.644
13/07/13	0.471	0.790	0.776	1.782	1.829	3.819
18/08/13	0.103	0.314	0.854	1.836	2.201	3.107
24/08/13	0.122	0.448	1.237	2.410	2.985	4.217
30/08/13	0.071	0.201	0.443	1.092	1.388	1.807
05/09/13	0.097	0.356	0.931	1.891	2.345	3.275
11/09/13	0.073	0.250	0.598	1.166	1.591	2.087
05/10/13	0.230	0.884	3.023	4.309	6.178	8.446
11/10/13	0.452	0.811	2.954	3.633	5.497	7.850
23/10/13	0.249	0.612	2.424	2.693	4.217	5.978
29/10/13	0.346	0.640	1.716	1.910	3.116	4.613
04/11/13	0.184	0.511	1.367	1.481	2.516	3.543
10/11/13	0.240	0.545	1.956	2.248	3.507	4.989
16/11/13	0.173	0.371	1.212	1.387	2.258	3.143
22/11/13	0.198	0.469	1.275	1.774	2.541	3.715
16/12/13	0.190	0.413	1.158	1.804	2.404	3.565
22/12/13	0.232	0.635	1.202	1.751	2.496	3.820
28/12/13	0.406	1.200	2.143	2.832	4.375	6.581
03/01/14	0.392	0.872	3.301	4.822	6.484	9.387
09/01/14	0.354	0.812	2.587	3.582	5.089	7.335
16/03/14	0.093	0.170	0.357	0.943	1.126	1.563
22/03/14	0.163	0.363	1.165	1.431	2.220	3.122
09/04/14	0.100	0.278	0.941	1.099	1.836	2.418
15/04/14	0.046	0.174	0.886	1.027	1.705	2.134
21/04/14	0.027	0.139	0.450	0.998	1.237	1.615
27/04/14	0.020	0.122	0.711	0.952	1.487	1.805
03/05/14	0.123	0.247	0.545	1.158	1.439	2.073
09/05/14	0.029	0.155	0.335	0.969	1.113	1.488
27/05/14	0.079	0.259	0.758	1.566	1.986	2.662
Annual						
min	0.02	0.12	0.34	0.94	1.11	1.49
max	0.93	1.30	3.30	4.82	6.48	9.39
Average	0.18	0.50	1.30	1.86	2.69	3.84
SD	0.18	0.35	0.83	0.93	1.42	2.01

Table A.3 Meteorological and pollutant data measured at the urban background site.

dd/mm/yy	Concentration (ng m^{-3})						
	PM_{10} (µg m^{-3})	**WS ($m\ s^{-1}$)**	**WD (Degree)**	**T (°C)**	**RH (%)**	**Rain (mm)**	**ACY**
02/05/13	29.0	0.9	206	33.2	58	0.0	0
08/05/13	28.7	0.7	218	32.0	65	0.0	0
20/05/13	30.7	0.6	203	29.9	74	0.0	0.139
26/05/13	23.6	0.8	193	30.6	68	0.0	0
01/06/13	29.8	0.5	204	30.8	63	0.5	0
07/06/13	33.2	0.5	199	28.8	75	0.1	0
13/06/13	35.6	0.2	209	19.2	90	0.6	0
19/06/13	23.3	1.0	208	28.9	73	0.1	0
07/07/13	21.4	0.6	169	20.2	82	0.5	0
13/07/13	18.9	1.0	221	29.8	71	0.7	0
19/07/13	25.2	1.0	221	28.6	71	0.1	0
12/08/13	21.1	0.3	196	29.5	79	1.3	0.012
18/08/13	29.0	0.6	219	29.0	73	0.0	0.021
24/08/13	30.8	0.7	213	27.9	82	0.8	0.020
30/08/13	26.1	0.8	204	28.3	77	1.2	0.019
05/09/13	25.1	0.5	204	29.7	68	0.0	0.022
11/09/13	54.9	0.4	145	27.5	77	1.4	0.034
23/09/13	20.8	0.7	215	26.7	80	0.0	0.018
29/09/13	22.0	0.4	206	27.7	79	0.4	0.013
05/10/13	56.6	0.2	177	28.1	76	1.5	0.019
11/10/13	77.0	0.2	232	28.7	75	0.5	0.034
17/10/13	30.9	0.3	123	25.9	87	0.1	0.016
23/10/13	40.4	0.2	165	28.8	70	0.0	0.018
29/10/13	57.0	0.3	188	28.5	72	0.0	0
04/11/13	49.0	0.2	89	28.9	51	0.0	0
10/11/13	44.7	0.2	205	28.2	70	0.0	0.021
16/11/13	26.4	0.2	207	25.7	76	0.0	0
16/12/13	38.6	0.6	196	29.0	71	0.0	0.015
22/12/13	75.3	0.2	216	22.8	54	0.0	0.020
28/12/13	89.5	0.2	167	22.4	54	0.0	0.020
03/01/14	124.2	0.2	238	26.0	60	0.0	0.034
08/02/14	27.2	1.1	185	28.0	68	0.0	0
14/02/14	59.0	1.0	185	28.6	67	0.0	0.032
21/02/14	91.4	0.5	141	25.0	63	0.0	0.068
26/02/14	42.7	1.2	192	28.4	69	0.0	0.025
16/03/14	42.3	1.0	183.4	28.2	71	0.0	0.027
22/03/14	43.5	0.8	175	28.0	74	0.0	0.030
28/03/14	38.5	1.4	177	31.1	64	0.0	0.022
03/04/14	26.5	1.3	185	31.3	65	0.0	0.023
09/04/14	61.9	1.0	190	32.1	56	0.0	0.024
15/04/14	29.6	0.4	223	29.8	67	0.0	0.019
21/04/14	25.2	1.1	183	32.3	59	0.0	0
27/04/14	19.7	1.2	190	32.5	61	0.0	0
03/05/14	28.2	0.8	167	30.6	40	0.0	0.025
09/05/14	23.1	1.0	192	31.8	46	0.0	0.026
15/05/14	33.1	0.9	209	32.8	52	0.0	0.034
Annual							
min	18.90	0.2	89	19.19	40	0.0	0.00
max	124.20	1.4	238	33.22	90	1.5	0.14
Average	39.80	0.6	192	28.52	68	0.2	0.02
SD	22.17	0.3	28	3.02	11	0.4	0.02

dd/mm/yy	Concentration (ng m^{-3})						
	ACE	**FLU**	**PHE**	**ANT**	**FLT**	**PYR**	**BaA**
02/05/13	0	0.122	0.247	0	0.051	0.090	0
08/05/13	0	0	0.046	0	0.076	0.085	0
20/05/13	0	0.021	0.082	0	0.128	0.139	0.971
26/05/13	0	0	0.042	0	0.072	0.077	0
01/06/13	0	0.354	0.396	0	0.111	0.184	0
07/06/13	0.026	0	0.080	0	0.115	0.111	0.914
13/06/13	0	0.014	0.053	0	0.078	0.086	0.897
19/06/13	0.027	0.015	0.040	0	0.065	0.061	0
07/07/13	0	0.009	0.036	0	0.071	0.074	0
13/07/13	0	0.008	0.029	0	0.062	0.062	0
19/07/13	0	0.010	0.041	0	0.080	0.082	0.893
12/08/13	0	0.021	0.038	0.001	0.041	0.058	0.029
18/08/13	0	0.023	0.061	0.007	0.068	0.084	0.073
24/08/13	0.015	0.024	0.059	0.006	0.066	0.082	0.070
30/08/13	0	0.023	0.041	0.005	0.049	0.073	0.062
05/09/13	0	0.025	0.041	0.003	0.049	0.069	0.049
11/09/13	0	0.036	0.111	0.018	0.130	0.145	0.127
23/09/13	0	0.028	0.057	0.008	0.058	0.081	0.072
29/09/13	0	0.031	0.045	0.005	0.049	0.079	0.044
05/10/13	0	0.111	0.084	0.017	0.107	0.135	0.057
11/10/13	0	0	0.141	0.029	0.157	0.192	0.086
17/10/13	0	0.102	0.087	0.024	0.086	0.122	0.074
23/10/13	0	0.037	0.085	0.015	0.101	0.130	0.068
29/10/13	0	0.144	0.110	0.016	0.131	0.139	0.068
04/11/13	0	0	0.074	0.011	0.097	0.128	0.075
10/11/13	0	0	0.105	0.021	0.100	0.158	0.088
16/11/13	0	0	0.087	0.011	0.076	0.115	0.072
16/12/13	0	0	0.091	0.010	0.067	0.100	0.050
22/12/13	0	0	0.182	0.018	0.218	0.204	0.085
28/12/13	0	0.028	0.300	0.021	0.402	0.299	0.086
03/01/14	0	0.063	0.208	0.040	0.172	0.233	0.124
08/02/14	0	0	0.051	0.005	0.022	0.049	0.028
14/02/14	0	0	0.146	0	0	0.080	0
21/02/14	0	0	0.258	0	0	0.166	0
26/02/14	0	0	0.064	0	0	0.053	0
16/03/14	0	0	0.078	0	0	0.067	0
22/03/14	0	0	0.064	0	0	0.076	0
28/03/14	0	0	0.035	0	0	0.044	0
03/04/14	0	0	0.032	0	0.042	0.047	0
09/04/14	0	0	0.043	0	0	0.064	0
15/04/14	0	0	0.027	0	0	0.038	0
21/04/14	0	0	0.031	0	0.032	0.043	0.051
27/04/14	0	0	0.023	0	0.026	0.040	0.046
03/05/14	0	0	0.046	0	0.052	0.068	0.065
09/05/14	0	0	0.046	0	0.055	0.068	0.070
15/05/14	0	0	0.051	0	0.065	0.088	0.082
Annual							
min	0.00	0.00	0.02	0.00	0.00	0.04	0.00
max	0.03	0.35	0.40	0.04	0.40	0.30	0.97
Average	0.00	0.03	0.09	0.01	0.07	0.10	0.12
SD	0.01	0.06	0.08	0.01	0.07	0.06	0.25

dd/mm/yy	Concentration (ng m^{-3})						
	CHR	**BbF**	**BkF**	**BaP**	**IP**	**DBA**	**BP**
02/05/13	0.358	0	0	0	0	0	0.640
08/05/13	0.173	0.503	0	0.306	0.587	0	0.628
20/05/13	0.251	0.807	0	0.450	0.858	0	0.900
26/05/13	0.184	0.451	0	0.254	0.355	0	0.406
01/06/13	0.201	0	0	1.153	0	0	1.158
07/06/13	0.269	0.783	0	0.531	0.934	0	0.981
13/06/13	0.197	0.699	0	0.456	0.798	0	0.876
19/06/13	0.172	0.448	0	0.282	0.394	0	0.469
07/07/13	0.180	0.511	0	0.350	0.565	0	0.588
13/07/13	0.163	0.467	0	0.311	0.521	0	0.557
19/07/13	0.194	0.802	0	0.564	1.273	0	1.265
12/08/13	0.049	0.140	0.043	0.073	0.133	0.010	0.143
18/08/13	0.084	0.329	0.102	0.244	0.376	0.032	0.423
24/08/13	0.090	0.373	0.138	0.257	0.469	0.039	0.503
30/08/13	0.070	0.253	0.082	0.195	0.263	0.021	0.333
05/09/13	0.072	0.238	0.074	0.157	0.267	0.024	0.286
11/09/13	0.197	0.743	0.255	0.432	0.751	0.052	0.818
23/09/13	0.094	0.358	0.106	0.207	0.370	0.024	0.444
29/09/13	0.063	0.217	0.064	0.119	0.204	0.020	0.233
05/10/13	0.119	0.354	0.098	0.137	0.433	0.025	0.294
11/10/13	0.150	0.623	0.166	0.292	0.785	0.062	0.762
17/10/13	0.118	0.525	0.143	0.257	0.570	0.035	0.504
23/10/13	0.113	0.386	0.103	0.165	0.523	0.037	0.379
29/10/13	0.116	0.420	0.124	0.152	0.497	0.033	0.368
04/11/13	0.124	0.458	0.111	0.201	0.530	0.042	0.348
10/11/13	0.127	0.520	0.143	0.265	0.638	0.051	0.566
16/11/13	0.097	0.368	0.104	0.179	0.452	0.027	0.325
16/12/13	0.067	0.192	0.063	0.111	0.406	0.020	0.282
22/12/13	0.143	0.441	0.123	0.207	0.732	0.064	0.582
28/12/13	0.228	0.622	0.165	0.286	0.813	0.071	0.650
03/01/14	0.152	0.622	0.175	0.335	1.113	0.084	0.836
08/02/14	0.025	0.085	0.027	0.046	0.286	0.009	0.135
14/02/14	0	0.292	0	0.153	0.803	0.073	0.202
21/02/14	0	0	0	0.350	1.966	0.188	0.765
26/02/14	0	0	0	0.104	0.702	0	0.105
16/03/14	0	0	0	0.101	0.692	0	0.098
22/03/14	0	0	0	0.171	0.822	0.076	0.244
28/03/14	0	0	0	0.118	0.715	0	0.150
03/04/14	0	0	0	0.128	0.743	0	0.167
09/04/14	0	0	0	0.130	0.744	0	0.157
15/04/14	0	0	0	0.088	0.676	0	0.083
21/04/14	0	0.143	0.082	0.104	0.712	0	0.140
27/04/14	0.037	0.113	0.069	0.110	0.666	0	0.084
03/05/14	0.065	0.301	0.120	0.161	0.870	0.077	0.280
09/05/14	0.052	0.213	0.098	0.158	0.790	0	0.206
15/05/14	0.074	0.354	0.144	0.192	0.935	0.084	0.358
Annual							
min	0.00	0.00	0.00	0.00	0.00	0.00	0.08
max	0.36	0.81	0.25	1.15	1.97	0.19	1.27
Average	0.11	0.33	0.06	0.24	0.62	0.03	0.45
SD	0.09	0.25	0.07	0.19	0.34	0.04	0.30

dd/mm/yy	Concentration (ng m-3)					
	3-ring	**4-ring**	**5-ring**	**6-ring**	**7PAHs**	**15PAHs**
02/05/13	0.369	0.498	0.000	0.640	0.358	1.507
08/05/13	0.046	0.333	0.808	1.215	1.568	2.402
20/05/13	0.243	1.489	1.256	1.758	3.337	4.747
26/05/13	0.042	0.333	0.706	0.761	1.245	1.842
01/06/13	0.750	0.495	1.153	1.158	1.354	3.557
07/06/13	0.106	1.409	1.314	1.915	3.430	4.744
13/06/13	0.067	1.258	1.155	1.674	3.047	4.154
19/06/13	0.082	0.298	0.730	0.863	1.296	1.973
07/07/13	0.045	0.325	0.860	1.154	1.605	2.384
13/07/13	0.037	0.286	0.778	1.078	1.462	2.180
19/07/13	0.051	1.249	1.365	2.538	3.725	5.203
12/08/13	0.072	0.177	0.267	0.276	0.478	0.792
18/08/13	0.112	0.308	0.708	0.799	1.240	1.927
24/08/13	0.124	0.308	0.808	0.971	1.436	2.211
30/08/13	0.088	0.254	0.551	0.596	0.946	1.488
05/09/13	0.091	0.239	0.494	0.553	0.882	1.377
11/09/13	0.200	0.598	1.482	1.569	2.556	3.849
23/09/13	0.111	0.305	0.695	0.815	1.231	1.925
29/09/13	0.095	0.236	0.420	0.437	0.731	1.187
05/10/13	0.231	0.417	0.614	0.726	1.222	1.989
11/10/13	0.204	0.584	1.143	1.547	2.164	3.478
17/10/13	0.229	0.401	0.959	1.074	1.721	2.663
23/10/13	0.156	0.412	0.691	0.903	1.395	2.161
29/10/13	0.269	0.455	0.730	0.865	1.411	2.319
04/11/13	0.085	0.424	0.812	0.878	1.541	2.198
10/11/13	0.147	0.473	0.979	1.204	1.833	2.803
16/11/13	0.098	0.359	0.677	0.777	1.297	1.910
16/12/13	0.116	0.284	0.387	0.688	0.910	1.475
22/12/13	0.220	0.651	0.836	1.314	1.796	3.021
28/12/13	0.369	1.015	1.145	1.463	2.272	3.992
03/01/14	0.345	0.681	1.216	1.949	2.604	4.190
08/02/14	0.056	0.124	0.167	0.422	0.506	0.768
14/02/14	0.178	0.080	0.519	1.005	1.322	1.781
21/02/14	0.326	0.166	0.537	2.730	2.503	3.760
26/02/14	0.088	0.053	0.104	0.807	0.806	1.052
16/03/14	0.105	0.067	0.101	0.791	0.794	1.063
22/03/14	0.094	0.076	0.247	1.066	1.069	1.483
28/03/14	0.057	0.044	0.118	0.865	0.833	1.084
03/04/14	0.056	0.089	0.128	0.910	0.871	1.182
09/04/14	0.068	0.064	0.130	0.900	0.873	1.162
15/04/14	0.047	0.038	0.088	0.759	0.763	0.931
21/04/14	0.031	0.126	0.328	0.852	1.091	1.337
27/04/14	0.023	0.149	0.292	0.750	1.041	1.214
03/05/14	0.071	0.250	0.660	1.150	1.660	2.131
09/05/14	0.071	0.245	0.470	0.996	1.382	1.783
15/05/14	0.086	0.308	0.774	1.294	1.865	2.462
Annual						
min	0.02	0.04	0.00	0.28	0.36	0.77
max	0.75	1.49	1.48	2.73	3.73	5.20
Average	0.14	0.40	0.66	1.08	1.51	2.28
SD	0.13	0.36	0.39	0.50	0.79	1.16

Appendix B

PM_{10} sampling sites

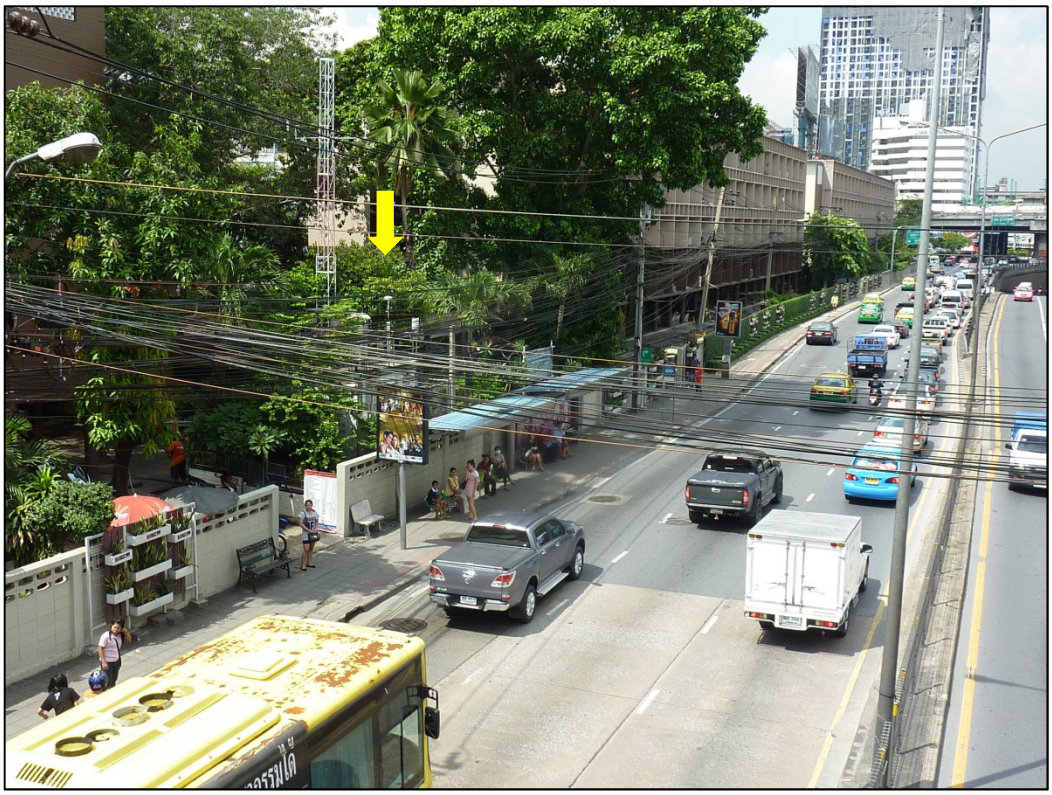


Figure B.1 Ambient air monitoring station at the roadside site.

Figure B.2 PM_{10} sampling equipment at the roadside site.

Figure B.3 Satellite image showing the roadside site (yellow spot) in Bangkok.

Figure B.4 Ambient air monitoring station at the industrial site.

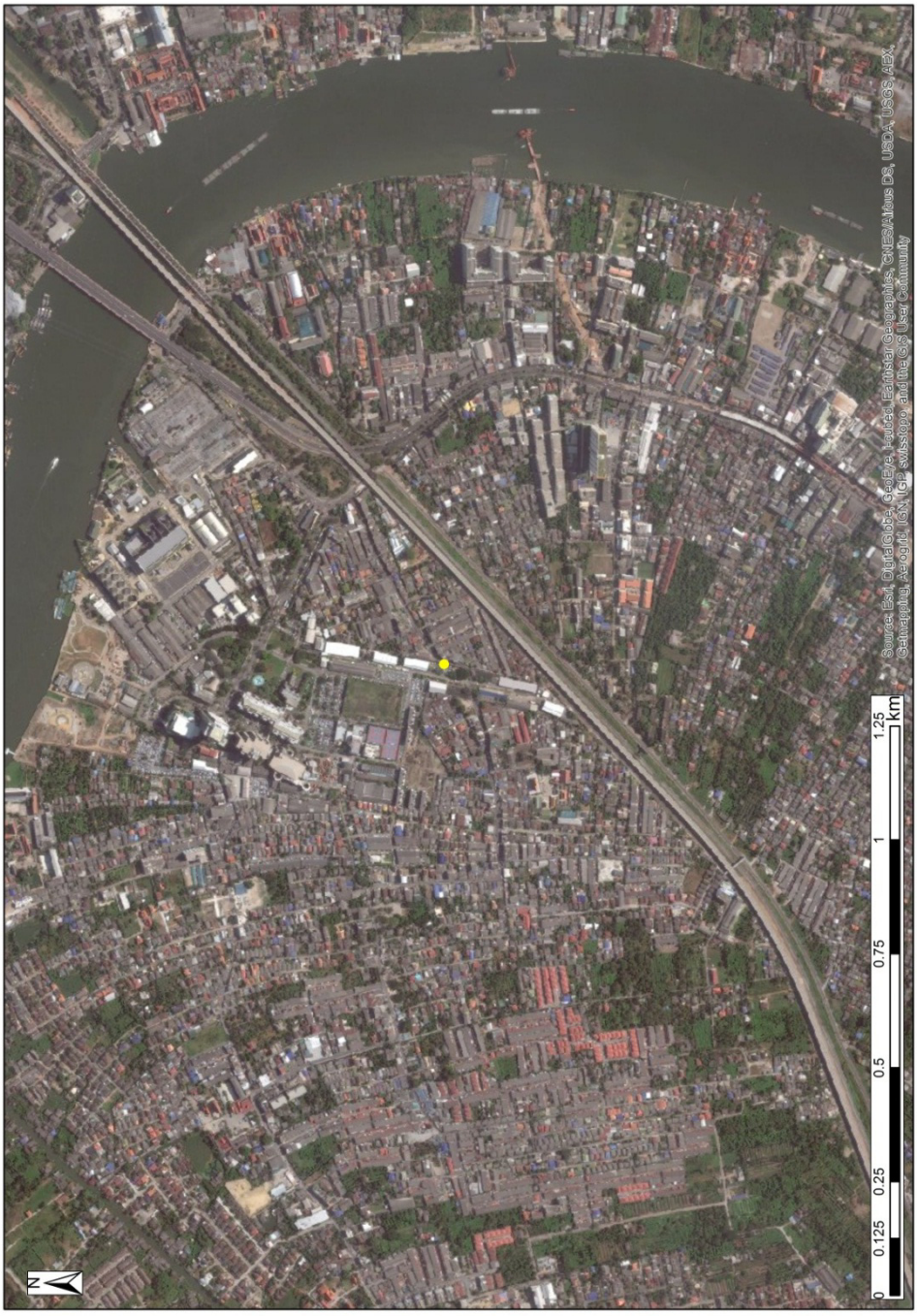


Figure B.5 Satellite image showing the industrial site (yellow spot) in Nonthaburi Province.

Figure B.6 Ambient air monitoring station at the urban background site.

Figure B.7 PM_{10} sampling equipment at the urban background site.

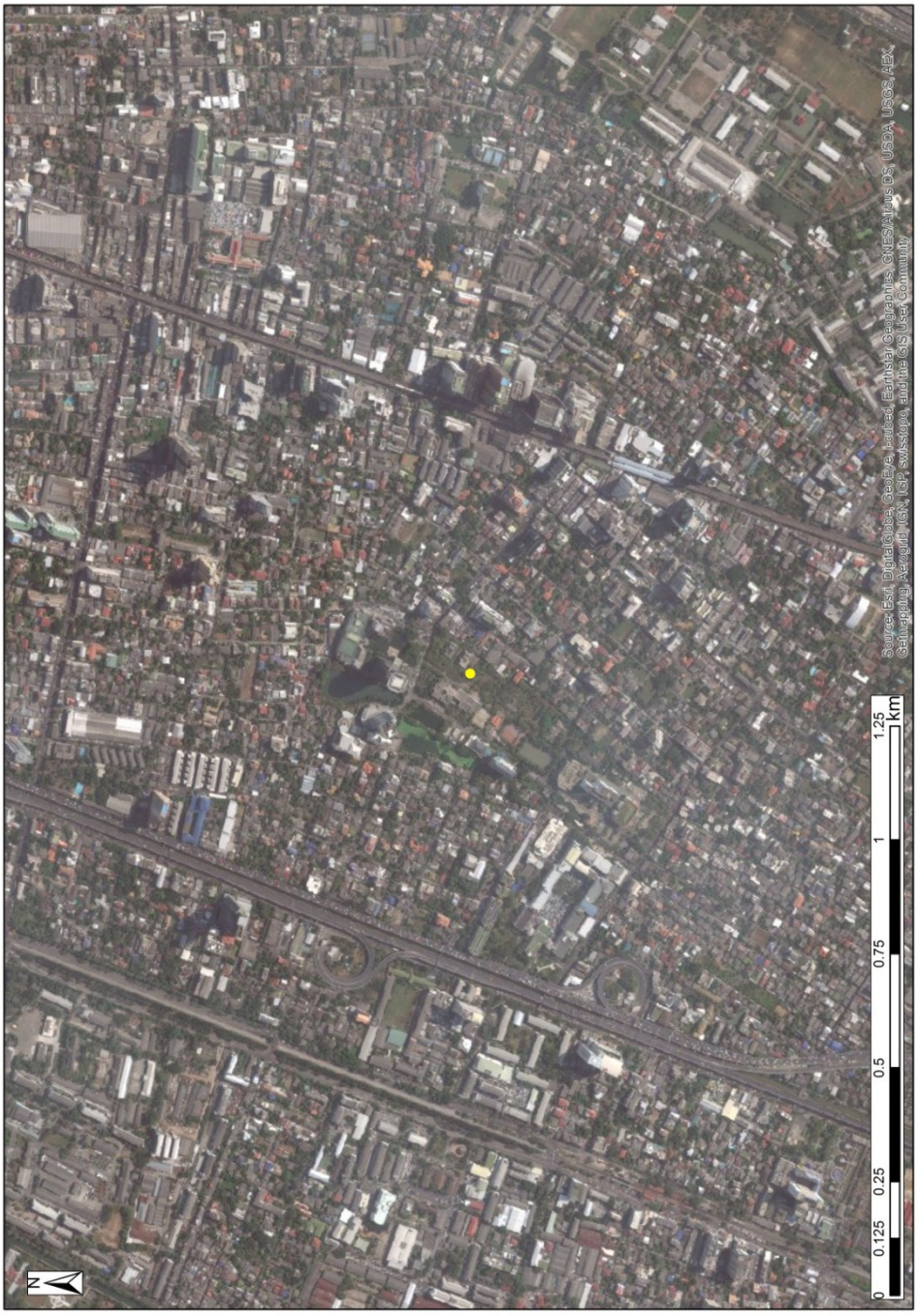


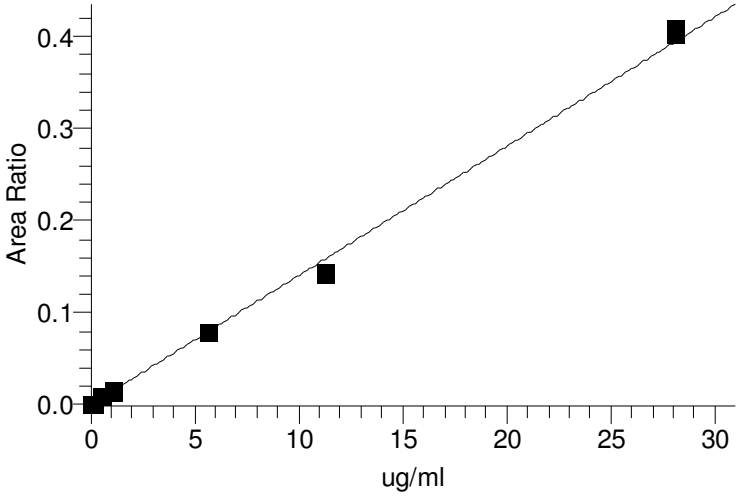
Figure B.8 Satellite image showing the urban background site (yellow spot) in Bangkok.

Appendix C

GC-QMS Calibration curves

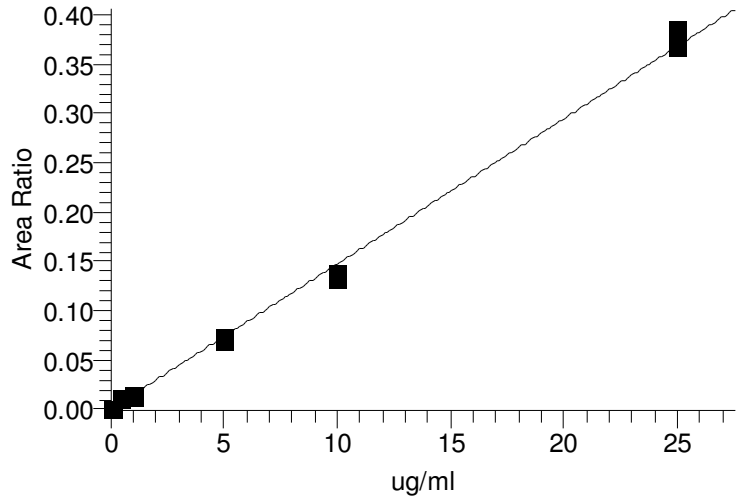
D8-Naphthalene

Y = 1.35975e-005+0.0140418*X R^2 = 0.9960 W: 1/X



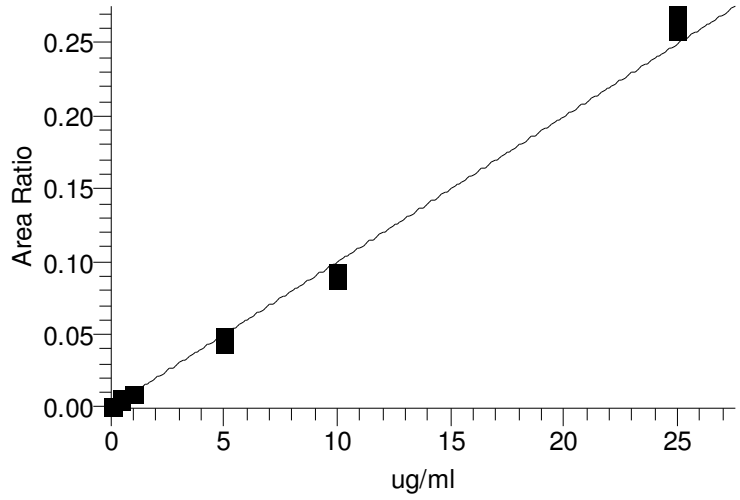
Naphthalene

Y = 3.92708e-005+0.0147302*X R^2 = 0.9959 W: 1/X



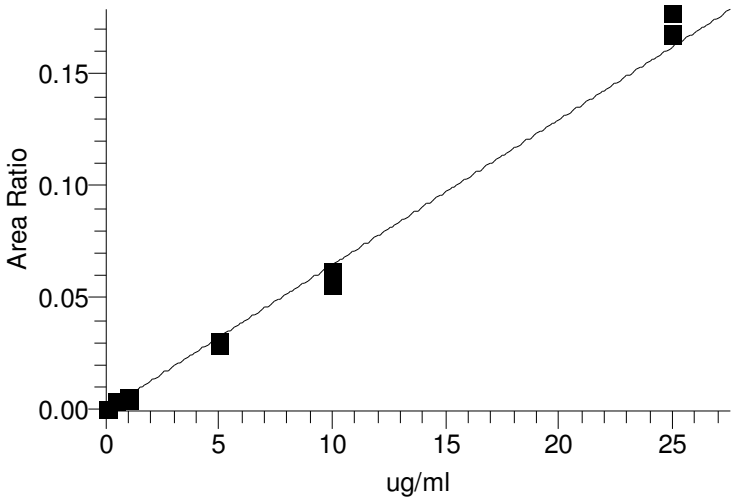
Acenaphthylene

Y = -3.2341e-005+0.00999105*X R^2 = 0.9934 W: 1/X



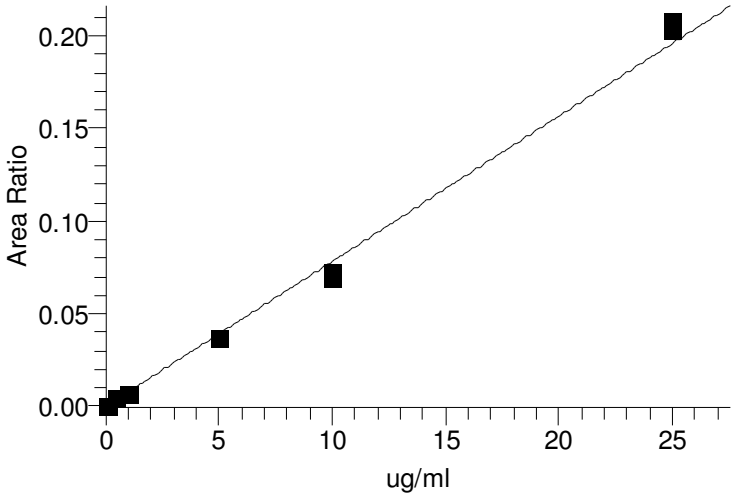
Acenaphthene

Y = -1.79901e-005+0.00648631*X R^2 = 0.9936 W: 1/X



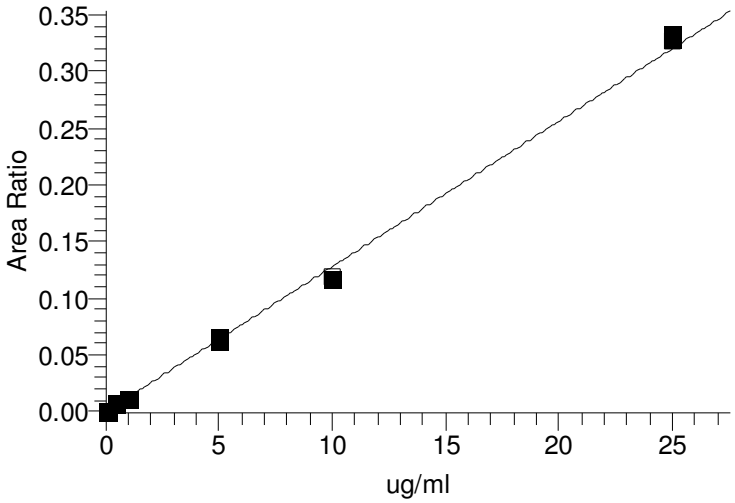
Fluorene

Y = -1.89533e-005+0.00784641*X R^2 = 0.9951 W: 1/X



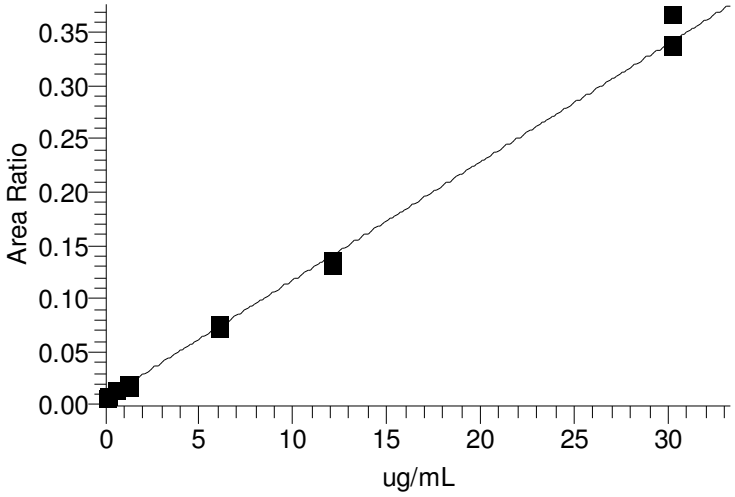
Phenanthrene

Y = -0.000144911+0.0128355*X R^2 = 0.9965 W: 1/X



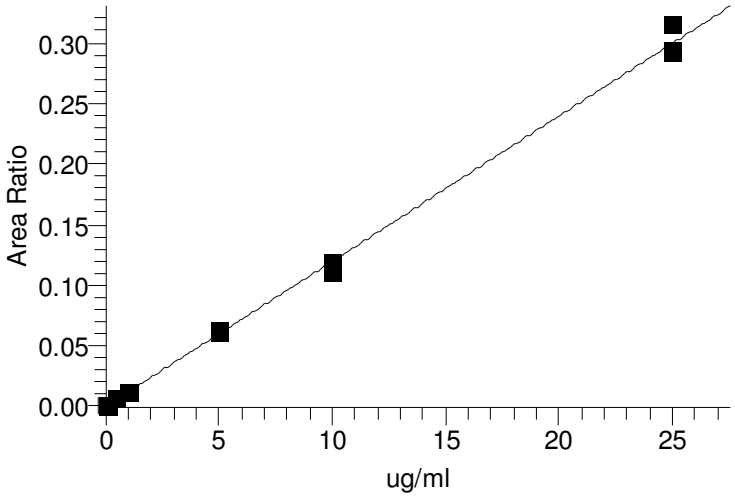
D10-Anthracene

Y = 0.00640493+0.0111024*X R^2 = 0.9960 W: 1/X



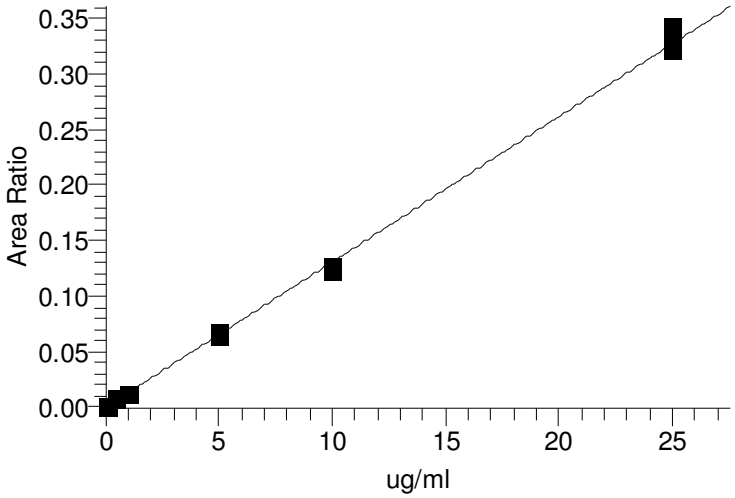
Anthracene

Y = -2.92843e-006+0.0119887*X R^2 = 0.9974 W: 1/X



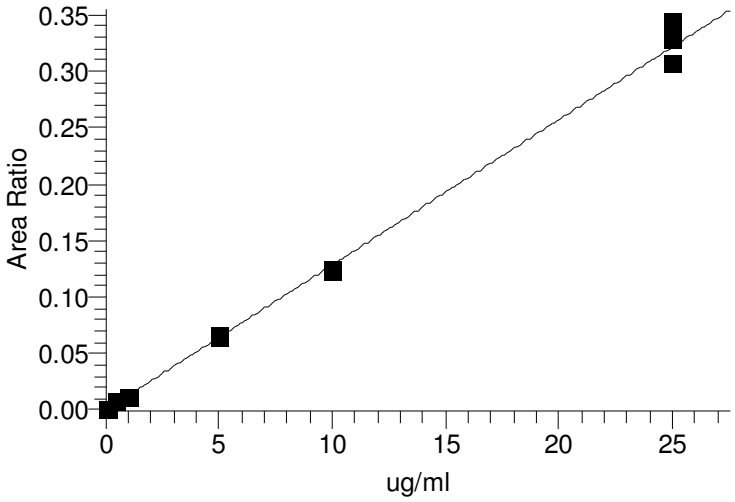
Fluoranthene

Y = -3.65082e-005+0.0131042*X R^2 = 0.9975 W: 1/X



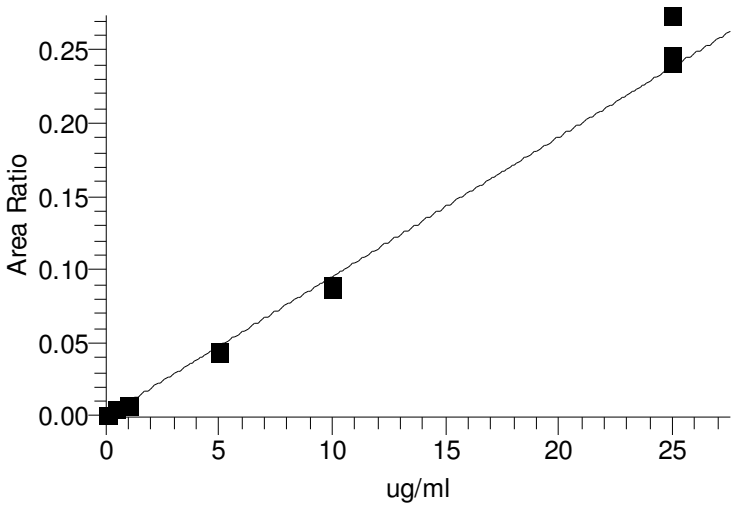
Pyrene

Y = -3.55466e-005+0.0128747*X R^2 = 0.9971 W: 1/X



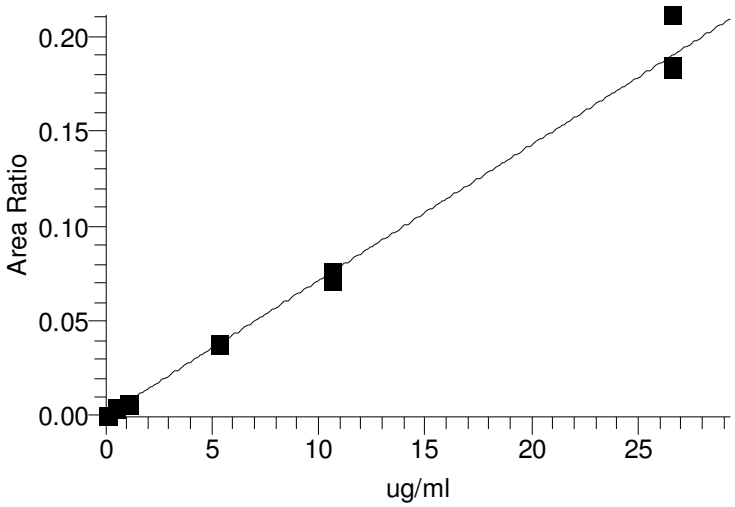
Benz(a)anthracene

Y = -0.000162127+0.00954162*X R^2 = 0.9907 W: 1/X



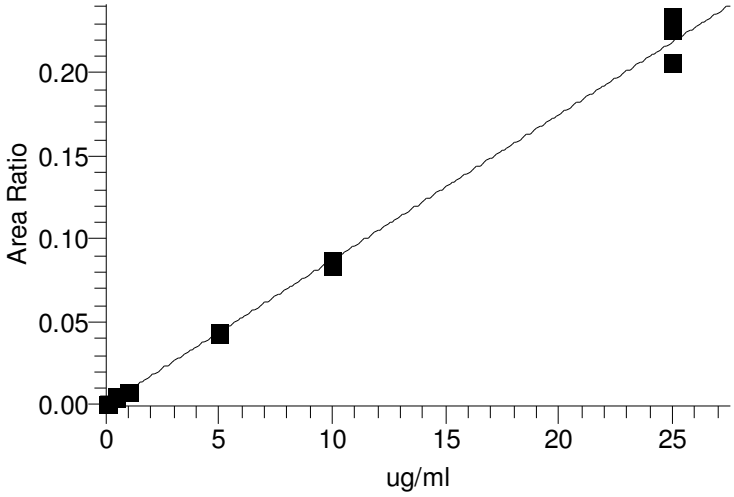
D12-Chrysene

Y = -8.3652e-005+0.00714189*X R^2 = 0.9956 W: 1/X



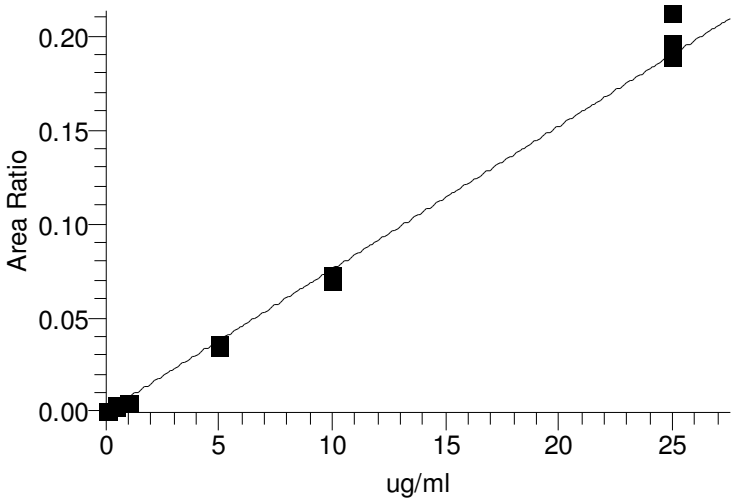
Chrysene

Y = -9.2986e-005+0.0087628*X R^2 = 0.9968 W: 1/X



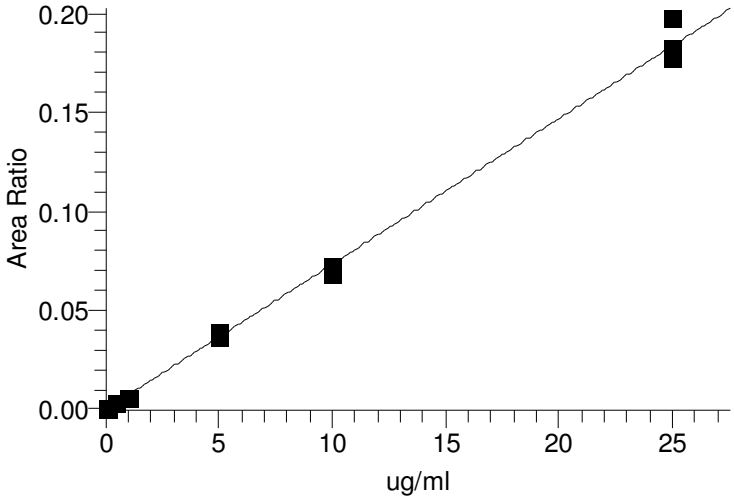
Benzo(b)fluoranthene

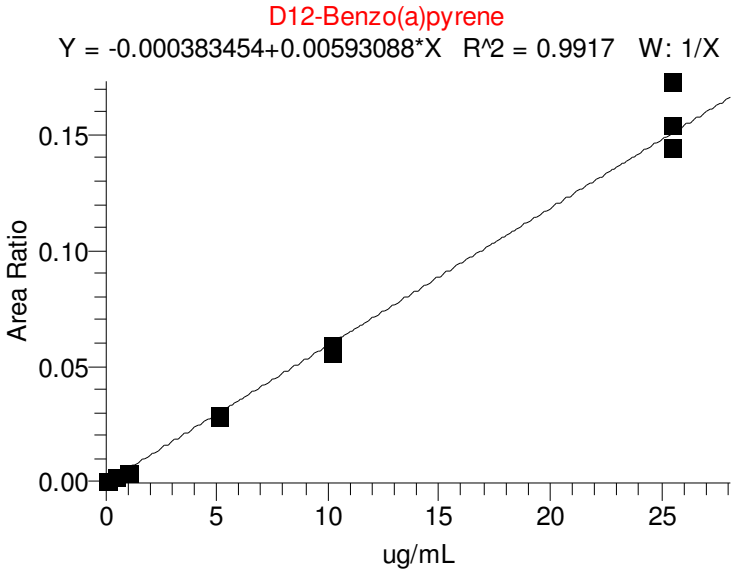
Y = -0.000443698+0.00762377*X R^2 = 0.9933 W: 1/X

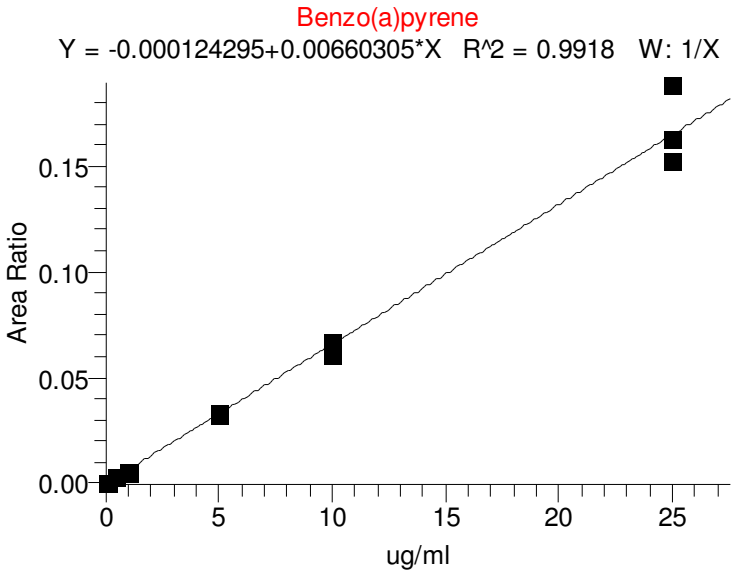


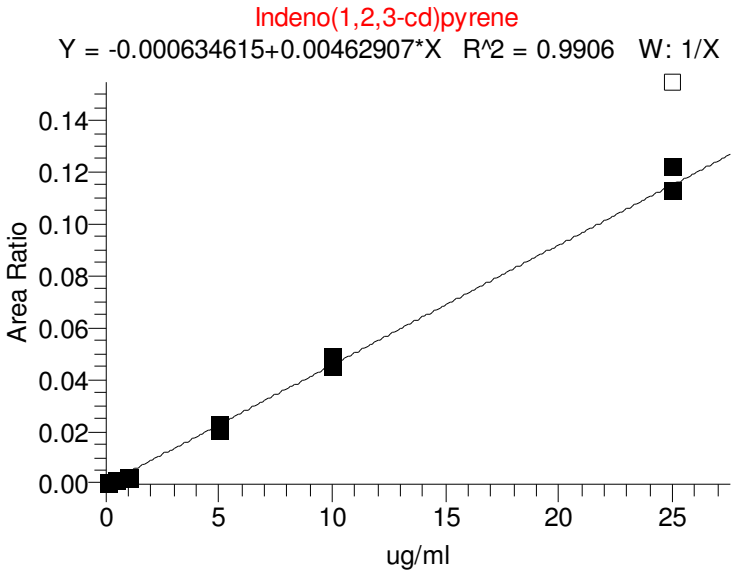
Benzo(k)fluoranthene

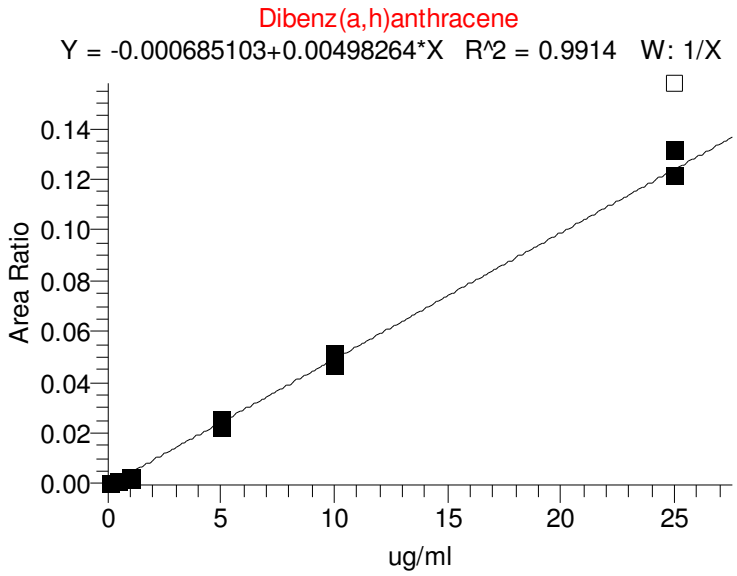
Y = -0.000338643+0.00735866*X R^2 = 0.9970 W: 1/X

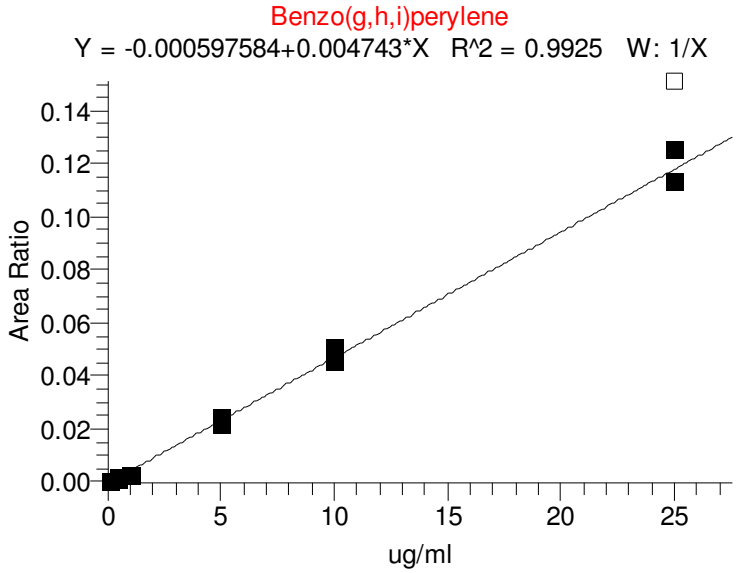



D12-Benzo(a)pyrene
Y = -0.000383454+0.00593088*X R^2 = 0.9917 W: 1/X
Area Ratio
0.15
0.10
0.05
0.00
0
5
10
15
20
25
ug/mL


Benzo(a)pyrene
Y = -0.000124295+0.00660305*X R^2 = 0.9918 W: 1/X
Area Ratio
0.15
0.10
0.05
0.00
0
5
10
15
20
25
ug/ml


Indeno(1,2,3-cd)pyrene
Y = -0.000634615+0.00462907*X R^2 = 0.9906 W: 1/X
Area Ratio
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
25
ug/ml


Dibenz(a,h)anthracene
Y = -0.000685103+0.00498264*X R^2 = 0.9914 W: 1/X
Area Ratio
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
25
ug/ml


Benzo(g,h,i)perylene
Y = -0.000597584+0.004743*X R^2 = 0.9925 W: 1/X
Area Ratio
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
25
ug/ml