Distribution and characteristics of black carbon from biomass burning in the middle- and low-latitude Asian and its impact on regional climate and monsoon precipitation

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Preface

I was delighted to respond to an invitation from Prof. Dr. Junji Cao, a deputy director of Institute of Earth Environment, Chinese Academy of Sciences (IEECAS) to join an international project funded by National Natural Scineces Foundation of China (NSFC) and Thailand Research Fund (TRF) under the topic of Climate Change & Climate Variability Research in Monsoon Asia. It is a topic well enough investigated by Western researchers in the past, but has become increasingly important during these early years of the 21st Century in Asian countries. I believe therefore that there is a place for a geochemist like me and that notwithstanding the immense activity in the research area the report will have a reasonable shelf life. This is because it constantly connects the argumentation to the fundamentals of physics and chemistry associated with aerosols and other environmental compartments, and these do not change with time.

To have appreciated each and every one of the previous studies I have drawn on would not only have lengthened the report to no real purpose but, more seriously, might even have been a distraction to a reader. I wish that this appreciation in the preface of such sources will suffice.

I am hopeful that graduate students will benefit from the report as well as those already professionally involved with atmospheric pollution, climate sciences, atmospheric chemistry, paleoclimate and limnology. I am very much hoping that it will of use to those involved in argumentation of such matters in the media. I shall be delighted to hear from readers who have comments or suggestions to make.

Siwatt P

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Chapter I

Introduction

1.1 Research Background

Biomass burning (BB) has been a pollution source for over 300 million years in history. It plays a role of ‘catalyst’ affecting the whole ecosystem on earth. BB emitting large amounts of trace gases and aerosol particles that play important roles in atmospheric chemistry and climate (1). Carbonaceous aerosol (including organic carbon/OC and black carbon/BC) is the major pollutant produced by BB, accounting for 60-80% of the total pollutants.

BC affect the Earth's temperature and climate by altering the radiative properties of the atmosphere. The magnitude of the direct radiative forcing from black carbon itself exceeds that due to CH4, suggesting that black carbon may be the second most important component of global warming after CO2 in terms of direct forcing [Jacobson, 2001]. Estimates of the direct radiative effect of BC complied by Bond et al. [2013] range between 0.1 and 1.63 W/m2. Besides, BC mixed with other aerosol components can serve as cloud condensation nuclei. These particles may thus substantially influence cloud microphysical and optical properties. An effect that could have repercussions for the radiation budget and the hydrological cycle in the tropics. However, OC is often held responsible for light scattering effect which can lead to global cooling. Thus, a number of researches indicate that the OC/EC ratio can be used as an index for the aerosol radiation effect. In addition, brown carbon, the absorbing component of OC associated with biomass burning absorbs light primarily at the low visible wavelengths and the near ultraviolet range of the spectrum; therefore, BrC also has significant radiative forcing impacts on the Earth’s atmospheric energy balance and even climate change (2, 3).

Although BC is a minor component of aerosol (usually it only accounts for a few to ten percent), due to its unique physical and chemical properties as well as the synergy with other aerosol, it still have significant impacts on air quality and global climate system. The different percentage of BC from aerosol mass showed geographical divergence, closely related to the emission source (4). Tropical Southeast (SE) Asia is an active biomass-burning region as a result of the increasing deforestation and agricultural activities [Stott, 1988; Christopher and Kimberly, 1996]. BB serves to clear land for shifting cultivation, to convert forests to agricultural and pastoral lands, and to remove dry vegetation in order to promote agricultural productivity and the growth of higher yield grasses, with the characteristics of large-emission, high-diversity, and relative concentration of burning time in the region. Christopher and Kimberly [1996] have identified east-central India and the region containing Thailand, Laos, Cambodia and Vietnam as the two major areas of biomass burning in India and SE Asia (5). The BC emission from SE Asia could be transferred to the downwind areas (including the east coast of China and even high-altitude region) under the guidance of the monsoon (see Fig. 1.1), and its impact is a key concern. In recent years, scientific attention has shifted from the role of black carbon as a pollutant to its importance as a driver of climate change in SE Asia. For instance, Lau, Kim and Kim (6) suggest that increased dust loading coupled with black carbon emission from local sources in northern India during late spring may lead to an advance of the rainy periods and subsequently an intensification of the Indian summer monsoon. The enhanced rainfall over India is associated with the development of an aerosol-induced large-scale sea level pressure anomaly pattern, which causes the East Asia (Mei-yu) rain belt to shift northwestward, suppressing rainfall over East Asia and the adjacent oceanic regions; thinning of glaciers over the Himalayas caused by BC deposition (7).

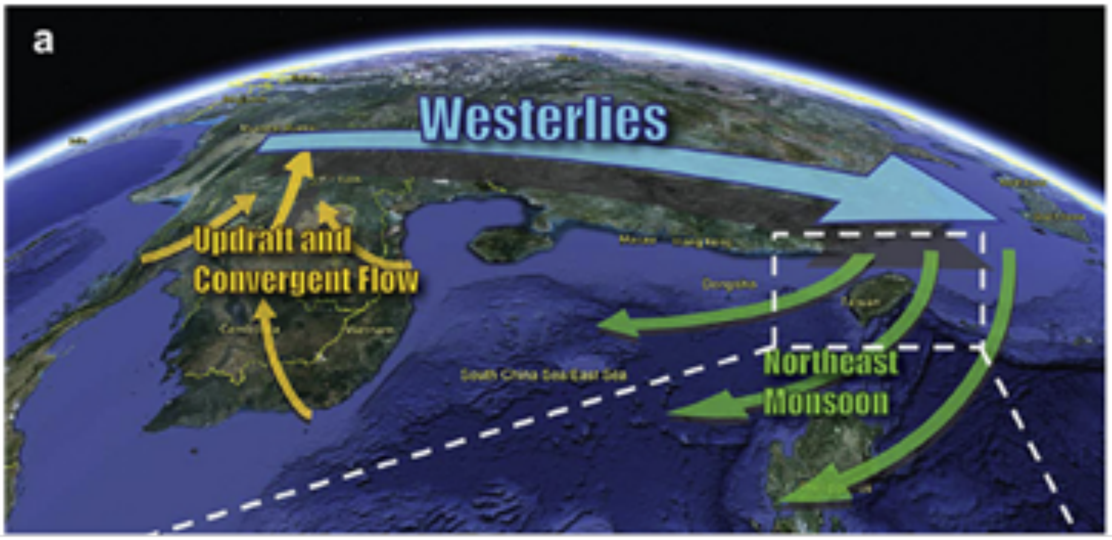


Figure. 1.1. Conceptual model for climatological circulation pattern in March for high-altitude and low-level transport pathways by westerly and northeast monsoon flows (8)

Although earth's atmospheric energy balance owing to BC has been recognized widely, great uncertainty still exists in assessing the climate change effects of BB emitting BC in SE Asia region; the main bottleneck are that 1) no sufficiently long-term and targeted ground-based observations in Southeast Asia; 2) the lack of assessment in different combustion ways; 3) the climate effects of black carbon and homology pollutants from BB are still controversial. Firstly, most researches of BC and its climate effects are conducted in South Asia (mostly in Indo-Gangetic plain), but rarely in SE Asia. Secondly, two different combustion ways (flaming combustion and smoldering combustion) have been found having divergent results of emission. Flaming combustion has been found having more BC while the smoldering has more OC. Moreover, as to PAHs, flaming contributes more than smoldering does. This divergence causes different effects on radiation, climate as well as monsoon precipitation. Finally, biomass burning in SE Asia is an important source of BC and other homologous contaminants (organic carbon, sulfates, and gas precursors) in this region. Climate effects of BC and homologous pollutants shows not only opposing effects but also regional differences, such as, positive radiative forcing from BC but negative from other homologous aerosols. And aerosol demonstrates a stronger effect on continents than marine, on high latitude than low one, on East Asia than other regions at the same latitude.

At present, the urgent need for understand BC and its climate change effects have been recognized by scientists as well as governments, and research projects has been taken in SE Asia gradually. For example, BASE-ASIA (Biomass-burning Aerosols in South-East Asia: Smoke Impact Assessment) and the 7-SEAS (7-South-East Asian Studies)/Dongsha Experiment were conducted during the spring seasons of 2006 and 2010 in northern SEA, respectively, to characterize the chemical, physical, and radiative properties of biomass-burning emissions near the source regions, and assess their effects. Chuang, Chou, Sopajaree, Lin, Wang, Sheu, Chang and Lee (9) is the first study to characterize the chemistry of biomass-burning aerosols near the source region in the northern SEA, i.e., border of Thailand and Myanmar (at Doi Suthep, near Chiang Mai city) where highly intense fires happen nearby. Their results suggest the biomass-burning aerosols are mainly produced by smoldering softwood. The biomass-burning plume from northern SEA was sampled at several locations along the transport pathway. Plume signatures were observed at LABS in central Taiwan (10), above boundary layer over Hong Kong (5, 11), and possibly even near the surface in the southern Taiwan (12). These studies provide the first relatively complete dataset of aerosol chemistry and physical observations conducted in the source/sink region in the northern SE Asia, with particular emphasis on the marine boundary layer and lower free troposphere. However, reviewing these researches, most of them are short-term observations and lacking of specificity (e.g. feedback mechanisms between BC and Asian monsoon cycle, etc.), which impedes further discussions on characteristics and the impact of BC producing from biomass burning in SE Asia.

For a better understanding of direct and indirect climate effects from biomass combustion BC, and improve the accuracy of model simulation in predicting future climate change trends, it’s necessary to explore the history of biomass burning through BC in sediment. Before the industrialization, biomass combustion was the only source of BC in atmosphere. Therefore, to study the history of biomass combustion can facilitate us to understand the effect of BC exerted on climate; also assist us to predict the future climate change and biomass combustion trend. In Asia however, on one hand we lack the history log of the long-term biomass burning, on the other, the majority of previous biomass combustion history were restructured through charcoal, so the divergence of combustion methods were never considered by any researchers before. Hence, researches on the connection between climate change and carbonaceous aerosol emission are limited.

Recently, the applicant reconstructed the combustion history of flaming combustion and smoldering combustion in North America via experiments with different types of char-soot (13). Soot is a common residue of smoldering combustion, which reserves the features of the original organic substance. Char, by contrast, can be found rich after flaming combustion. Although in previous researches most of them claim that char is the primary form of BC while the sediments and soil researches emphasize on soot, in fact, whatever aerosol or sediments, those two forms of carbon compounds are ubiquitous. However, due to the difference in physi-chemical characteristics, the transport trajectories are different. To be more specific, the transport of char often occurs in a relatively short distance in regions, while the soot always travels far across continents. Furthermore, our research will involve the verification on the hypothesis that soot in sediments are from atmosphere. Also because of the divergence of OC/EC between char and soot, we reconstruct atmospheric soot concentration history through that in sediments. This serves as a new approach of predicting the long-term OC/EC ratios and also makes it possible for understanding and quantifying the interactive effect between carbonaceous aerosol and climate change. In addition, the applicants also found that flaming combustion often occurred in dry area, smoldering by contrast often happened in wet area. Therefore, we generated a hypothesis that more flaming wildfires occurring in dry regions, more smoldering wildfires in wet regions. They have different OC and BC emissions, especially, higher OC/BC in wet regions and lower OC/BC in dry regions. Thus, OC/BC ratios, which are the key factor influencing on climatic effects of carbonaceous aerosols (14), can be evaluated, and this can be used in modeling studies. What we want to do is to confirm this hypothesis through the comparison of wildfire history (the Holocene), smoldering and flaming, in both wet, say Thailand, and dry regions, say western China. The comparison of carbonaceous aerosol compositions will be also conducted to support our hypothesis. In addition, biomass burning source emissions will be tested in different fuels and different loading (wet and dry).

In spite of various studies associated with OC/EC in atmospheric particles around the world, the number of publications related with carbonaceous aerosols in Thailand is strictly limited. In 2013, Pongpiachan et al (2013) reported the estimation of gas-particle partitioning coefficients (Kp) of carcinogenic polycyclic aromatic hydrocarbons in carbonaceous aerosols collected at Chiang-Mai, Bangkok and Hat-Yai, Thailand by using Dachs-Eisenreich model (15). This is the first study to assess the diurnal variation of OC/EC in PM10 collected at three different altitudes in urban atmosphere of Southeast Asian cities. Dachs-Eisenreich model highlights the crucial role of adsorption in gas-particle partitioning of low molecular weight PAHs, whereas both absorption and adsorption tend to account for gas-particle partitioning of high molecular weight PAHs in urban residential zones of Thailand. Interestingly, the absorption mode alone plays a minor role in gas-particle partitioning of PAHs in Chiang-Mai, Bangkok and Hat-Yai. Recently, Pongpiachan et al (2015) published the study of effects of day-of-week trends and vehicle types on PM2.5-bounded carbonaceous compositions in Science of the Total Environment (16). The application of diagnostic binary ratios of OC/EC and estimations of secondary organic carbon (SOC) coupled with autocorrelation plots (Box and Jenkins) highlight the enhanced impacts of traffic emissions, especially from diesel vehicles, on PM2.5-bound carbonaceous compositions on weekdays relative to weekends. Hierarchical cluster analysis (HCA) coupled with principal component analysis (PCA) underline the importance of diesel emissions as the primary contributors of carbonaceous aerosols, particularly during weekdays. The spatial and temporal distribution of carbonaceous PM10 was assessed in eight air quality observatory sites in Bangkok from February to December 2007 (17). The relatively low OC/EC ratios observed in Bangkok highlight the influence of transportation sector in governing carbonaceous aerosols, particularly in heavy traffic congestion area. Three-dimensional plots of principal components (PCs) successfully discriminate “traffic emission” group from those of “urban residential background” group. Over the past decades, there are many studies analyze OC/EC coupled with PAHs in core sediments in different locations around the world. Since PAHs are widely considered as a consequence of imperfect combustions of hydrocarbon, various investigations have been attempted to connect PAHs with historical trends of atmospheric black carbon in lake sediment record (18-20). Despite the countless number of publications associated with

PAHs in various environmental compartments in different countries, there are only a few studies related with this topic in Thailand (21-26).

Above all, the impact of black carbon aerosols on climate has become one of the hot topics in the international atmospheric research field. However, the divergent regional climate effects are generated by such a large amount of biomass combustion in SE Asia, especially the medium-term and long-term effects on regional climate exerted by different combustion modes are still poorly understood. Therefore, it is urgent for us to carry out a more systemic and in-depth research in this field. This will provide scientific basis for China and SE Asia in sustainable social and economic development and ecological management. On the other hand the severe particulate air pollution from BB in SE Asia, provides a unique platform for scientists worldwide to obtain new insights into many aspects of atmospheric chemistry and physics and its climate effects. This calls for international collaboration.

This proposed project is based on the collaborative research project "Climate Change (Climate Change & Climate Variability Research in Monsoon Asia)" of National Natural Science Foundation of China (NSFC) and Thailand Research Foundation (TRF) in 2016. And the proposed topic is in line with ‘2.2 Land surface, their impacts and interactions with climate’ application requirements in the guide of TRF.

This project is proposed by Siwatt Pongpiachanof the School of Social and Environmental Development, National Institute of Development Administration (NIDA), Thailand, and Yongming Han, a professor from the Institute of Earth Environment, Chinese Academy of Science. The applicant, Siwatt Pongpiachan, has devoted himself to the study on air quality in Thailand, especially the environmental and health effects of VOCs in carbonaceous aerosols, since he worked in the School of Social and Environmental Development, National Institute of Development Administration (NIDA). Thanks to his diverse abroad study experience, his group established a good cooperative relationship with world-famous scientific institutions in Japan, England and China (Hongkong included), and became one of the best groups on aerosol study in Thailand. The Chinese partner, the

Key Laboratory of Aerosol Chemistry and Physics (KLACP) at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS), focuses on chemical nature and sources of particulate matter as well as model studies of air pollution in China. With over 50 publications per year and around 2000 citations of their work per year, the KLACP is recognized as one of the world-leading groups in the characterization of chemical and physical properties of aerosol particles and their sources in urban, rural, mountain, desert, and pristine Tibet-Qinghai regions, as well as modelling studies of air pollution with regional and global models e.g., WRF-CHEM, CMAQ, MOZART. Since 1980's, KLACP has accomplished aseries of aerosol observation campaigns around China. Tens of representative urban and rural sites were established, among which 10 are for continuous observations, including Sanya and Yulong Mountain sites in this project. Over the past 10 years, the KLACP has coordinated several large field measurement campaigns with world-leading groups including the Desert Research Institute, University of Minnesota, University of Washington, NOAA, PSI and the Polytechnic University of Hong Kong. The KLACP was also the first laboratory established in China for carbonaceous aerosol studies. The KLACP pioneered the first nationwide summertime and wintertime carbonaceous aerosol studies in China (14 cities) in 2003, leading to the first picture of particulate air pollution in China (Cao et al., 2007) (27). Multi-discipline techniques, including systematic observation, analytical method development, record re-construction, and numeral simulation, were integrated in this lab to enrich the fundamental understanding of black carbon climatology.

Since 2010, when Siwatt Pongpiachan began his post-doctoral research in KLACP, a strong collaboration has successfully been established between his group and the KLACP at CAS. In January 2015, the President of NIDA, Assoc. Prof. Pradit Wanarat visited the KLACP and signed a Memorandum Of Understanding (MOU) with IEECAS, reaching a consensus about all-dimensional cooperation in the exchange of faculty members and students, joint research activity, organization seminars, etc. With the support of this agreement, a PhD candidate in the KLACP, Wei Chong, firstly conducted an aerosol observation experiment for a month from March to May 2015 in Thailand. Recently, Prof. Cao Junji in the KLACP was invited to attend the first International Conference on Disaster

Management: From the Polar Regions to the Local Communities and give a plenary presentation. During the conference, Prof. Cao discussed the joint project in depth with Assoc. Prof. Dr. Siwatt Pongpiachan, which further strengthened the collaboration between these two groups and will be a perfect basis for a successful joint Chinese-Thailand project.

1.2 Objectives

In this study, we will do researches on three subjects. The first one focuses on the history of biomass burning in the past 2000 years from lake sediments, its emissions, and their relations with climate change, which will provide a understanding of the mechanical relationship between biomass burning and climate change. The second one is the distribution and physicochemical characteristics of black carbon by aerosol observations, which will provide the key parameters for radiative forcing simulations and will test the hypothesis in paleo-wildfire study. The last one is the impacts of biomass burning on the radiation and monsoon precipitation in Asia from model simulations. Thus, this research has three objectives listed below:

1) We will collect 6 lake sediment cores in different climatic zones and reconstruct the wildfire history including both flaming and smoldering combustion in the Asia in the middle- and low-latitude Asian regions covering the past 2000 years. The relationship among the climatic zones, vegetation types, the combustion types, and carbonaceous aerosol emissions from biomass burning will be put forward.
2) We will find out the transport and evolution characteristics of black carbon; obtain the particle size distribution, mixing state, optical property, and hygroscopic characteristics of black carbon at a high time resolution scale; and establish the connection between aerosol radioactive forcing and these characteristics of black carbon mentioned above.
3) Using the WRF-Chem model, we will find out the radiative effects of carbonaceous aerosol emitted from biomass burning in the middle- and low-latitude Asian regions; discuss its influence on monsoon precipitation, and

forecast the trend of biomass burning, its emissions and their direct and indirect climate effects in the next 30 years.

1.3 Expected Outcomes

1) The variations of wildfires overview map or based historical map
2) The intrinsic mechanism of the occurrences of biomass burning with climate change
3) WRF-Chem dynamical and chemical transport model
4) Biomass burning distribution maps
5) Impacts of carbonaceous aerosols
6) Decision making guidelines for local government
7) 2-4 international high-quality papers
8) Corroborations between Thailand and China.
9) Capacity building; research assistants, student
10) Websites

Chapter II

Research Methodology

2.1 Research Methodology

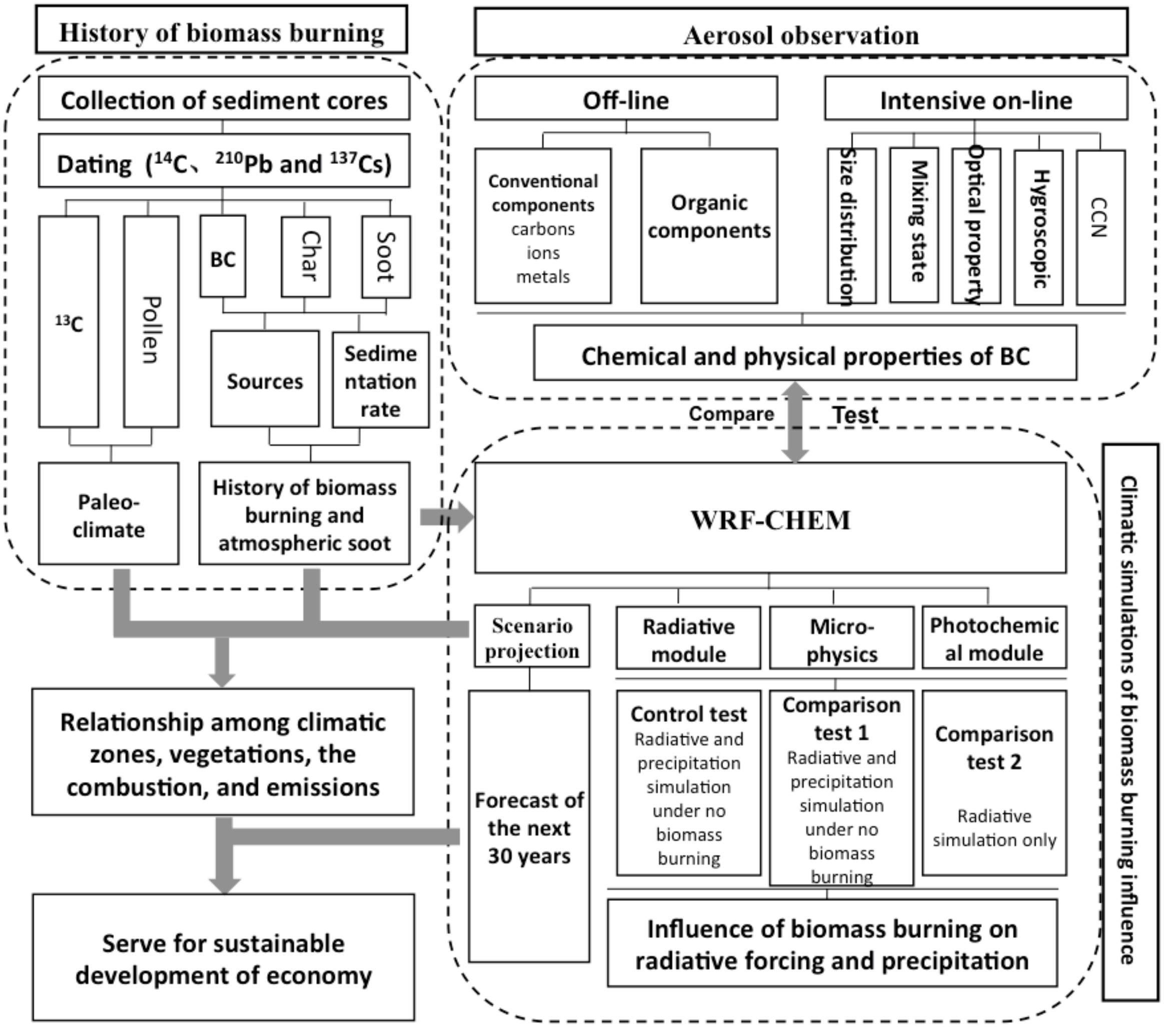


Figure 2.1. A flowchart of research methodology

This study was composed with three phases. Firstly, the history of biomass burning and atmospheric soot was carefully studied by the collection of lake sediment cores. Paleoclimate parameters such as ^{14}C, ^{210}Pb and ^{137}Cs coupled with OC/EC were deliberately characterized and statistically analyzed. Secondly, the chemical characterization of $PM_{2.5}$ were conducted by using GC-MS/MS and DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT). All physicochemical properties (e.g. hygroscopic, CCN, optical property, mixing states, and size distribution) were monitored online. Thirdly, the climatic simulation of biomass burning influence was assessed by using WRF-CHEM model, which is composed of photochemical module, microphysics and radiative module. In addition, the schematic diagram of research methodology was clear illustrated in Fig. 2.1.

2.1.1 History of biomass burning in the past 2000 years, its emissions, and their relations with climate change

12 sediment cores covering the past ~2,000 years will be collected from 6 lakes (three from Tailand, namely, Phayao Lake, Bueng Ken Lake, and Songkhla Lake; and three from China, namely, Qinghai Lake, Lugu Lake, and Tengchong Maar Lake) with different climatic zones and different annual precipitation rates using a kind of gravity core. Two parallel cores will be collected from each lakes. Sampling slices will be done in the field works at 0.5-3 cm intervals with approximately time resolutions of ~3-20 years. ^{14}C (radiocarbon) analysis from selected charcoal materials of sediment cores will be used for chronology reconstruction. ^{137}Cs and ^{210}Pb analysis will be conducted to date the chronology of the different sediment cores for the past ~150 years.

Black carbon (BC), char, and soot concentrations will be measured using the thermal-optical method, which will be used for the historical reconstruction of wildfires, flaming and smoldering combustion, and atmospheric soot concentrations in the past 2,000 years. ^{13}C stable isotope and pollen will be quantified to reconstruct the paleo-climate variations. PAHs, and OPAHs will be analyzed for recent sediments covering the past ~150 years to compare with the BC, char and soot results to test the effectiveness of our reconstruction of the wildfire history since both BC and PAHs originate mainly from burning. The relative contributions of flaming and smoldering combustion will be found out by the char/soot ratios in sediment cores. Meanwhile, the relative emissions of carbonaceous aerosol (organic and black carbon) from biomass burning will be evaluated from the relative contributions of flaming to smoldering fires in the past 2,000 years. The comparison of wildfire history including both flaming and smoldering combustion with paleo-climate (wet and dry) parameters indicated by pollen and ^{13}C data in different zones will give us the mechanism understanding the relationship between will fire and climate.

2.1.2 Distribution and physicochemical characteristics of black carbon

In this subject, we plan to take one year-round $PM_{2.5}$ samples simultaneously at low latitude area of Asian, Phuket, Thailand, as well as Sanya, Sansha, and Mt. Yulong, China. The concentrations of black carbon will be quantified to investigate their temporal and spatial distribution. The ME-2 receptor model will be used to study the contributions of different sources on black carbon mass, while the regional atmospheric chemistry model will be used to quantify the contributions from local and regional transport. The regional atmospheric chemistry model will also be used to understand the evolution characteristics of black carbon during monsoon and non-monsoon. The intrinsic relationship between the physical and chemical properties of black carbon aerosol and the aerosol radiative forcing will be investigated to improve the key parameters in the radiative transfer model.

2.1.3 Impacts of biomass burning on the radiation and monsoon precipitation in Asia

We will apply the state-of-art regional WRF-Chem dynamical and chemical transport model and emission inventories of biomass burning estimated by MODIS monitoring to assess the impacts of biomass burning in Southeast Asia on Asian climate. In order to better separate the direct and indirect climate effects of biomass burning on the radiation and monsoon precipitation in Asia, an aerosol-radiation module, photochemistry module and a new activation algorithm for cloud condensation nuclei (CCN)/ ice nuclei (IN) are developed in WRF-Chem model. In this proposal, we will also evaluate the potential impacts of biomass burning on Asian climate due to the activity data and emission control in the next decades.

2.2 Chemical analysis of PAHs

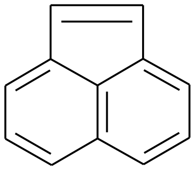
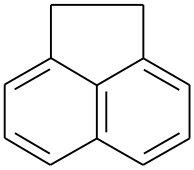
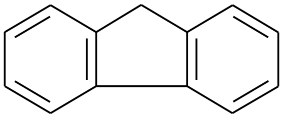
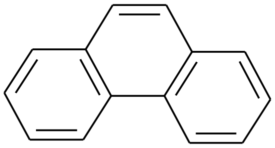
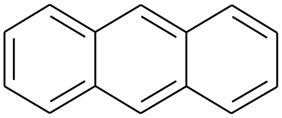
2.2.1 General information of PAHs

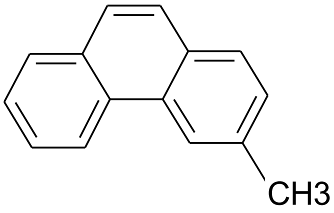
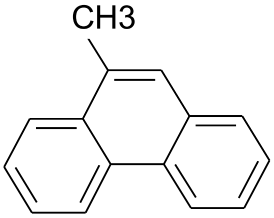
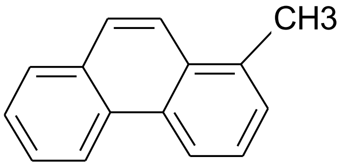
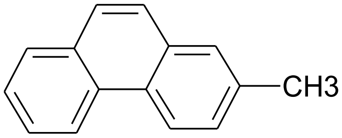
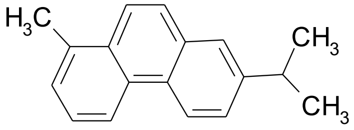
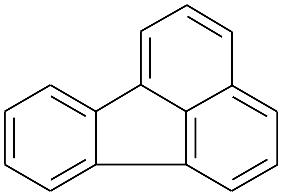
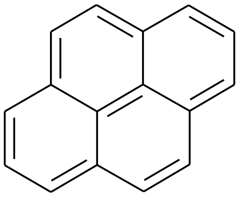
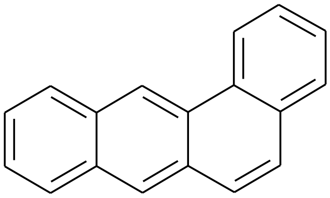
PAHs are a class of very stable organic molecules made up of only carbon and hydrogen and contain two to eight fused aromatic rings. PAHs are formed during incomplete combustion of organic materials such as fossil fuels, coke and wood. These molecules were oriented horizontal to the surface, with each carbon having three neighboring atoms much like graphite. The structures of a variety of representative PAHs can be seen in Table 2.1. Epidemiological evidence suggests that human exposures to PAHs, especially B[a]P are high risk factors for carcinogenic and mutagenic effects. There are hundreds of PAH compounds in the environment, but only 16 of them are included in the priority pollutants list of US EPA. Many PAHs have also been identified as cancer-inducing chemicals for animals and/or humans. In 1775, the British surgeon, Percival Pott, was the first to consider PAHs as toxic chemicals with the high incidence of scrotal cancer in chimney sweep apprentices. Occupational exposure of workers by inhalation of PAHs-both volatile and bound to respirable particulate matter- and by dermal contact with PAHs-containing materials, occurs at high levels during coke production, coal gasification, and iron and steel founding. Coke oven workers have a 3- to 7- fold risk increase for developing lung cancer.

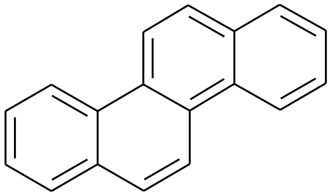
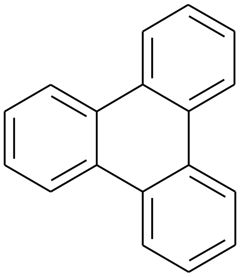
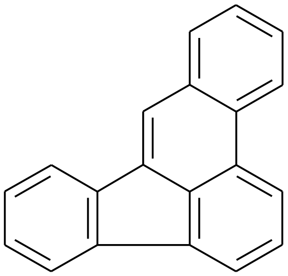
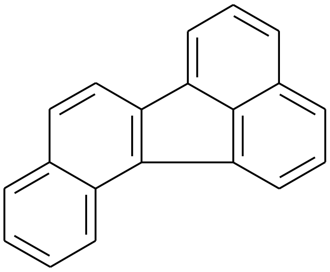
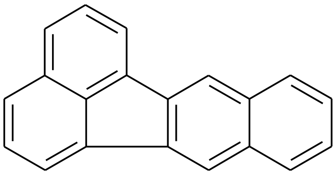
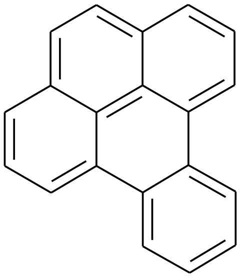
For this reason, the monitoring of PAHs in environmental media is a reasonable approach to assess the risk for adverse health effects. Since the fate of PAHs in the natural environment is mainly governed by its physiochemical properties, the study of general properties of the compounds is of great concern. It is well known that aqueous solubility, volatility (e.g. Henry's law constant of air/water partition coefficient, octanol/air partition coefficient), hydrophobicity or lipophilicity (e.g., n-octanol/water partition coefficient) of PAHs vary widely (Mackay and Callcot, 1998), the differences among their distribution in aquatic systems, the atmosphere, and the soil are significant. Molecular weight and chemical structure influence physical and chemical properties between individual PAHs.

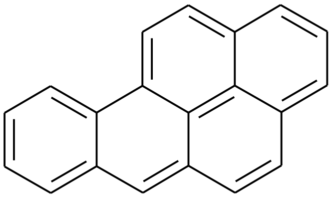
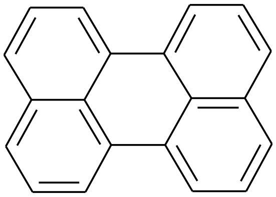
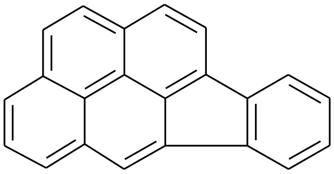
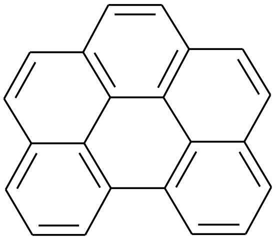
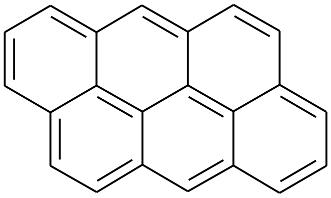
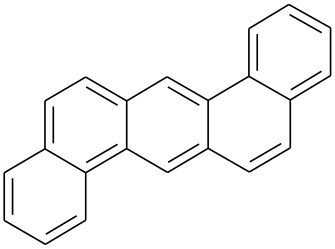
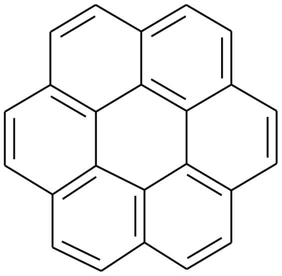
The vapour pressure and water solubility basically decrease with the increasing molecular weight. The fate of PAHs in the environment is largely determined by physiochemical property, as a result, high mobility of low molecular weight species can be expected. On the other hand, PAHs are also quite involatile, and have relatively low vapour pressure and resistance to chemical reactions. As a consequence PAHs are persistent in the environment and demonstrate a tendency to accumulate in biota, soils, sediments, and are also highly dispersed by the atmosphere. Furthermore, PAHs become more resistant to biotic and abiotic degradation as the number of benzene rings increase.

Table 2.1. Chemical structures of PAHs.

Congener	Abbreviation	M.W. [g]	Chemical Structure
Acenaphthylene	Ac	152	
Acenaphthene	Ace	154	
Fluorene	Fl	166	
Phenanthrene	Ph	178	
Anthracene	An	178	

3-Methyl Phenanthrene	3-MePh	192	
9-Methyl Phenanthrene	9-MePh	192	
1-Methyl Phenanthrene	1-MePh	192	
2-Methyl Phenanthrene	2-MePh	192	
1-methyl-7-isopropyl phenanthrene (Retene)	Ret	234	
Fluoranthene	Fluo	202	
Pyrene	Py	202	
Benz[*a*]anthracene	B[*a*]A	228	

Chrysene	Chry	228	
Triphenylene	Tri	228	
Benzo[*b*]fluoranthene	B[*b*]F	252	
Benzo[*j*]fluoranthene	B[*j*]F	252	
Benzo[*k*]fluoranthene	B[*k*]F	252	
Benzo[*e*]pyrene	B[*e*]P	252	

Benzo[*a*]pyrene	B[*a*]P	252	
Perylene	Per	252	
Indeno[*1,2,3-cd*]pyrene	Ind	276	
Benzo[*g,h,i*]perylene	B[*g,h,i]*P	276	
Anthanthrene	Ant	276	
Dibenzo[*a,h*]anthracene	D[*a,h*]A	278	
Coronene	Cor	300	

2.2.2 Chemical extraction of PAHs

2.2.2.1 Materials

All solvents are HPLC grade, will be purchased from Fisher Scientific. The EPA 16 PAH surrogate cocktail in methanol (100 µg ml^{-1}) which will be used as internal standard will be obtained from Greyhound/Chemserve. Silica gel (0.040–0.063 mm) will be purchased from Merck. Soxhlet thimbles and glass fiber filters will be obtained from Whatman (Maidstone, UK). All materials used (silica gel, glass and cotton wool, GFFs etc.) were Soxhlet extracted with DCM for 24 h, and kept dry (in desiccator) until use. Quartz fibre filters will be cleaned by baking at 550 °C overnight. All glassware will be cleaned by washing with decanted water before drying at 55 °C, and rinsed with DCM just before use.

2.3.2 Sampling Extraction

The extraction of PAHs will be conducted using 250 ml of Soxhlet extractors. After $PM_{2.5}$ determination, the QMFs will be divided in to two parts using stainless scissors. After that, the Soxhlet extraction of $PM_{2.5}$ filter samples and $PM_{2.5}$ filter blanks will be placed inside the Soxhlets, spiked with a known amount of internal standard (deuterated PAHs), and extracted with DCM for 24 h.

2.3.3 Fractionation/cleanup and Blow-down Process

The fractionation/cleanup process followed the method reported by Gogou et al (1996). After the extraction, the DCM solvent will be concentrated to dryness by a combination of rotary evaporation and blowing under a gentle nitrogen stream (see Fig. 2.2). The concentrated extract is then diluted in 10 ml of n-hexane before application to the top of a disposable silica gel column. The extract is then fractionated into individual compound classes by flash chromatography on silica gel as follows: The concentrate will be applied to the top of a 30 x 0.7 cm diameter column, containing 1.5 g of silica gel (activated at 150 ºC for 3 h). Nitrogen pressure will be used to in order to obtain a flow of 1.4 ml min^{-1} at the bottom of the column. The following solvents will be used to elute the different compound classes: (1) 15 ml n-hexane (fraction 1, light molecular weight PAHs); (2) 15 ml toluene-n-hexane (5.6:9.4) (fraction 2, middle and heavy molecular weight PAHs). In consideration of the toxicity of the solvent and the solubility of PAHs, toluene will be selected for the study. After the fractionation, the eluates will be concentrated by using rotary evaporator followed by the evaporation under a gentle nitrogen stream (set flow rate at 1.0 mbar). Because of the low dissipation capability of toluene, a percentage (5-25%) of acetone will be added to increase the volatility. The sample will be further reduced to incipient prior to being made up to volume with cyclohexane prior to GC/MS analysis.

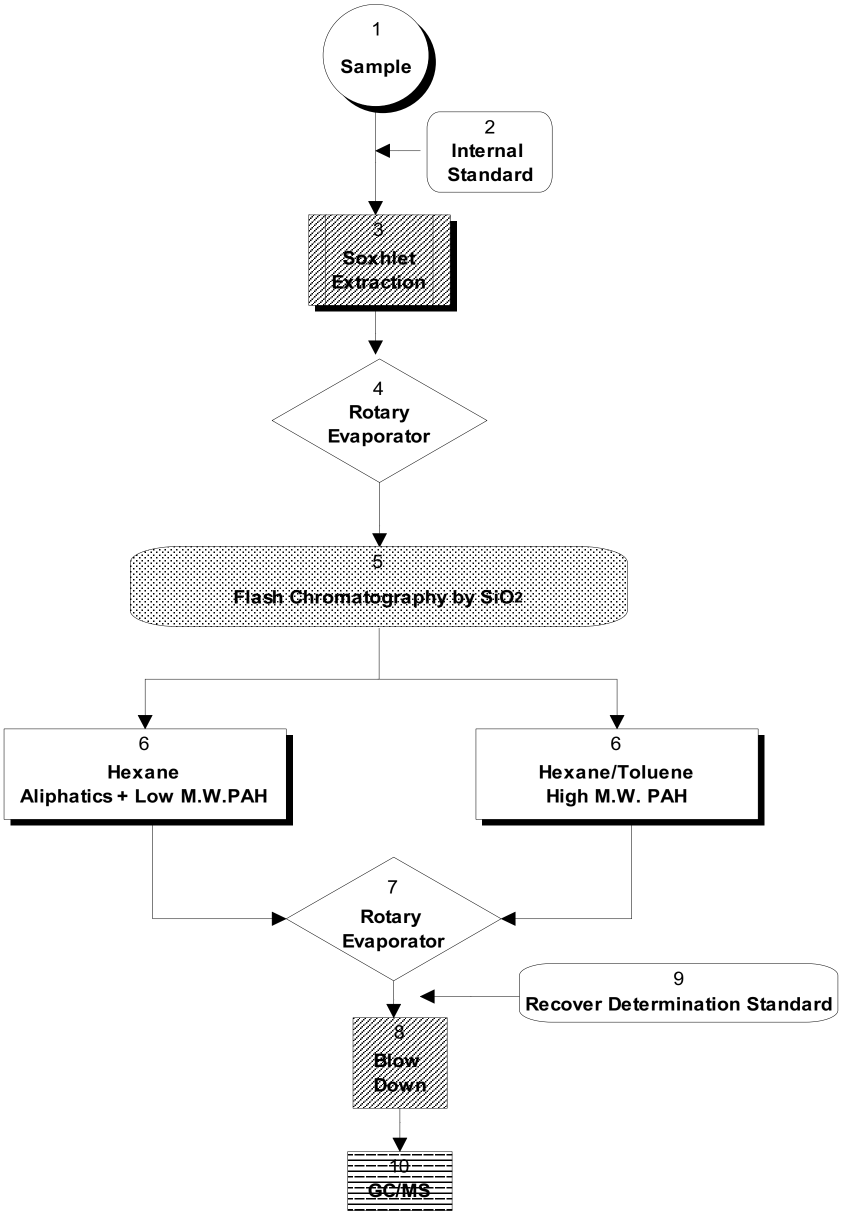


Figure 2.2. A flowchart of chemical analysis of PAHs

2.2.3 Water Soluble Ionic Species (WSIS) Analysis

All filter samples were stored in a refrigerator at about 4 ºC as soon as possible after sampling was completed. This was necessary to prevent any negative artifacts caused by losses of semi-volatile. Also field blank filters were collected to subtract the positive artifacts due to adsorption of gas phase organic compounds onto the filter during and/or after sampling. The analysis of water soluble particulate anion species including Cl^-, NO_3^- and SO_4^{2-}ion was performed by using an ion chromatography (Dionex DX-100) equipped with an IonPac AS4A-SC 4mm (10-32 P/N 43174) anion specific column, an AG4A-SC 4 mm (10-32 P/N 43175) guard column and a 25 µl sample loop (Msibi, 1992). Filters were cut, placed in a polyethylene vial (20 ml), and extracted with 10 ml of deionized water for 30 min. The extract was filtered through 0.2 µm pore size Millipore Teflon filters for cleanup. The GP40 gradient pump was used to set the ratio of two eluents (i.e. distilled water (mobile phase A) and NaOH solutions (mobile phase B)) pumped through the column at rate of 2 ml min^{-1}. The nitrogen gas was applied for generating the flow rate and set at 2 PSI. The mixture of standard solutions was made up by dissolving NaCl (1.646 g), $NaNO_3$ (1.373g) and $(NH_4)_2SO_4$ (1.376 g) into 1L of distilled water (1000 ppm). In addition, all the WSIS analysis had been conducted at the Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences (IEECAS), Xi'an, People Republic of China (PRC).

2.2.4 OC/EC Analysis

Carbon analysis was carried out at the Key Laboratory of Aerosol Chemistry and Physics, IEECAS, Xi'an, PRC. The calibrations and QA/QC of the measurements were conducted by Dr. Wang Qiyuan, a research scientist at the IEECAS. The samples were analyzed for OC and EC using DRI Model 2001 (Thermal/Optical Carbon Analyzer) with the IMPROVE thermal/optical reflectance (TOR) protocol. The protocol heats a 0.526 cm^2 punch aliquot of a sample quartz filter stepwise at temperatures of 120 ºC (OC1), 250 ºC (OC2), 450 ºC (OC3), and 550 ºC (OC4) in a non-oxidising helium atmosphere, and 550 ºC (EC1), 700 ºC (EC2), and 800 ºC (EC3) in an oxidising atmosphere of 2% oxygen in a balance of helium. When oxygen is added, the original and pyrolised black carbon burnt and the reflectance increase. The amount of carbon measured after oxygen is added until the reflectance achieves its original value is reported as optically-detected pyrolised carbon (OP).

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Chapter-III
Results & Discussion

Effects of Agricultural Waste Burning on $PM_{2.5}$-Bound Polycyclic Aromatic Hydrocarbons, Carbonaceous Compositions, and Water-Soluble Ionic Species in the Ambient Air of Chiang-Mai, Thailand

ABSTRACT

$PM_{2.5}$ is widely regarded as a major air pollutant due to its adverse health impacts and intimate relationship with the climate system. This study aims to characterize the chemical components (e.g., organic carbon (OC), elemental carbon (EC), water soluble ionic species (WSIS) and polycyclic aromatic hydrocarbons (PAHs)) in $PM_{2.5}$ collected at Doi–Inthanon in Chiang-Mai, Thailand, the highest mountain in Thailand. All samples (*n*=50) were collected by MiniVolTM portable air samplers from March 2017 to March 2018. The OC/EC ratio from this study was 6.8±3.0, and the decreasing order of the WSIS concentrations was $SO_4^{2-}>Na^+>Ca^{2+}>NH_4^+>NO_3^->K^+>Cl^->NO_2^->Mg^{2+}> F^-$. The concentration of total PAHs was 2,360 ± 2,154 pg m^{-3}. Principal component analysis (PCA) highlights the importance of vehicular exhaust, biomass burning, diesel emissions, sea-salt aerosols and volatilization from fertilizers as the five dominant potential sources that accounted for 51.6%, 16.2%, 10.6%, 5.20% and 3.70% of the total, respectively. The rest of the 12.7% variance probably is associated with unidentified local and regional sources such as incinerators, joss paper/incense burning, and domestic cooking. Interestingly, the results from the source estimations from the PCA underlined the importance of vehicular exhaust as the major contributor to the $PM_{2.5}$ concentrations in the ambient air of Chiang-Mai. However, it is crucial to emphasize that the impacts of agricultural waste burning, fossil fuel combustion, coal combustion and forest fires on the variations of OC, EC and WSIS contents were not negligible. This study not only enhances the knowledge of aerosol chemical characterizations but also provides information for health risk assessments of inhalation exposure to PAHs in the context of the local inhabitants of northern Thailand.

Keywords: $PM_{2.5}$, PAHs, Carbonaceous Compositions, Water Soluble Ionic Species**,** Biomass Burning

3.1 INTRODUCTION

Particulate matter (PM) or aerosols are defined as very small diameter solids or liquids that remain suspended in the atmosphere (Cooper, 2002), and they are a significant worldwide environmental issue, are well known as public health and climate hazards (Harrison and Yin, 2000; Metzger et al., 2004; Dai et al., 2013; Pani et al., 2016a, 2016b; Tsay et al., 2016; Chen et al., 2017; Pani et al., 2018) and cause visibility degradation (Tao et al., 2009). Over the past decades, international attention has been paid to fine particles discharged as a consequence of open biomass burning. Agricultural waste burning has usually operated to clean land before the next crop cycle (Pongpiachan et al., 2017). Biomass burning (BB) is reported almost every year with varying intensities during the dry season in northern Thailand and in neighbouring countries, such as Myanmar, Laos, Cambodia and Vietnam, due to agricultural waste burning (Tsay et al., 2016; Pongpiachan et al., 2017; Pani et al., 2018), and emits substantial amounts of $PM_{2.5}$ and trace gaseous species into the atmosphere (Chantara et al., 2012; Wiriya et al., 2013; Tsay et al., 2016; Pani et al., 2018; Punsompong and Chantara, 2018; Thepnuan et al., 2019). BB emits substantial amounts of trace gaseous species and PM into the atmosphere (Jian and Fu, 2014) and its contribution to carbonaceous aerosols at urban sites (Fine et al., 2001; Lanz et al., 2008) has been identified to be significant.

BB emissions contain significant amounts of water-soluble ionic species (WSIS), such as NH_4^+, K^+, and NO_3^- (Ryu et al., 2007; Mkoma et al., 2013; Lee et al., 2016; Khamkaew et al., 2016; Pani et al., 2018). Chemical analyses of smoke aerosols during forest fires have shown that potassium (K^+) and ammonium ions (NH_4^+) are the dominant cations and that sulphate ions (SO_4^{2-}) are the most abundant anions (Pio et al., 2008). It is also crucial to highlight that biomass burning is the major source of OC, EC, NO_3^-, NH_4^+, SO_4^{2-} and K^+ (Niemi et al., 2004). Multiple studies have confirmed the role of K^+ as a biosmoke tracer (Duan et al., 2004; Zhang et al., 2010; Lee et al., 2011; Cheng et al., 2013).

In recent years, scientists around the world have paid more attention to carbonaceous particulates because they influence global warming, cloud microphysics (Seinfeld and Pandis, 1998; Lyamani et al., 2006), global climate change (Hitzenberger et al., 1999; Dan et al., 2004) and have adverse effects on human health (Na et al., 2004). Moreover, cardiovascular mortality and morbidity rates are associated with increased levels of urban carbonaceous particulate matter (Ito et al., 2011). Furthermore, several organic compounds such as PAHs and PCBs are found in OC mixtures, which possess carcinogenic and mutagenic effects (WHO, 2013). Currently, most studies have highlighted the behaviour of particulate PAHs in tropical countries and in northern Thailand (Bourotte et al., 2005; Boonyatumanond et al., 2007; Vasconcellos et al., 2010; Pongpiachan, 2013a,b, 2015; Pongpiachan et al., 2013a,b, Pongpiachan et al., 2015a). Despite countless measurements of PAH compositions in coarse and fine particles around the world, there is inadequate information focusing on the characterization of particulate PAHs in tropical atmospheres. Most studies have targeted estimations of source apportionment (Wan et al., 2006;

Gupta et al., 2011; Dvorská et al., 2012; Hu et al., 2012; Pongpiachan et al., 2009). Unfortunately, there is limited information associated with $PM_{2.5}$-bound OC, EC, WSIS and PAHs in northern Thailand.

Chiang-Mai is the third-largest province in Thailand, covering an area of 20,107 square kilometres. It is the second-largest province in the country in terms of population and also attracts many millions of visitors each year. Due to its mountainous geographical features, Chiang-Mai has suffered from poor air quality, especially during the dry season, for decades. Previous studies have indicated that biomass burning, vehicular emissions, industrial emissions, and anthropogenic activities are the main contributors for air pollutants (Tsai et al., 2013; Janta and Chantara, 2017; Pani et al., 2018; Thepnuan et al., 2019). The understanding of atmospheric aerosol compositions and their major sources is undoubtedly essential for reducing ambient PM levels and improving air quality. This study was carried out to evaluate the emission sources and chemical characteristics of the OC, EC, WSIS and PAHs components in $PM_{2.5}$. Overall, the main objectives of this study are to (*i*) characterize the chemical compounds (e.g. OC, EC, OC/EC, WSIS, and PAHs) from $PM_{2.5}$ samples collected in Chiang-Mai; (*ii*) statistically analyse the chemical composition of $PM_{2.5}$ and its relationships to source identification; and (*iii*) perform source apportionment of the chemical composition of $PM_{2.5}$ using hierarchical cluster (HCA) and principal component analysis (PCA).

3.2. MATERIALS & METHODS

3.2.1. Sampling site

The air quality observatory site is located at the National Astronomical Research Institute of Thailand (NARIT) at the summit of Doi–Inthanon, Chiang-Mai province (see Fig. 3.1). It is important to mention that Doi-Inthanon is the highest mountain in Thailand. The sampling location is at 18 54’40.5”N and 99 13’01.4”E. Chiang-Mai is the third-largest province in Thailand, covering an area of 20,107 square kilometres. It is the second-largest in the country in terms of population, with 1,746,840 people currently residing in Chiang-Mai. The city is a popular destination among travellers. Chiang-Mai has relatively cool weather throughout the year. There has been an increasing number of articles related to air quality in northern Thailand (Wiwatanadate and Liwsrisakun, 2011; Pongpiachan S, 2013b). These can be correlated with the $PM_{2.5}$ levels, which are caused by large-scale ‘hot spot’ locations. The pollutant sources can be identified, for example, pollutants from forest fires, burning of agriculture waste, and trans-boundary haze pollution.

Source : Field survey.
Printed by GEO-Informatics Research Center for Natural Resource and Environment, Prince of Songkla University, Thailand.

Figure 3.1. Map of the Air Quality Observatory Sites in this Study

All samples (*n*=50) were collected on quartz-fibre filters using MiniVolTM portable air samplers (Airmetrics) through 47 mm filters at flow rates of 5 L min^{-1}. All samples were collected over a period of 72 h, and then, sample collections were halted for 24 h and were then followed by another collection session of 72 h; this pattern was repeated throughout the study period. After the sample collections, the filters were carefully kept in Petri slide dishes that were individually wrapped in aluminium foil to avoid any loss from photodegradation and were stored in a freezer at 4°C to maintain their chemical stability until subsequent analysis. The quartz-fibre filter samples were divided into two segments. One of the filters was analysed for OC/EC, and the other one was analysed for PAHs and WSIS. This monitoring campaign was conducted from March 2017 to March 2018.

3.2.2. Carbonaceous aerosol analyses: Thermal analysis protocols

The carbonaceous aerosol components, OC and EC, were quantified using a Desert Research Institute (DRI) Model 2001 carbon analyser (Atmoslytic Inc., Calabasas, CA, USA). The IMPROVE_A thermal/optical reflectance (TOR) protocol was used for the analyses (Chow et al., 2007a). The thermal/optical carbon analyser bases its analysis on the oxidation of organic carbon (OC) compounds and of elemental carbon (EC) at different temperatures.

Carbonate carbon is determined by estimating the CO_2 acidification from organic sample that punches before the normal carbon analysis procedure. This protocol uses seven temperature programmes for seven different fractions. The temperature protocol is applied for separating OC and EC. It is the same as that for the TOR and TOT burning correction. This protocol includes total OC, total EC, and total carbon, which are monitored by both reflectance (OPR) and transmittance (OPT). This protocol is dependent on the thermal/optical analysis that is applied for quantification of the thermally derived sub-fractions of OC and EC.

Thermal analysis using heat (thermal/optical carbon analyser) follows the IMPROVE protocol (Interagency Monitoring of Protected Visual Environments) using the thermal/optical reflectance (TOR) method. There are eight types of carbonaceous compounds that are differentiated by their combustion temperatures, namely, OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP. Total OC was defined as the sum of four OC fractions (OC1-OC4) plus OP, whereas the total EC was technically defined as the sum of three EC fractions (EC1-EC3) minus OP. In this study, TD-GC/MS was employed for both qualitative and quantitative analyses of PAHs. Injection port thermal desorption (TD), coupled with gas chromatography/mass spectrometry (GC/MS), was applied to quantify the non-polar organic compounds in the $PM_{2.5}$ samples. The details of the analytical procedures have been provided in previous publications and will not be further mentioned here (Ho and Yu, 2004; Chow et al., 2007b; Ho et al., 2008).

3.2.3. Statistical analysis

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used for the classification and source apportionments of OC, EC, WSIS and PAHs using the Statistical Package for Social Sciences (SPSS) version 13 software. Data preprocessing consisted first of subjecting all data to a logarithmic transformation. This technique is the most common approach for transforming environmental data, as it is robust for non-normal data distributions (Field et al., 1982). PCA enables multivariate data reduction by transforming the data into orthogonal components that are linear combinations of the original variables. Therefore, PCA reduces multidimensional data to fewer dimensions. Hence, this method is used to identify trends and clusters within the data. In addition, the correlation coefficients of OC, EC and WSIS are regularly used to identify the relationships between aerosol components (Kocak et al., 2004 and Hegde et al., 2007) and are used in this study to observe these relationships and to identify the sources of OC, EC and WSIS.

3.3. RESULTS & DISCUSSION

3.3.1. Mass concentrations of carbonaceous compounds (OC and EC)

The average mass concentrations of atmospheric $PM_{2.5}$ and its carbonaceous chemical components (OC and EC) in Chiang-Mai were collected from March 2017 to March 2018. The concentrations of the average compositions of each carbon fraction relative to the total carbon (TC), OC and EC levels in Chiang-Mai are summarized in Table 3.1. The average concentrations of the carbonaceous chemical components are 9.98±8.00, 8.38±6.41, 1.60±1.65, 0.10±0.08, 1.26±1.02, 3.60±2.54, 2.57±2.49, 2.28±1.95, 0.16±0.07 and 0.02±0.05 µg m^{-3} for TC, OC, EC, OC1, OC2, OC3, OC4, EC1, EC2 and EC3, respectively.

Table 3.1. Summary of the concentrations of TC, OC and EC in Chiang-Mai, Thailand

Species	**Unit**	**Mean ± SD (n=50)**	**Minimum**	**Maximum**
TC	µg m^{-3}	9.98±8.00	0.74	32.81
OC	µg m^{-3}	8.38±6.41	0.67	26.82
EC	µg m^{-3}	1.60±1.65	0.07	7.26
OC1	µg m^{-3}	0.10±0.08	0.00	0.30
OC2	µg m^{-3}	1.26±1.02	0.16	4.69
OC3	µg m^{-3}	3.60±2.54	0.40	11.37
OC4	µg m^{-3}	2.57±2.49	0.08	10.46
EC1	µg m^{-3}	2.28±1.95	0.01	7.10
EC2	µg m^{-3}	0.16±0.07	0.05	0.34

EC3	µg m^{-3}	0.02±0.05	0.00	0.24

In Chiang-Mai, Pani et al (2019) presented the concentrations of carbonaceous compounds in $PM_{2.5}$ at Doi Ang Khang (DAK) and at Chiang Mai University (CMU) during the dry season of 2015. The TC mass concentrations were 54.9 ± 15.8 and 56.0 ± 22.4 µg m^{-3} at DAK and at CMU, respectively. The percentage contributions from OC were 87% and 83% at DAK and CMU, respectively. In addition, the percentage contribution of OC obtained from this study was 84%. This result is consistent with previous studies indicating that BB might have been the principal source of carbonaceous substances (Khamkaew et al., 2016; Pani et al., 2018; Thepnuan et al., 2019). In contrast, the EC fractions were regarded as being relatively lower than the OC fractions. Since EC has a chemical structure similar to impure graphite, it appears reasonable to assume that vehicle exhaust is the major source of EC. As a consequence, the most important sources of EC are fossil fuel combustion and biomass burning (Gelencsér, 2004).

OC can either be directly emitted into the atmosphere from the incomplete combustion of organic compounds or can form by the condensation of compounds produced by atmospheric photooxidation and polymerization of organic species (Jimenez et al., 2008), including thousands of organic compounds (e.g., aromatic compounds, carboxylic compounds with polar substituents and aliphatic compounds) with a variety of physical and chemical properties. OC may be emitted directly from sources such as industrial processes and by natural occurrences (e.g. primary OC) or can form in the atmosphere due to gas-to-particle conversion of semi- and low-volatility organic compounds (e.g., secondary OC). Quantification of the contributions of primary and secondary organic carbon is quite difficult to determine through direct chemical analysis, since OC contains a complex mixture of many compounds. Particles containing OC might show a significant risk to human health, as well (Mauderly and Chow, 2008). The carbonaceous compounds or total carbon

(TC) in the atmosphere represent one of the main components of the total mass of suspended fine particles. They are composed of organic carbon (OC) with a contribution of 70–80% (Seinfeld and Pandis, 2006).

In the case of four OC fractions, OC3 was the most abundant (3.60±2.54 μg m^{-3}), followed by OC4 (2.57±2.49 μg m^{-3}), OC2 (1.26±1.02 μg m^{-3}) and OC1 (0.10±0.08 μg m^{-3}). Additionally, EC1 was the major fraction (2.28±1.95 μg m^{-3}) in the EC. Chuang et al (2013b) reported that OC3 can be used as a biomass burning tracer adjacent to emission sources, while OC2 is the most abundant fraction of OC released from coal combustion (Chow et al., 2004) and motor vehicle exhaust (Cheng et al., 2015). Biomass burning combustion sources are considered to be the greatest contributors to primary carbonaceous particle levels in the atmosphere (Zheng et al., 2005; Cao et al., 2005; Cheng et al., 2013; Chen et al., 2017) and many studies have used their fractions for source apportionment of biomass burning (Chow et al., 2004; Cao et al., 2005; Han et al., 2007, 2009b, 2010).

3.3.2. The OC/EC ratios, Atmospheric Concentrations of Water-Soluble Ionic Species (WSIS) and PAHs in $PM_{2.5}$.

3.3.2.1. OC/EC ratios

The ratio of OC to EC (OC/EC) is often used to obtain information on emission sources (Chow et al., 2004; Dan et al., 2004; Cao et al., 2005; Han et al., 2007, 2009). Table 3.2 shows the literature values of particulate OC/EC ratios reported for different emission sources. The average OC/EC ratio from this study was 6.8±3.0 (Table 2).

Table 3.2. The binary ratios of OC to EC for different emission sources.

Emission source	EC	OC	OC/EC ratio	References
Ambient $PM_{2.5}$[a]	2.1±1.0	10.8±4.9	5.2±2.7	Kwangsam Na et al., 2004

Light-duty gasoline vehicles[a]	22.6	50.1	2.20	Hildemann et al., 1991
Light-duty gasoline vehicles[b]	13.5±8.02	30.1±12.3	2.20	Watson et al., 1994
Heavy-duty diesel vehicles[a]	40.5	32.6	0.80	Hildemann et al., 1991
Tunnels[c]	25.5±4.90	19.2±8.46	0.76	Gillies et al., 2001
Tunnels[b]	16.9	16.8	N.A.	Pant et al., 2016
Paved road dust[b]	1.12±0.30	14.7±2.00	13.1	Watson et al., 1994
Residential wood combustion[b]	12.3±4.20	51.3±11.7	4.15	Watson et al., 2001
Meat charbroiling[a]	0.0±0.5	33.8±2.0	N.A.	Schauer et al., 1999
Natural gas home appliances[a]	6.70	84.9	12.7	Hildemann et al., 1991
Forest fires[a]	3.23±1.80	46.8±15.6	14.51	Watson et al., 2001
Ambient PM2.5[b]	1.60±1.65	8.38±6.41	6.8±3.0	This study

Note: N.A.=not applicable.

[a] Mass % of fine particle mass.

[b] Mass concentration.

[c] mg per vehicle-kilometre.

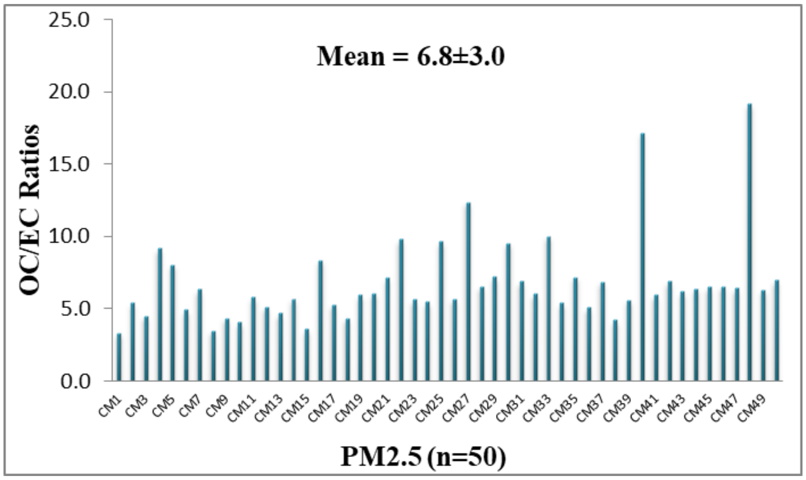

Figure 3.2. Temporal variations in the OC/EC ratios for 50 samples from Chiang-Mai from March 2017 to March 2018

OC/EC ratios can be used to classify the main sources of air pollutants (Wang et al., 2015). Some studies have reported that OC/EC ratios greater than two indicate SOC formation (Chow et al., 1996; Chow et al., 2004). Table 3.3 shows that the OC/EC ratios from both vehicle exhaust and biomass burning range from 4.0 to 60 (Pio et al., 2008; Zhang., 2008, Chuang et al., 2013;

Chuang et al., 2014; Chuang et al., 2016; Ferek et al., 1998; Lee et al., 2016; Andreae and Merlet, 2001; Cachier et al., 1989; Mazurek et al., 1991; Ward et al., 1992; Cao et al., 2005), the ratios for motor vehicles (diesel and gasoline) range from 0.02 to 4.0 (Dallmann et al., 2014; Kwangsam Na et al., 2004; Turpin and Huntzicker, 1995; Schauer et al., 2001; Kirchstetter et al., 2001,2004; Cadle et al., 1999), the ratios for fossil fuel combustion range from 1.1 to 4.1 (Watson et al., 2001; Koch, 2001; Cao et al., 2005), the ratios for coal combustion range from 2.7 to 12.0 (Watson et al., 2001 and Cao et al., 2005), the ratios for forest fires show a range of 14.51- 16.0 (Watson et al., 2001), the ratios secondary organic carbon show a range of 3.3-33 (Saarikoski et al., 2008; Boreddy et al., 2018b), the ratios for long-range transport show a range of 3.01-12 (Pani et al., 2017; Saarikoski et al., 2008) and cooking emissions ratios show a range of 4.3–7.7 (See and Balasubramanian, 2008). It is important to emphasize that the PM $_{2.5}$-bound OC/EC ratios collected during the dry season at Doi Ang Khang and at Chiang Mai University were 6.8±0.6 and 5.2±1.3, respectively (Pani et al., 2019). As a consequence, the OC/EC ratio obtained from this study (e.g., 6.8±3.0) is surprisingly consistent with the results of Pani et al (2019), thus emphasizing that biomass burning is the major source of carbonaceous compounds in this region.

Table 3.3 The literature values of the OC to EC (OC/EC) ratios for different emission sources

Emission sources	**OC/EC**	**References**
Biomass burning	5.1	Pio et al., 2008
	4.0-8.0	Zhang., 2007
	5.7	Chuang et al., 2013
	6.7	Ferek et al., 1998
	6.8	Lee et al., 2016
	5–8	Andreae and Merlet., 2001
	9	Cachier et al., 1989
	10	Mazurek et al., 1991
	12	Ward et al., 1992
	12.3	Cao et al., 2005
	16.7	Ward et al., 1992
	60.3	Cao et al., 2005
Fossil fuel combustion	1.1	Watson et al., 2001
	4	Koch., 2001
	4.1	Cao et al., 2005
Coal combustion	2.7	Watson et al., 2001
	3.0 and 12.0	Cao et al., 2005
Forest fires	~ 16.0	Watson et al., 2001
	14.51	Watson et al., 2001
Vehicle exhaust	0.06	Dallmann et al., 2014
	0.8	Kwangsam Na et al., 2004
	0.3	Turpin and Huntzicker., 1995
	0.8	Hildemann et al., 1991
	0.02	Dallmann et al., 2014
	1.0-4.0	Schauer et al., 1999,2002
	0.9	Kirchstetter et al., 2004
	2.2	Kwangsam Na et al., 2004
	2.05–2.36	Cadle et al., 1999
Secondary organic carbon	3.3	Saarikoski et al., 2008
	21–33	Boreddy et al., 2018b
Long-range transport	3.01 and 3.58	Pani et al., 2017
	12	Saarikoski et al., 2008
Traffic	0.7	Saarikoski et al., 2008
Cooking emissions	4.3–7.7	See and Balasubramanian., 2008

3.3.2.2. Secondary Organic Carbon (SOC) Contributions

Carbonaceous aerosols with OC/EC values greater than two can be considered to contain significant quantities of SOC (Chow et al., 1996; Gray et al., 1986). According to Castro et al. (1999), the SOC contribution can be estimated by calculating the minimum values of the OC/EC ratios in all samples. The SOC was computed from equation 1:

$$SOC = OC_{total} - EC \times (OC/EC)_{min}$$

Equation 1

where SOC is the secondary OC, OC_{total} denotes the total OC, and $(OC/EC)_{min}$ is the average of the three minimum OC/EC ratios. Ji et al. (2016) described the formation and influencing factors of SOC, which show that photochemical oxidation and atmospheric temperatures play important roles in the formation of SOCs. SOCs are distributed in a particle phase after the oxidation of volatile organic carbon (VOC) by active radicals in the atmosphere (Li et al., 2018). Chemical reactions involving gas–particle conversion occur during long-distance transport of aerosol particles (Zhang et al., 2012).

In this study, there was a high correlation between OC-EC and K^+. Normally, OC, EC and K^+ are generated from biomass burning and from in $PM_{2.5}$. It is crucial to note that the high OC/EC ratios (6.8±3.0), coupled with the high SOC contents (8.12±0.26 $\mu g\ m^{-3}$) detected at Chiang-Mai, highlight the dominant effects of biomass/agricultural waste burning in northern Thailand. These findings are consistent with the comparatively high SO_4^{2-}, NH_4^+, K^+ levels observed at Chiang-Mai. Strong positive correlations of OC *vs.* K^+ (r=0.95) and EC *vs.* K^+ (r=0.90) were also detected (see Fig. 3.4). BB is another possible means for forming SOC (Mancilla et al., 2015) and it has been common in Chiang-Mai to burn biomass for farming preparation.

3.3.2.3. Water Soluble Ionic Species (WSIS)

WSIS dominate major portions of atmospheric particles (Harrison et al., 2004; Querol et al., 2001) and they may be harmful to human health as they can easily enter human lungs and trigger respiratory diseases (Adamson, 1999). For this particular reason, chemical characterizations of WSIS have been conducted worldwide by many researchers using various types of analytical techniques (Morales et al., 1998; Wang and Shooter, 2001; Lin, 2002; Chandra Mouli, et al., 2003). Most of these studies have investigated the major ions, such as NH_4^+, Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. It is well known that BB emissions are responsible for relatively large amounts of WSIS in atmospheric particles (Chuang et al., 2013; Lee et al., 2016; Pani et al., 2018). Since BB releases great amounts of carbonaceous aerosols, coupled with WSIS, into the atmosphere (Cao et al., 2005; Lee et al., 2011; Chuang et al., 2013; Mkoma et al., 2013), the assessment of WSIS, OC, and EC can provide valuable information regarding their formation, characteristics, and potential emission sources.

As previously mentioned, the most dominant species in this study was SO_4^{2-}, which mainly converts SO_2 gaseous precursors into particles. Fig. 3.3 presents the concentrations of ten WSIS species in $PM_{2.5}$. The results showed that SO_4^{2-}, Na^+, Ca^{2+}, NH_4^+, NO_3^-, K^+, Cl^-, NO_2^-, Mg^{2+} and F^- were the dominant WSIS species, which accounted for 44%, 14%, 11%, 10%, 6%, 6%, 4%, 3%, 1% and 1% of the total mass of ions, respectively. Secondary inorganic aerosols (SIA), including SO_4^2, NH_4^+, and NO_3^-, were the major ions found in this study. This finding suggests that SIA are mainly present in fine particles, which is in good agreement with previous studies (Kong et al., 2010; Long et al., 2014; Pani, et al., 2019). It is also crucial to note that Na^+, Ca^{2+}, Mg^{2+} and F^-

can be used as geochemical tracers representing maritime aerosols (Chan et al. 1997; Wang and Shooter, 2001).

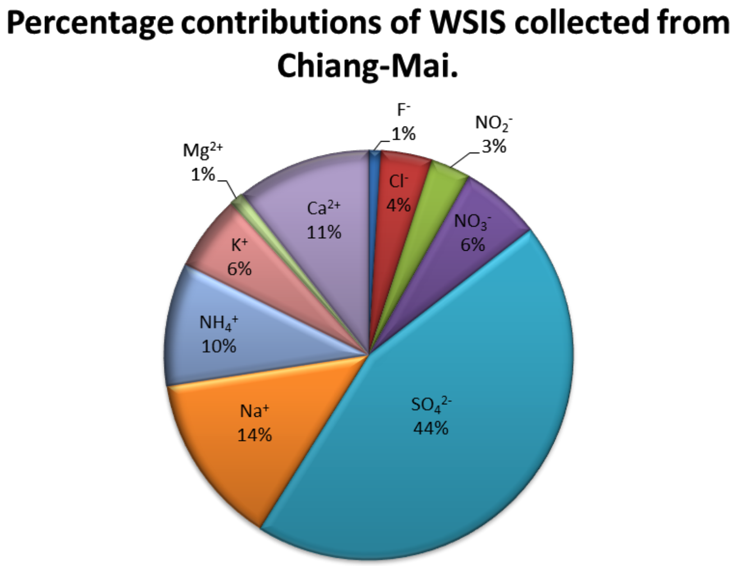

Figure 3.3. Percentage contributions of WSIS collected from Chiang-Mai

For this study, the individual WSIS concentrations of the $PM_{2.5}$ samples in Chiang-Mai during March 2017 to March 2018 were in a decreasing order of SO_4^{2-}>Na^+>Ca^{2+}>NH_4^+>NO_3^->K^+> Cl^- >NO_2^->Mg_2^+>F^-. These data indicate that traffic (e.g., SO_4^{2-}) and long-range atmospheric transport of maritime aerosols (e.g., Na^+) are the two major contributors to WSIS in $PM_{2.5}$. SO_4^{2-}, and NO_3^- and NH_4^+ mainly form in the atmosphere by gas-to-particle conversion from their precursor gases (e.g., SO_2, NO_x and NH_3). Although the major source of NO_x is traffic emissions, in particular, incomplete combustion of fossil fuels from diesel engines and cement kiln manufacturing can be another major source of NO_x emissions (Mousavi et al., 2014). Kalaboukas et al. (1999) and Yao et al. (2016) reported that SO_4^{2-} is normally created mainly from fossil fuel combustion by the photochemical formation of SO_2 from traffic and industrial activity. In contrast, Pengchai et al. (2009) indicated that vehicle exhaust and biomass burning were two major sources of SO_4^{2-} in the ambient air of northern Thailand. Consequently, it seems reasonable to conclude that the PM$_{2.5}$-bound SO$_4^{2-}$ obtained in this study could be derived from mixed sources between biomass burning and fossil fuel combustion.

3.3.2.4. Pearson correlation analysis of OC-EC and WSIS

The Pearson correlations of OC, EC and WSIS in PM$_{2.5}$ were investigated and the results are shown in Fig 3.4. The OC concentrations were strongly correlated with EC (*r*=0.95). The SO$_4^{2-}$ concentrations were greatly correlated with NH$_4^+$ (*r*=0.91). The K$^+$ concentrations were positively correlated with OC (*r*=0.95) and EC (*r*=0.89). Pani et al (2019) reported that strong correlations were also found between SO$_4^{2-}$ and NH$_4^+$ (*r* =0.95) from studies in Chiang-Mai during the dry period. The result of this study also demonstrated the similar patterns observed in previous investigations conducted in Chiang-Mai province.

	OC	EC	F$^-$	Cl$^-$	NO$_2^-$	NO$_3^-$	SO$_4^{2-}$	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}
EC	**.953****										
F$^-$	.630**	.621**									
Cl$^-$	-0.261	-.291*	-0.034								
NO$_2^-$	-.297*	-.288*	-0.099	0.216							
NO$_3^-$	.685**	.639**	.615**	-0.016	0						
SO$_4^{2-}$	.656**	.584**	.307*	-0.259	-0.183	.536**					
Na$^+$	.689**	.618**	.611**	0.085	-0.014	.606**	.606**				
NH$_4^+$	.608**	.515**	0.256	-0.219	-0.047	.612**	**.909****	.531**			
K$^+$	**.952****	**.897****	.534**	-0.278	-0.209	**.717****	**.785****	**.706****	**.769****		
Mg^{2+}	.317*	0.26	0.222	.429**	0.261	.563**	.339*	.603**	.448**	.406**	
Ca^{2+}	**.721****	.679**	.439**	0.024	-0.044	.549**	.537**	.634**	.460**	.693**	.532**

Bold: R > 0.7

Figure 3.4. Pearson correlation analysis of OC, EC and WSIS in PM$_{2.5}$

3.3.2.5. Concentrations of PAHs

The concentrations of PAHs are summarized in Table 3.4 for the concentrations of ∑PAHs (e.g., the sum of 19 PAH contents) for the annual averages, the standard deviations (SD) and the ranges for 19 PAHs examined in this study. The concentration of total PAHs was 2,360±2,154 pg m^{-3}. The values in this study were lower than those measured in other areas such as Beijing and

Guangzhou, which are often known as heavily polluted areas in China (Zhou et al., 2012; Wang et al., 2016).

Table 3.4. Summary of PAHs concentrations in Chiang-Mai, Thailand

PAHs (pg m^{-3})	Mean	S.D.	Min.	Max.
Ace	39.6	41.8	5.2	225
Fl	32.4	37.8	7.6	219
Phe	125	199	21.7	1038
Ant	19.9	22.3	6.0	121
Fluo	53.8	46.0	8.2	205
Pyr	54.2	47.8	5.9	183
B[a]A	122	91.8	18.8	470
Chry	51.6	48.9	2.2	180
B[b]F	176	167	5.8	732
B[k]F	203	202	1.3	929
B[a]F	27.6	26.4	1.7	117
B[e]P	96.0	84.4	4.8	381
B[a]P	169	167	8.8	703
Per	19.2	17.1	1.3	76.6
Ind	467	380	3.8	1712
B[g,h,i]P	398	321	4.4	1403
D[a,h]A	103	86.5	1.5	405
Cor	144	108	1.2	467
D[a,e]P	54.8	55.5	0.7	273
ΣPAHs*	2360	2154		

*Note that ΣPAHs is the sum of Ace, Fl, Phe, Ant, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]F, B[e]P, B[a]P, Per, Ind, B[g,h,i]P, D[a,h]A, Cor, and D[a,e]P.

Over the past few decades, numerous studies concerned with source identifications, quantitative source apportionments, and ecological risk assessments of PAHs in the ambient air of Thailand have conducted intensive investigations (Pongpiachan, 2013a,b, 2014, 2015 a,b). In the northern part of Thailand, agricultural waste and biomass burning during cold periods have released large amounts of particulate matter, especially ultra-fine particles, including $PM_{2.5}$-bound PAHs, into the atmosphere. There are a number of recent studies that use PAHs data to obtain inferences of particulate pollution sources (Yunker et al., 2002; Marchand et al., 2004; Bourette et al., 2005;

Akyuz and Cabuk, 2008). Nine of the 16 USEPA priority PAHs are related to combustion processes such as those of coal, petroleum and diesel. These PAHs are known as combustion PAHs (CPAH), namely, Flu, Pry, B[a]A, Chry, B[b]F, B[k]F, B[a]P, B[g,h,i]P and Ind (Ravindra et al., 2008). The ratios of the concentrations of these CPAHs have been used in many studies to identify potential sources of PAHs in aerosols (Manoli et al., 2004). In this study, relatively high abundances of Ind and B[g,h,i]P were detected, indicating that traffic emissions, petroleum combustion and industrial waste burning can be considered as the emission sources of PAHs for the ambient air of Chiang-Mai (Zhou et al., 1999; Ravindra et al. 2008).

3.3.3. Source identification and pattern recognition

To identify the potential sources of the OC, EC, WSIS and PAHs, two multivariate statistical analyses are introduced in this section. In section 3.2.4, the relatively high correlation coefficients of K^+ *vs.* OC and K^+ *vs.* EC indicate that biomass burning is the main contributor to carbonaceous aerosols. Furthermore, the relatively high abundance of Ind and B[g,h,i]P suggests that motor vehicle exhaust can be considered as one of the major emission sources of PAHs in this region. In this section, source identification, coupled with quantitative source apportionment of targeted chemical species, is investigated by using two multivariate statistical analyses, namely, hierarchical cluster analysis (HCA) and principal component analysis (PCA).

3.3.3.1. Classification of Chemical Compounds by Hierarchical Cluster Analysis (HCA)

HCA was performed to identify the homogeneous groups of carbonaceous aerosol components, including OC, EC, WSIS and 19 individual PAHs in $PM_{2.5}$. The hierarchical dendrogram is shown in Fig 3.5. Three major groups of carbonaceous aerosol components were clearly distinguished.

The first group contains F^-, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, K^+, Na^+, Ca^{2+}, NH_4^+, EC, SO_4^{2-}, TC, OC, B[a]F, Per, Ace, Ant, Fl, Fluo, Pyr, Chry, D[a,e]P, all OCs, EC and WSIS. This indicates that the major sources are mixtures of biomass burning, fossil fuel, coal combustion, and industrial emissions (Kong et al., 2010; Long et al., 2014; Pani, et al., 2019). In addition, the pyrogenic sources, namely, the motor vehicle emissions from both gasoline and diesel emissions and the leakage of used oil and road dust have been previously identified as the original sources of this group (Dahle et al., 2003; Fang et al., 2009; Liu et al., 2009). In accordance with previous literature reports, 3–4 ring PAHs have been found in the road dust in urban cities (Zakaria et al., 2002; Boonyatumanond et al., 2007). The second group consists of B[b]F, B[a]P, B[k]F, B[e]P, D[a,h]A, Cor, B[a]A and Phe, which are the high-molecular-weight PAHs with 5–6 rings. This group usually originates from road-paving asphalt, crude oil, bitumen (Ahrens and Depree, 2010) and road dust (Larsen and Baker, 2003). The last group consists of Ind and B[g,h,i]P, which are the anthropogenic PAHs from the use of petroleum products, motor vehicles, oil combustion and industrial waste incinerators (Zhou et al., 1999; Ravindra et al. 2008).

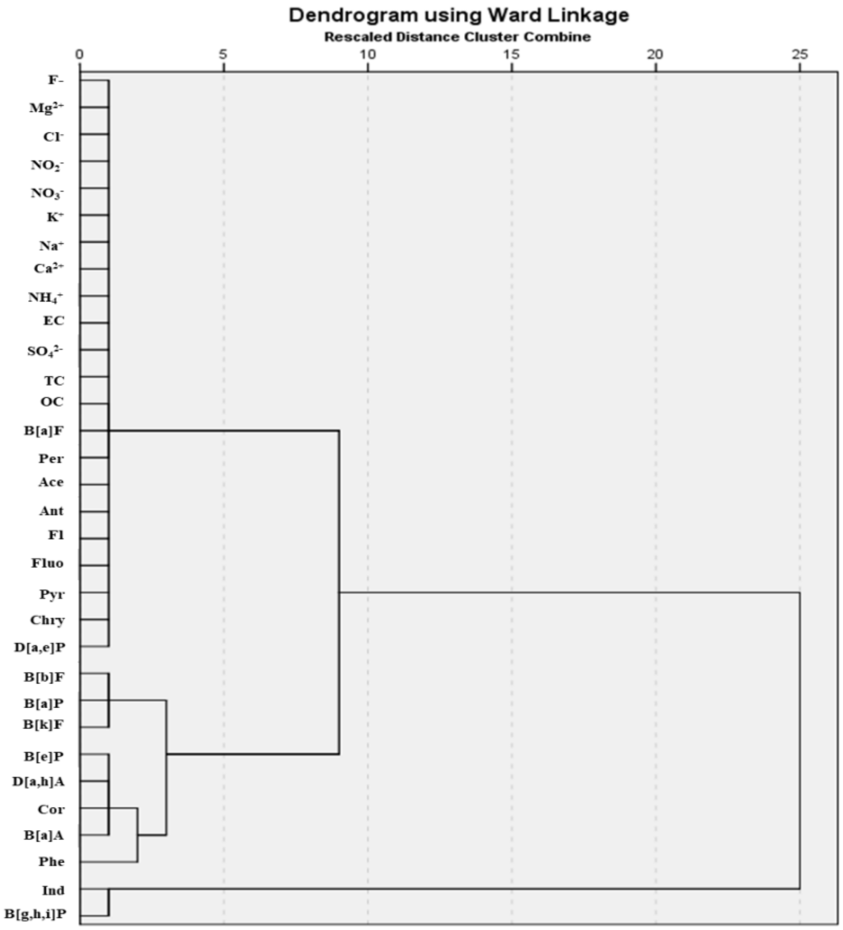

Figure 3.5. Hierarchical Cluster Analysis (HCA) of carbonaceous compounds, water soluble ionic species and 19 individual PAHs in PM2.5 at Chiang-Mai, Thailand.

3.3.3.2. Source estimations from PCA

As is widely known, PCA is a multivariate technique. PCA achieves multivariate data reduction by transforming the data into orthogonal components that are linear combinations of the original variables. Hence, PCA reduces multidimensional data into fewer dimensions. (Wold et al, 1987). In this study, the concentrations of OC-EC, WSIS and 19 individual PAHs from 50 samples were selected as the active variables. The majority of the variance (87.3%) of the scaled data was explained by five eigenvectors/principal components. The first principal component (PC1) explains 51.6% of the total variance, while the second principal component (PC2) accounts for

16.2% of the total variance. Interestingly, PC3, PC4, and PC5 describe 10.6%, 5.20%, and 3.70% of the total variance, respectively (see Table 3.5).

Table 3.5. Rotated Component Matrix[a] of carbonaceous compounds, water soluble ionic species and 19 individual PAHs in $PM_{2.5}$ at Chiang-Mai, Thailand

Compositions	**Principal components (PC)**				
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
TC	.303	**.836**	.284	-.219	.104
OC	.310	**.834**	.296	-.205	.115
EC	.265	**.812**	.227	-.266	.054
F^-	.102	**.742**	.156	-.057	-.395
Cl^-	-.186	.002	-.105	**.740**	-.329
NO_2^-	.070	-.164	-.195	.656	.078
NO_3^-	.039	**.818**	.060	.131	.111
SO_4^{2-}	.239	.602	.127	-.100	.643
Na^+	.061	**.830**	.116	.220	.078
NH_4^+	.161	.606	-.028	-.018	**.711**
K^+	.263	**.827**	.251	-.145	.340
Mg^{2+}	-.059	.570	-.058	.684	.210
Ca^{2+}	.303	.697	.200	.218	.116
Ace	.118	.204	**.944**	-.123	-.003
Fl	.092	.060	**.817**	.013	.283
Phe	.116	.286	**.918**	-.117	-.103
Ant	.182	.219	**.915**	-.126	-.090
Fluo	.566	.538	.501	-.143	-.013
Pyr	.673	.543	.350	-.139	-.009
B[a]A	.508	.409	.658	-.204	-.023
Chry	**.770**	.520	-.004	-.215	.048
B[b]F	**.914**	.352	.008	-.087	.058
B[k]F	**.925**	.304	.008	-.063	.070
B[a]F	**.946**	.288	.007	-.075	.037
B[e]P	**.929**	.286	.179	-.074	.043
B[a]P	**.924**	.332	-.075	-.096	.052
Per	**.947**	.277	.056	-.071	.063
Ind	**.960**	.016	.149	.017	.063
B[g,h,i]P	**.919**	.055	.327	-.001	.018
D[a,h]A	**.972**	.047	.149	.007	.045
Cor	**.882**	-.076	.296	.056	.050
D[a,e]P	**.861**	-.094	.203	.115	.069

Variance [%]	**51.6**	**16.2**	**10.6**	**5.20**	**3.70**
Estimated source	**Vehicular Exhaust**	**Biomass Burning**	**Diesel Emissions**	**Sea-Salt Aerosols**	**Agricultural Emissions**

a Rotation Method: Varimax with Kaiser Normalization.
b Bold loading > 0.70

PC1 represents high loading factors of Chry, B[b]F, B[k]F, B[a]F, B[e]P, B[a]P, Per, Ind, B[g,h,i]P, D[a,h]A, Cor and D[a,e]P, which can be described as the high molecular weight 4-6 ring PAHs. Since these congeners are deeply connected with vehicle exhaust, it is reasonable to conclude that traffic emissions explain 51.6% of the total variance. It is also worth mentioning that B[k]F and B[g,h,i]P have been used as tracers of vehicle emissions (Miguel and Pereira, 1989; Harrison et al., 1996). While B[g,h,i]P and Cor are related to gasoline vehicles (Khalili et al., 1995; Schauer et al., 2002), B[a]P, B[k]F and B[g,h,i]P are identified as tracers of diesel/gasoline emissions (Teixeira et al., 2013). Chry and B[k]F can be considered as geochemical markers for identifying coal combustion (Smith and Harrison, 1998; Ravindra et al., 2008). While B[b]F and Ind can be used as biomarkers for oil combustion, D[a,h]A, Per, B[a]P and B[e]P are widely considered as tracers for discriminating the air pollutants released from industrial stacks (Ravindra et al., 2008).

PC2 is related to biomass burning, accounting for 16.2% of the total variance, with a high loading factor for OC, EC and WSIS. This PC is believed to be the biomass burning source of carbonaceous compositions. OC, EC and K^+ are generated from biomass burning. BB emissions contain a significant amount of WSIS, such as NH_4^+, K^+, and NO_3^- (Chuang et al., 2013; Mkoma et al., 2013; Lee et al., 2016; Pani et al., 2018). Moreover, BB also emits significant amounts of carbonaceous aerosols that are composed of both OC and EC into the atmosphere (Cao et al., 2005; Chuang et al., 2013; Mkoma et al., 2013).

PC3 accounts for 10.6% of the total variance and has high loading factors for Ace, Fl, Phe and Ant. Several studies have reported that the most significant PAH compound from diesel engine exhaust was Phe (Nelsen, 1989; Lim et al., 2005; Szewczyńska et al., 2017). As a consequence, PC3 can be attributed to vehicle exhaust, particularly diesel emissions. This interpretation is consistent with the fact that Pyr and Fluo can also be considered as chemical tracers of vehicle emissions (Szewczyńska et al., 2017).

PC4, which explains 5.20% of the total variance, is associated with sea-salt aerosols because of relatively high loading factors of Cl^-. The results suggest a strong influence from maritime aerosols in $PM_{2.5}$. This explanation is in good agreement with previous studies conducted in Brisbane, Australia and in Auckland, New Zealand, highlighting Cl^- as a chemical tracer of maritime aerosols (Chan et al., 1997; Wang and Shooter, 2000).

The last group, PC5, shows a relatively high loading factor from NH_4^+. It is the only WSIS that possesses a high correlation coefficient (r=0.71) with PC5. It is well known that volatilization from fertilizer is the main source of NH_4^+ in particulate matter (Lee and Hopke, 2006; Sheppard et al., 2010). Thepnuan et al. (2019) reported the photochemical formation of SO_2 from both traffic/industrial activities and biomass burning because of the high affinity of SO_4^{2-} for NH_4^+. SO_4^{2-}, NO_3^- and NH_4^+ mainly form in the atmosphere by gas-to-particle conversion from their precursor trace gaseous species (e.g. SO_2, NO_x and NH_3) (Mousavi et al., 2014).

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Chapter-IV
Results & Discussion

Impacts of Vehicular Exhausts on Variations of Particulate Chemical Compounds in Ambient Air of Bangkok, Thailand

Abstract

In this study, a chemical characterization of $PM_{2.5}$-bounded carbonaceous compositions (OC, EC), water-soluble ionic species (WSIS), and polycyclic aromatic hydrocarbons (PAHs) in the ambient air of Bangkok was carefully investigated. The arithmetic mean of $PM_{2.5}$ concentration was 77.0±21.2 μg m^{-3}. The average concentrations of TC, OC and EC were 10.65±5.39, 8.03±4.02 and 2.62±1.49 μg m^{-3}, respectively. The comparatively high OC/EC ratio (i.e. 3.52±1.41) coupled with strong positive correlation between K^+ and other carbonaceous compositions (i.e. K^+ *vs.* OC (r=0.86), K^+ *vs.* EC (r=0.87), K^+ *vs.* Char-EC (r=0.82)) suggest that biomass burnings are one of the major contributors in sampling area. The ∑PAHs concentrations (e.g. the sum of 19 PAH profiles) was 2.78±1.48 μg m^{-3}, which the highest concentration of B[g,h,i]P and Ind were determined as 0.516±0.271 μg m^{-3} and 0.404±0.221 μg m^{-3}, respectively.

Hierarchical cluster analysis (HCA) indicated that the main source was a mixture from numerous combustion activities (e.g. biomass burning, vehicular exhausts, fossil fuel, coal and industrial). It is also remarkable to underline that Principal Component Analysis (PCA) successfully classified five principal sources of $PM_{2.5}$ samples, including vehicular exhaust, biomass burning, sea salt aerosols, power plants and industrial emission, which clarified for 43.7%, 24.0%, 10.5%, 6.48% and 4.46%, respectively. As a consequence, the results indicated that the effects of both local (e.g. vehicular exhausts) and regional (e.g. agricultural waste

burnings) sources play an important role in governing the level of $PM_{2.5}$ in Bangkok's atmosphere. In addition, policy markers can benefit tremendously from this study to launch an effective air quality control strategy based on the source apportionment analysis.

Keywords: $PM_{2.5}$, PAHs, Carbonaceous Compositions, WSIS, Backward Trajectories, HCA, PCA

4.1. Introduction

Over the past decades, it has been acknowledged that air pollution is one of significant environmental problems because of emissions from energy use (World Energy Council, 2013; Arbabi and Mayfield, 2016) and biomass burning (Guofeng et al., 2012; Pongpiachan et al., 2017a) in urban and rural areas. In general, the main sources of air pollutants were activities that required energy consumption, such as land transportation (Silva, 2005), electricity generation (Dung, 1996; Akunne et al., 2006) and industry (Gocht et al., 2001), especially in the mega cities, including Bangkok (Vichit-Vadakan and Vajanapoom, 2011; Guo et al., 2014, Pongpiachan et al., 2017b).

It is well known that the air quality problem in Bangkok's atmosphere is caused by high traffic emissions which greatly affects people's health (Muttamara and Leong, 2000; Pongpiachan et al., 2014a; 2015). Besides the emissions from biomass burning, particularly during the burned sugar cane period is also significant environmental problems (Junpen et al. 2018; Kim Oanh, et al., 2018). During dry seasons, Bangkok is affected by the plumes of smoke originating from long-range transport from surrounding provinces. The biomass burning and traffic emissions release large amounts of particulate matters, including PAHs, OC-EC and WSIS (e.g. NH_4^+, K^+ and NO_3^-) that may lead to an increased the environmental effects as well as the heath impact (Dan et al., 2004; Harrison and Yin, 2008; Zhao et al., 2013; Pongpiachan et al., 2014a; Irei et al., 2016; Tsay et al., 2016; Chen et al., 2017; Pani et al., 2018).

Atmospheric $PM_{2.5}$-bound carbonaceous aerosol compositions have been intensively studied in several previous and comprehensively considered as persistent organic pollutants (POPs) (Jones and Voogt, 1999; Dachs and Eisenreich, 2000). Several reports highlight the adverse health impacts of PAHs as carcinogenic and/or mutagenic substances (e.g. chronic respiratory diseases, lower respiratory diseases and allergic reaction in skin, as well as skin, lung, bladder and gastrointestinal cancers) (Bach et al., 2003; Unwin et al., 2006; Campo et al., 2010; Diggs et al., 2011). PAHs have been widely used as geochemical tracers to identify potential sources of $PM_{2.5}$ based on the concept of receptor model (Boonyatumanond et al., 2007; Dvorská et al., 2012; Hu et al., 2012; Pongpiachan, et al., 2013a,b, 2015; Choochuay et al., 2020).

Over the past few decades, it is also worth mentioning that $PM_{2.5}$-bound carbonaceous aerosol compositions have been extensively evaluated in the northern and central parts of Thailand (Pongpiachan et al., 2017a; Pani et al., 2018; Thepnuan et al., 2019; Choochuay et al., 2020). A previous study reported that the annual mean concentrations of OC and EC at numerous PCD air quality observatory sites located in Bangkok were 18.8 ± 9.18 (n=94) and 6.65 ± 2.94 $\mu g\ m^{-3}$ (n=94), respectively (Pongpiachan et al., 2015). Some previous studies have also investigated the annual mean of $PM_{2.5}$-bound carbonaceous aerosol compositions in Bangkok (Pongpiachan et al., 2014a; Phairuang et al. 2019). It is emphasized that biomass burning is also the main source of OC-EC and WSIS (e.g. K^+, NH_4^+ ,SO_4^{2-} and NO_3^-) , which K^+ is widely used as a biomass marker (Chuang et al., 2013; Lee et al., 2016; Khamkaew et al., 2016; Pani et al., 2018; Choochuay et al., 2020).

Therefore, the atmospheric behavior of $PM_{2.5}$-bounded chemical compositions and their potential sources is definitely important for decreasing PM levels and improving air quality in ambient air of Bangkok. Overall, the main principles of this research are to (*i*) quantitatively characterize the carbonaceous compositions, PAHs, and WSIS in $PM_{2.5}$; (*ii*) apply the diagnostic binary ratios of PAHs for potential source classification; and (*iii*) employ HCA and PCA for execute the source apportionment of $PM_{2.5}$ in Bangkok.

4.2. Materials and Methods

4.2.1. Air Quality Observatory Area

The Aerosol sampling at Bangkok was located at ValayaAlongkorn Rajabhat University. The mini-vol air sampler is settled up at the rooftop of Science Center Building (5th Floor). The latitude of Bangkok sampling area is 14.13383 and the longitude is 100.61604. It located in the central of Thailand that is roughly 1,500 km^2, which on the riverside of Chao Phraya and close to the Gulf of Thailand, as well as its low-lying geography of approximately 1.5 meters average elevation upper mean sea level. It has a tropical atmosphere under the effect of the South Asian monsoon regularity which has three seasons, namely, summer, rainy, and winter, although weathers are rather hot year-round.

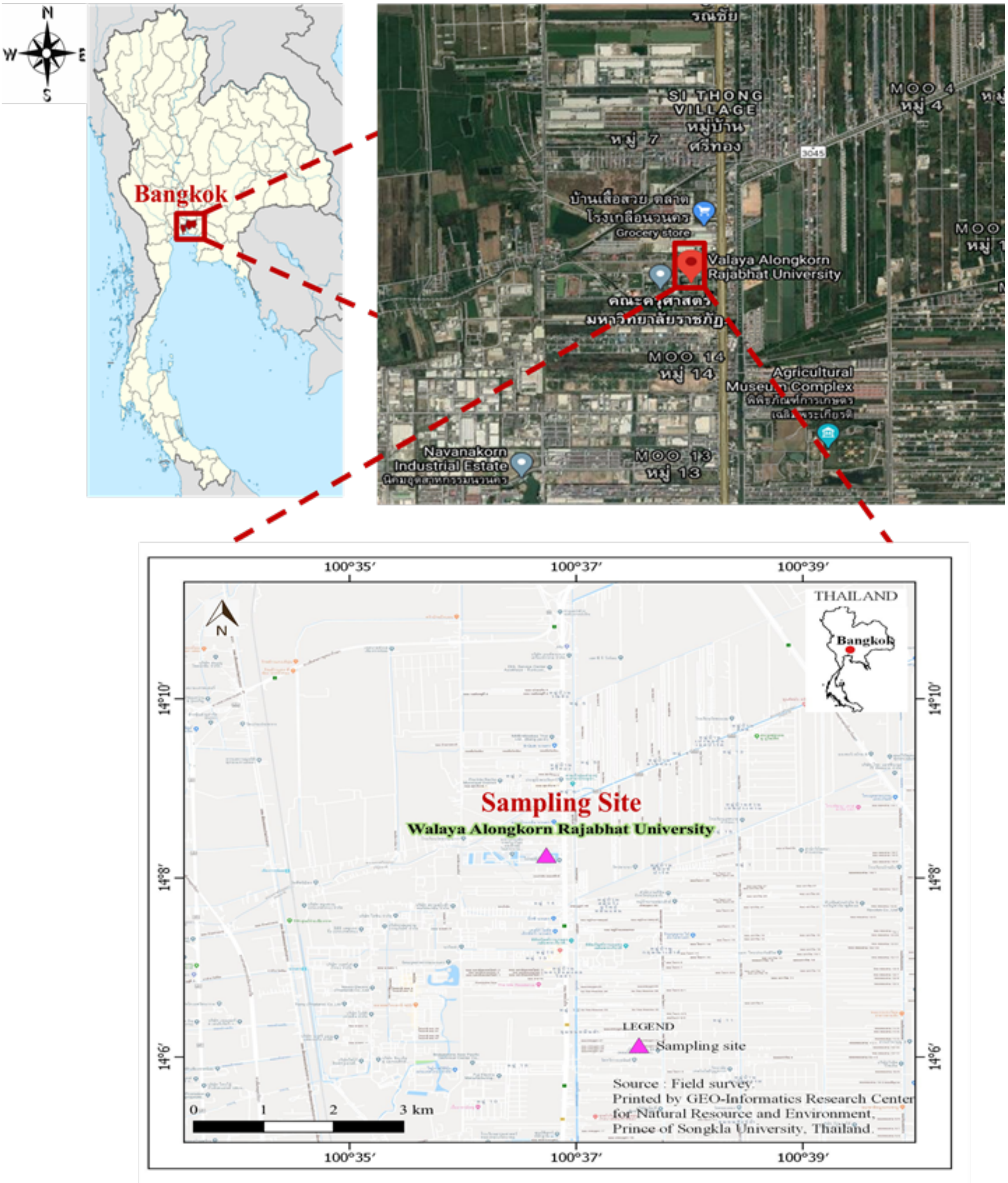

Figure 4.1. Description of air sample observatory area in Bangkok

PM$_{2.5}$ samples (n=43) were conducted from Bangkok, which described in Fig. 4.1. All PM$_{2.5}$ samples were conducted on a 47 mm Whatman quartz fiber-filter, each quartz fiber-filter were pre-heated in a furnace at 550 °C for 6 hours before sampling to eliminate the residual carbon. In sampling process, we used a MiniVol portable air sampler with a flow rate of five lite per minute for 72 consecutive hours. Each $PM_{2.5}$ sample was reserved in petri slide dish and stored them in a refrigerator till the next step of analysis. After the sample preservation, all $PM_{2.5}$ samples have been analyzed for PAHs, OC-EC and WSIS.

4.2.2. Measurement data in Bangkok

4.2.2.1. The measurement of OC-EC

For each sample was clarified for carbonaceous aerosol concentrations, following the thermal/optical reflectance procedure and applied a Desert Research Institute Model 2001 carbon analyzer (Chow et al., 1993). Eight carbonaceous fractions, including four organic carbons (OC1-OC4), a pyrolyzed carbon fraction (OP), and three elemental carbons (EC1-EC3) were formed from the carbon analyzer (Chow et al., 2007a).

The quality control and quality assurance (QA/QC) procedures for the OC and EC measurements that were followed previous studies (Cao et al., 2003). Concisely, methane with known quantity was used every day for calibration of analyzer. One of ten samples used for replicate measurements and the variation was below 5% for TC (total carbon) and 10% for OC and EC.

4.2.2.2. The measurement of WSIS

Each $PM_{2.5}$ sample was identified for WSIS, five cations including Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} and five anions including Cl^-, F^-, NO_2^-, NO_3^- and SO_4^{2-}. The extraction of each $PM_{2.5}$ filter was used the ion chromatography (IC) that contains with a separation column for measure the concentration of WSIS in all $PM_{2.5}$ samples. The quality assurance/quality control (QA/QC) for this measurement, following the previous studies (Wang et al., 2005). Briefly, all solvents that applied for identification process were pesticide residue grade. All glassware that used in the process was rinsed by an ultrasonic and incubated at 450 degrees in furnace for six hours.

4.2.2.3. The measurement of PAHs

The $PM_{2.5}$ sample was clarified for PAHs concentration by TD-GC/MS, following the in-injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS) which applied for quantify of non-polar organic compounds as a concentration of PAHs. The quality assurance/quality control (QA/QC) for this measurement, following the previous studies (Chow et al., 2007b). Shortly, injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS), was applied to quantify 19 PAH profiles in the $PM_{2.5}$ samples. It responds as well as an alternative procedure of ancient solvent extraction performed by GC/MS analysis.

4.2.3. Statistical analysis

This study, statistical analysis was using SPSS system for windows version 22 (SPSS Inc., USA), including the minimum, maximum, mean, and standard deviations for the concentrations of OC, EC, WSIS and PAHs. The identify source appointment was applied by HCA and PCA, following the previous studies (Larsen and Baker, 2003; Hegde et al., 2007). Approximately, HCA was applied to cluster chemicals according to the coherent source of $PM_{2.5}$ samples in Bangkok. Whilst PCA was a statistics curtailment procedure helpful for outline or explain the transition in a batch of variant into less magnitude than there are variants in that data set.

4.3. Results and Discussion

4.3.1. Mass concentrations of $PM_{2.5}$, TC, OC and EC

The mass concentrations of $PM_{2.5}$, OC and EC are shown in Table 4.1. During the study period the concentrations of $PM_{2.5}$ mass varied from 34.8 to 143.5 µg m^{-3} with a mean of 77.0±21.2

µg m^{-3}, highlighting that the mean of $PM_{2.5}$ levels is much higher than the annual mean concentration of Thai National Ambient standard (25 µg m^{-3}) as well as USEPA standard. The average concentrations of TC, OC and EC were 10.65±5.39, 8.03±4.02 and 2.62±1.49 µg m^{-3}, respectively. While the mean mass concentrations of each carbon fraction including OC1, OC2, OC3, OC4, EC1, EC2 and EC3 were 0.07±0.09, 1.31±0.64, 3.67±1.88, 2.41±1.64, 2.97±1.32, 0.22±0.06 and 0.01±0.02 µg m^{-3}, respectively.

Table 4.1. The concentrations of TC, OC and EC in Bangkok

Species	**Minimum (µg m^{-3})**	**Maximum (µg m^{-3})**	**Mean ± SD (*n*=43)**
OC1	N.D.	0.30	0.07±0.09
OC2	0.38	3.57	1.31±0.64
OC3	1.53	10.73	3.67±1.88
OC4	0.46	8.16	2.41±1.64
EC1	0.24	6.25	2.97±1.32
EC2	0.14	0.41	0.22±0.06
EC3	N.D.	0.14	0.01±0.02
OC	2.64	22.75	8.03±4.02
EC	0.27	6.43	2.62±1.49
TC	2.99	29.06	10.65±5.39
$PM_{2.5}$	34.8	143.5	77.0±21.2

For OC fractions, OC3 was found the most (3.67±1.88 µg m^{-3}), followed by OC4 (2.41±1.64 µg m^{-3}), OC2 (1.31±0.64 µg m^{-3}) and OC1 (0.07±0.09 µg m^{-3}).While EC fractions, EC1 was found the most (2.97±1.32 µg m^{-3}), followed by EC2 (0.22±0.06 µg m^{-3}) and EC3 (0.01±0.02 µg m^{-3}), respectively. Several studies applied OC and EC to estimated emission sources from local and regional transport such as anthropogenic emissions and burning of biomass (Chuang et al., 2013; Cheng et al., 2015; Li et al., 2018). Previous studies reported that OC3 was a good relationship with gasoline emission (Cao et al., 2006) and burning of biomass (Chuang et al., 2013), while OC2 was a marker of vehicular exhausts (Cheng et al., 2015). Form the result of

EC fractions, EC1 was a strong correlation with vehicular exhausts (Cao et al., 2005) and EC2 was a good relationship with diesel emissions (Cao et al., 2006).

Several studies showed the result that agricultural burning such as rice straw and sugar cane in central and northeastern part of Thailand was creating the higher value of black carbon and organic carbon to the Bangkok area (Junpen et al. 2018; Kim Oanh, et al., 2018). Hence, the results of this study shows the higher level of $PM_{2.5}$ concentration might be came from the agricultural burning activities from another province nearby this area, which areas around 250 kilometers far from Bangkok. Thus, it is much more enough time to enrich the level of organic carbon and $PM_{2.5}$, which lifetime of black carbon was taking the atmospheric about one week (Cape et al., 2012)

OC can be released straight from various sources, including the man-made processes and natural germinations (e.g. primary OC) and/or also can produce in the ambience air because of gas-to-particle exchanging (e.g. secondary OC) (Mauderly and Chow, 2008). While, EC is released from incomplete combustion processes (e.g. the combustion biomass, the combustion of fossil fuels and biofuels) and usually applied as a marker of primary organic carbon (Turpin and Huntzicker, 1995).Generally EC is sub-divided into char and soot. Char-EC was consisted of submicron particles produced from low temperature combustion of biomass and Soot-EC was composed from aggregation of gas-phase precursors released from high temperature (>600 ºC) of fossil fuel combustion, which depend on the type of fuel and condition of combustion (Han et al., 2007, 2009a; Keiluweit et al., 2010). Hence, the ratio of OC/EC and Char-EC/Soot-EC can explain their environmental (Han et al., 2009a) and benefit in source estimation.

4.3.2. Distribution of OC/EC ratios and Char-EC/Soot-EC Ratios

Carbonaceous compounds are essential fraction of atmospheric aerosols (Putaud et al., 2004). The ratio of OC/EC and Char-EC/Soot-EC were applied to predicate the source of carbonaceous aerosols (Han et al., 2007, 2009b), as showed in Table 4.2. In this study the result showed that the OC/EC ratios ranged from 1.87 to 9.96 with an average value of 3.52±1.41, indicating that the source was gasoline and LPG exhausts (Chow et al., 2004), which the OC to EC ratio higher than two points that the secondary organic carbon has a significant to organic carbon (Turpin and Huntzicker, 1995).While the Char-EC/Soot-EC ranged from N.D. to 17.93 with a mean value of 6.94±3.70. Char-EC/Soot-EC ratio is cogitated a good marker of biomass burning more than OC/EC ratio because the primary emission sources can be effected to OC/EC ratio (Kumar and Attri, 2016). A high Char-EC/Soot-EC ratio represents the function of biomass burning participated Char-EC rising to total EC, on the other hand, the ratio less than one will intimates that Soot-EC from fossil fuel combustion outstandingly encourage to total EC. The result presented the high ratio of Char-EC/Soot-EC guided that the ambient aerosol was emerging from biomass burning activity in Bangkok area.

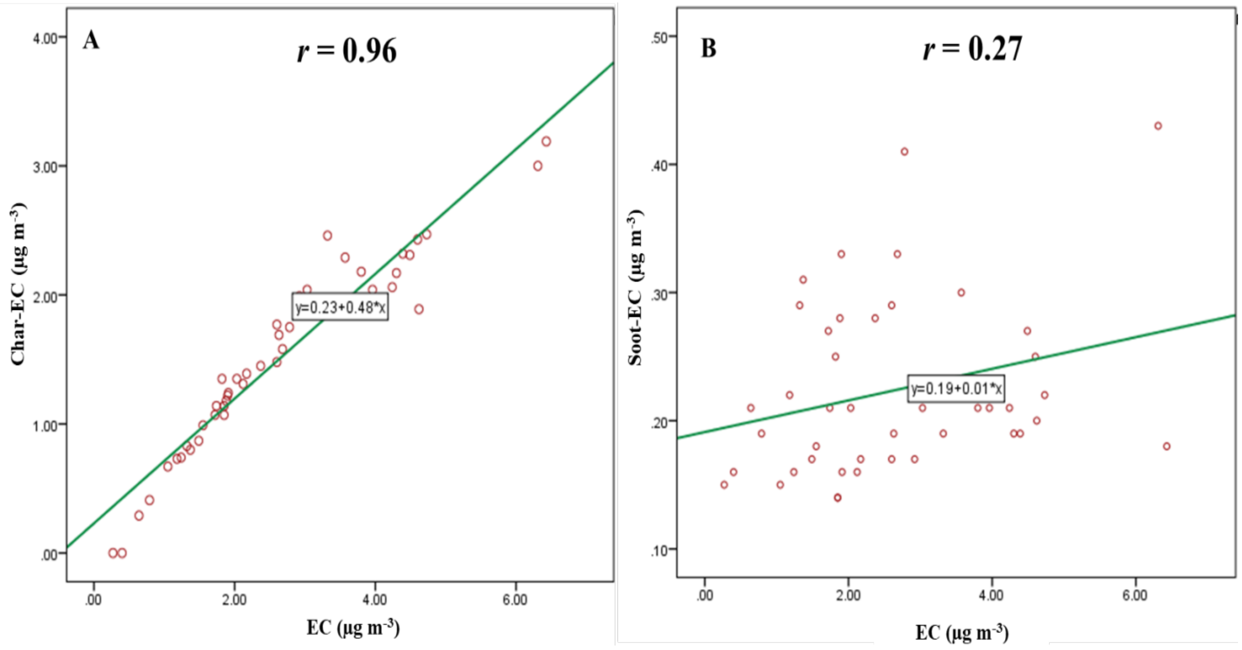

Figure 4.2. The correlation of Char-EC with total EC (A) and the correlation of Soot-EC with total EC (B) in PM$_{2.5}$ conducted at Bangkok

A strong correlation was found between Char-EC and total-EC (r = 0.96), while the correlation of Soot-EC with total-EC was weak (r = 0.27), correlation is significant at the 0.01 level (see in Fig. 4.2 (A) and (B)). This recommended that prominent raisings of Char-EC came from biomass burning to total-EC of the Bangkok's atmosphere. The correlations of this study were agreement with previous studies from China and India (Han et al., 2009; Kumar and Attri, 2016).

Table 4.2. Carbon composition and the average ratios of OC/EC, Char-EC/Soot-EC, OC, EC, and TC to particulate matter in Bangkok

Species	**Minimum**	**Maximum**	**Mean ± SD (*n*=43)**
OC/EC	1.87	9.96	3.52±1.41
Char-EC/Soot-EC	N.D.	17.93	6.94±3.70
OC/ $PM_{2.5}$	0.03	0.25	0.11±0.05
EC/PM2.5	N.D.	0.08	0.04±0.02
TC/ $PM_{2.5}$	0.03	0.33	0.15±0.07

For the result of OC/$PM_{2.5}$, EC/ $PM_{2.5}$ and TC/ $PM_{2.5}$ ratios were 0.11±0.05, 0.04±0.02 and 0.15±0.07, respectively. The ratios of OC/$PM_{2.5}$ and EC/$PM_{2.5}$ were closer to the resulted value of biomass burning that reported by previous studies from Mumbai, Beijing and Delhi (e.g. Zhang et al., 2013; Sharma et al., 2014a, b; Kumar and Attri, 2016). Noticeably, during the observation period were closer to the reported values of emission source from biomass burning.

4.3.3. Distribution of Secondary Organic Carbon (SOC)

The OC/EC ratio in section 3.2 was higher than two its points that the secondary organic carbon has a significant to organic carbon. Therefore, SOC was used to calculate by the minimum of OC/EC ratios, while EC is used as a primary organic carbon (POC) (Chow et al., 1996; Castro et al. 1999). It was followed from the equation 1:

$$SOC = OC_{total} - EC \times (OC/EC)_{pri} \quad (1)$$

Where, OC_{total} presents the value of total OC and $(OC/EC)_{pri}$ is the mean value of the three lowest OC/EC ratios

The average values of the three minimum OC/EC ratios (1.95) have been used in the equation for measure the SOC content of $PM_{2.5}$. The mean value of SOC in this study was 2.92±1.93 μg m^{-3}. The percentage contribution of SOC to OC_{total} was found 36.3%. This value is 2.3 times (84%) lower than the value that conducted in Milan, Italy (Lonati et al., 2007) and 1.6 times (59%) lower than the value that conducted in Birmingham (Harrison and Yin, 2008) and Beijing urban site (Dan et al., 2004). But it is higher 2.4 times (15.4%) than the value that conducted from southern Taiwan (Shen et al., 2020). However this value is close to the value that observed from roadside area in Hanoi, Vietnam (36.0%) (Thuy et al., 2018). Normally, the SOC content decreases in urban area and it increases in outlying areas (70–80% in Finokalia) (Shamjad et al., 2015). The result presented the ratio of SOC to OC at Bangkok had been contributed during the study period, where the high value maybe effected from the conversion of VOCs, which released from the traffic exhausts. (Sato et al. 2010).

4.3.4. Distribution of WSIS

The concentrations of WSIS in $PM_{2.5}$ are summarized in Table 4.3, which have been widely studied in different areas. Previous studies reported that SO_4^{2-} and Cl^- are mainly from marine aerosols, whereas NH_4^+ and K^+ are mainly from burning of biomass (Andreae, 1983; Kocaka et al., 2007; Park and Cho, 2011; Pongpiachan et al., 2014b). In this study we found the individual of WSIS concentrations were in a decreasing order of SO_4^{2-}>NO_3^->Na^+> Ca^{2+} >NH_4^+>K^+ >Cl^->NO_2^->Mg^{2+}>F^-. The mean concentration of total ten ions was 12.7±10.6 μg m^{-3}. By SO_4^{2-} (4.81±3.81 μg m^{-3}) was highest found in $PM_{2.5}$ mass, followed by NO_3^- (1.85±1.04 μg m^{-3}) and followed closely by Na^+ (1.78±0.59 µg m^{-3}), as 38%, 14% and 14% of the total measured ions, respectively.

Table 4.3. The concentrations of WSIS conducted in $PM_{2.5}$ at Bangkok

Ion Species	**Min. (µg m^{-3})**	**Max. (µg m^{-3})**	**Mean (µg m-3)**	**% mass of total ion content**
F^-	0.06	0.22	0.10±0.03	1%
Cl^-	0.28	6.86	0.59±0.99	5%
NO_2^-	N.D.	1.16	0.40±0.18	3%
NO_3^-	0.59	6.18	1.85±1.04	14%
SO_4^{2-}	0.80	21.40	4.81±3.81	38%
Na^+	1.10	4.51	1.78±0.59	14%
NH_4^+	0.20	3.61	0.97±0.85	8%
K^+	N.D.	1.60	0.65±0.41	5%
Mg^{2+}	0.08	2.53	0.18±0.37	1%
Ca^{2+}	0.60	16.20	1.36±2.33	11%
Total	-	-	**12.7±10.6**	**100%**

The higher value concentrations of SO_4^{2-} and NO_3^- that have found in this study could be related with high oxidation rates of SO_2 and NO_2 for the ambient air of Bangkok. Previous studies recommended that the aquatic phase oxidation of SO_2 by the catalysis of the transfer metals is probably a big role of SO_4^{2-} origination during the study period (Sun et al., 2013; Zhao et al., 2013; Park et al., 2016). While NO_3^- is generally produced through gas phase oxidation procedure of NO_2 and OH (Smith et al., 1995; Park et al.,2005; Park et al., 2016).

Several previous studies presented that K^+ and NH_4^+ are the major contributors of particles initiated from burning of biomass and agricultural waste, (Kocaka et al., 2007; Kundu et al., 2010; Park and Cho, 2011). At Bangkok, the result showed that the K^+ was a high relationship with OC (r=0.86), EC (r=0.87) and Char-EC (r=0.82), respectively. However K^+ was weakly related with those marine species (i.e., Na^+, Cl^-, Mg^{2+} and Ca^{2+}), indicating that K^+ mostly initiated from combustion activities that led to K^+ conjunction, so in this study K^+ was applied as a marker of biomass burning. Interestingly, a strong correlation between K^+ with NO_3^- (r=0.81) was also found in Bangkok area, as the major source of NO_3^- is originated from incomplete combustion, including traffic emissions and industrial emission (Mousavi et al., 2017). Thus, the result suggested that the combustion sources (e.g. biomass burning and vehicular exhausts) might be played a significant role in the higher organic carbon in $PM_{2.5}$ at Bangkok.

4.3.5. Distribution of PAHs

The statistical distributions of individual PAH obtained in Bangkok are plotted in panel as box and whisker plots were shown in Fig.4.3. In this study we found the individual concentrations of PAH that analyzed from $PM_{2.5}$ samples were in a decreasing order of B[g,h,i]P> Ind> B[k]F> B[b]F> B[a]P> B[e]P> Cor> Phe> B[a]A> Pyr> Chry> D[a,h]A> Fluo> D[a,e]P> B[a]F> Fl> Ace> Per> Ant. The ∑PAHs concentration (the sum of 19 PAH profiles) was 2.78±1.48 $\mu g\ m^{-3}$, which the highest concentration of B[g,h,i]P (0.516±0.271 $\mu g\ m^{-3}$), followed by Ind (0.404±0.221 $\mu g\ m^{-3}$) have been found in the $PM_{2.5}$ sample.

Previous studies in Bangkok reported that the dominant PAHs in ambient air were B[g,h,i]P, B[e]P, B[a]P, B[k]F, Pyr and Cor (Panther et al., 1999), and in the suburban Bangkok area, the significant PAHs were B[e]P, B[g,h,i]P, Ace, Acy (Kim Oanh et al., 2000).

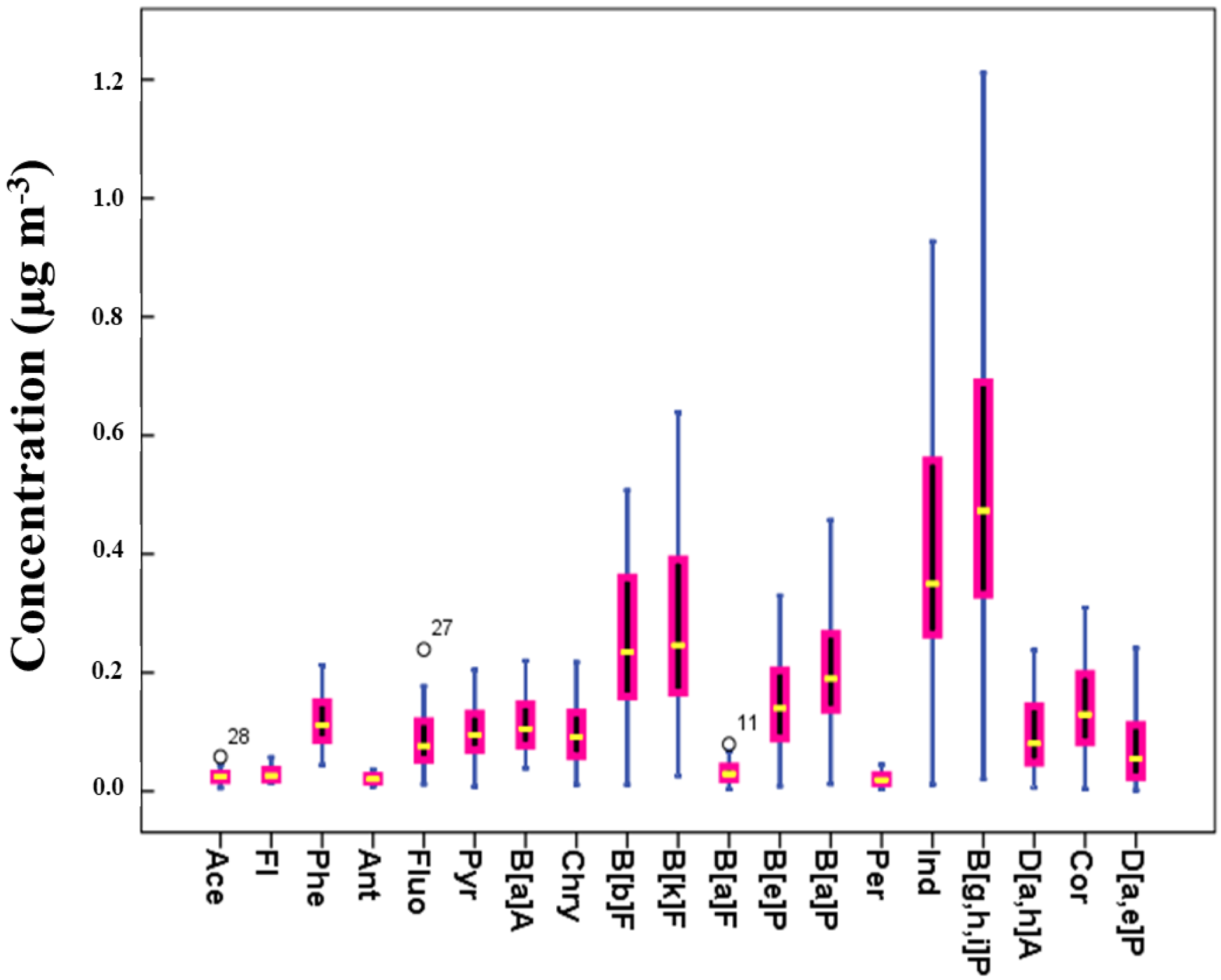

Figure. 4.3. Box-plot of individual concentration of 19 PAHs conducted in $PM_{2.5}$

In this study, B[g,h,i]P and Ind were presented the highest concentration, indicating that vehicular exhausts, industrial combustion and burning of waste might be reflected as the release sources of PAHs for the Bangkok's atmosphere (Zhou et al., 1999; Ravindra et al. 2008).

Several previous restudies have recommended the use of PAHs as markers to estimate the pollution sources. Those findings found B[g,h,i]P, Ind, B[a]P, B[b]F, B[k]F were the major PAHs, whereas smaller portions of B[a]A, Phe, Ant, Pyr, Fluo and Chry were found in the softwood burning emissions (Freeman and Cattel, 1990; Bari et al., 2010). Likewise, B[a]P have been used as a marker of biomass burning, while B[g,h,i]P and Ind used as tracers of vehicular exhaust

(Kulkarni and Venkataraman, 2000; Chuesaard et al., 2014). In addition, the high molecular weight PAH congeners (HMW-PAHs) (e.g. B[a]P and D[a,h]A) have been applied for the dominant emissions occurring from gasoline vehicles. Whilst other HMW-PAHs (e.g. B[a]P, B[g,h,i]P, Ind and D[a,h]A) released from diesel trucks at higher concentrations than duty vehicles (Miguel et al., 1989). Moreover, B[g,h,i]P also represented as a specific indicator for gasoline vehicles (Boström et al., 2002).

4.3.5.1. Diagnostic Ratios Analysis

Some PAH ratios have been applied as a descriptor to feature and separate the emission source (Yunker et al., 2002; Brown and Peake, 2006; Feng et al., 2006; Zhang et al., 2008) such as Ant/(Ant+Phe), Fluo/(Fluo+Pyr), B[a]A/(B[a]A+Chry) and Ind/(Ind+B[g,h,i]P), as Ant/(Ant +Phe) < 0.1 was suggest for petrogenic, or > 0.1 pyrogenic source. Fluo/(Fluo+Pyr) of 0.4–0.5 presented petroleum combustion (e.g. traffic emission and furnaces), > 0.5 combustion of biomass (e.g. combustion of grasses, wood and/or coal) source. For B[a]A/(B[a]A+ Chry), > 0.35 was indicated as the signal for pyrogenic source (e.g. combustion of biomass, coal, petroleum and mixed petroleum). Ind/(Ind+B[g,h,i]P), < 0.2 was considered as a petrogenic source, 0.4–0.5 was combustion of petroleum and > 0.5 related to the combustion of biomass. The diagnostic of the four ratios during the study periods are shown in Fig. 4.4.

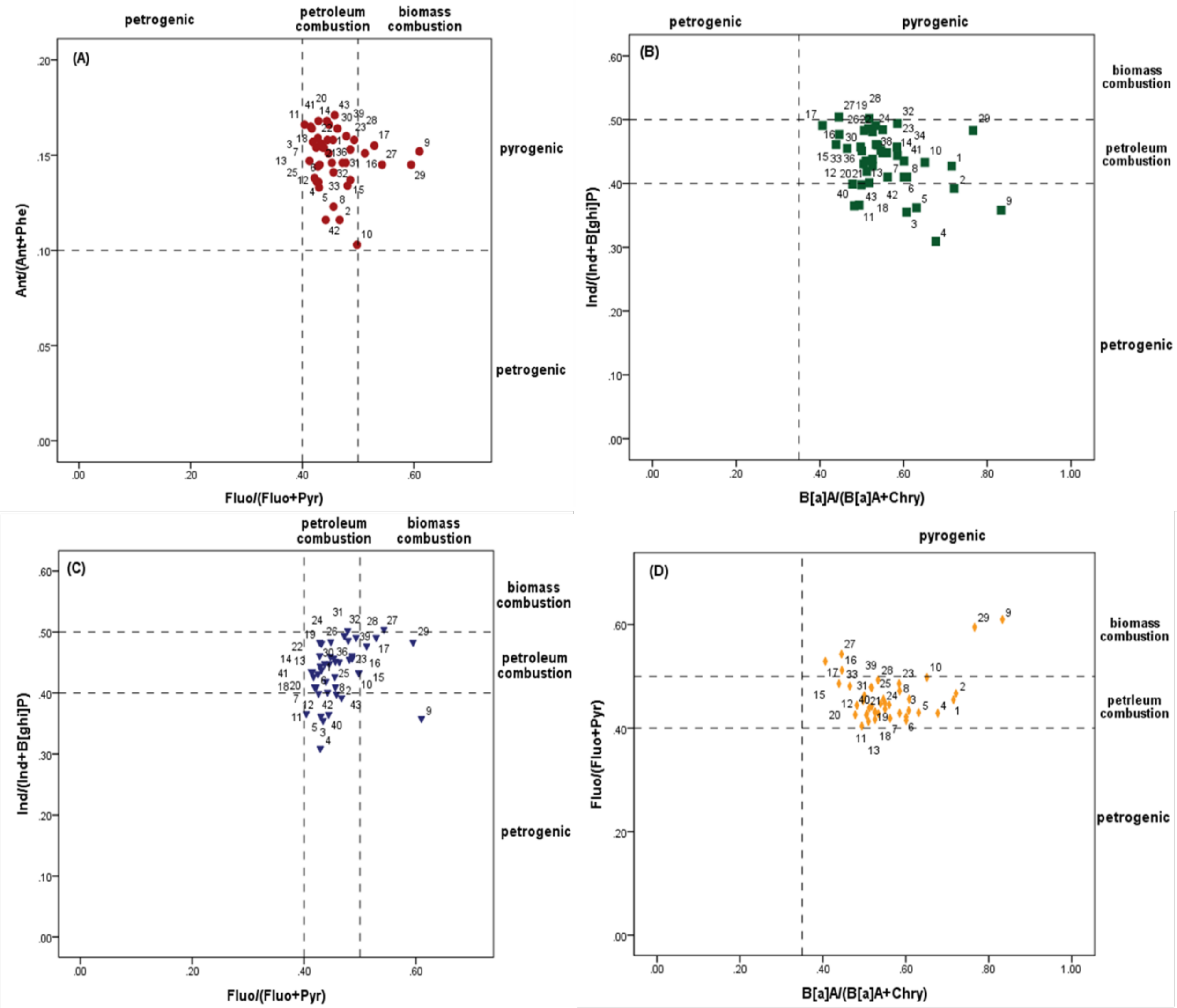

Figure 4.4. The diagnostic ratios of: (A) Fluo/(Fluo+Pyr) *vs.* Ant/(Ant+Phe); (B) B[a]A/(B[a]A+Chry) *vs.* Ind/(Ind+B[g,h,i]P) (C) Fluo/(Fluo+Pyr) *vs.* Ind/(Ind+B[g,h,i]P) and (D) B[a]A/(B[a]A+Chry) *vs.* Fluo/(Fluo+Pyr); conducted in Bangkok

In this study, the ratio of Ant/(Ant+Phe) ranged from 0.10 to 0.17, which applied to differentiate petrogenic (<0.1) and pyrogenic (>0.1). The plurality of portions accommodated a ratio greater than 0.1 designated a pyrogenic source. The Fluo/(Fluo+Pyr) has a range of 0.40 to 0.61 with a mean of 0.46. Most of sections rations in between 0.4 to 0.5, indicating petroleum combustion was a main source (e.g. combustion engines and furnaces). For B[a]A/(B[a]A+Chry) ranged from 0.41 to 0.83 with a mean of 0.55. It showed that the major source was pyrogenic (>0.35) (Dvorská et al. 2011), including coals, biomass, fossil and petrol fuels combustion. The

Ind/(Ind+B[g,h,i]P) ranged from 0.31 to 0.50 and a mean of 0.44. The majority of portions accommodated a ratio from 0.4 to 0.5, which indicates petroleum combustion was a major source. Overall, the result of the binary ratios showed that petroleum combustion and biomass burning, particularly vehicular exhausts and the effect of agricultural waste burning from another province surrounding Bangkok was a major contributor in Bangkok's atmosphere.

4.3.6. Classification of Air Mass Back Trajectories during the Aerosol Sampling Period

In order to identify the potential pollution sources in the receptor site, we investigated the air mass back trajectory using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Zhao et al., 2011; Stein et al., 2015; Kassambara, 2017; Moran et al., 2018). The backward air mass trajectories arriving at Bangkok during the study period in August (Fig. 4.5 (A)) presented that the southwest trajectory patterns were those having the marine pathways of air mass arriving the Bangkok area from over the sea. Thus, the marine air mass was initiated from the Indian Ocean and Andaman Sea and had a long distant marine and entered inland at the southern part of Myanmar and the western part of Thailand before arriving to Bangkok. These air masses can be carried sea salt aerosols to the Bangkok area, which is also demonstrated in the recreated mass produces. The majority backward air mass trajectories during October (Fig. 4.5 (B)) have passed over the northeastern trajectory (92% in total) and 8% from southwest trajectory patterns. Hence, the mainly air masses can be took from the long rang transportation of the biomass burning that initiated 48% in total from the northeastern regions of Thailand and 44% in total had a long distant pathway through China and a marine pathway over the Gulf of Vietnam, and then passing over Vietnam and Lao before arriving to Bangkok. During the study period in December (Fig. 4.5 (C)), all clusters of the air masses trajectory patterns have passed from the northeastern. Therefore, the essential sections of the air masses encouraged to the pollutants emitted from burning of biomass (e.g. agriculture waste, wood and/or grass) vehicles exhaust, combustion of fossil fuel and coal which transferred from Lao, Vietnam and China.

Interestingly, during the sugarcane harvests season in central and northern part of Thailand during November to February was related to high level of carbonaceous aerosols and air masses trajectory patterns from this study in December. From the previous study reported that the owning of five PAHs profile including B[a]A, B[b]F, B[k]F), B[a]P) and D[a,h]A in cachaça, Brazil which indicating that the samples that conducted from burnt sugar cane fields had higher significant PAHs levels more than those samples that conducted from non-burnt sugar cane fields (Tfouni et al., 2007) and the enriched K^+ and Cl^- were found the most abundant of WSIS in burnt sugar cane period as well (Álvareza et al., 2018). All chemical level concentrations measured in this study, including OC, EC, WSIS and PAHs are in a good agreement with the result which have been reported in Brazil (Lara et al., 2005; lvarez et al., 2016). The concentrations of TC, OC, EC, WSIS and PAHs during burned and non-burnt sugar cane fields were statistically different for both period, presenting statistical differences ($p < 0.05$) and ($p < 0.10$). Hence, it points that the burning of sugarcane leaf for the harvest period had a significant in December which is agreement with the high-level of chemical characterization of $PM_{2.5}$-bounded carbonaceous aerosols in the ambient air of Bangkok.

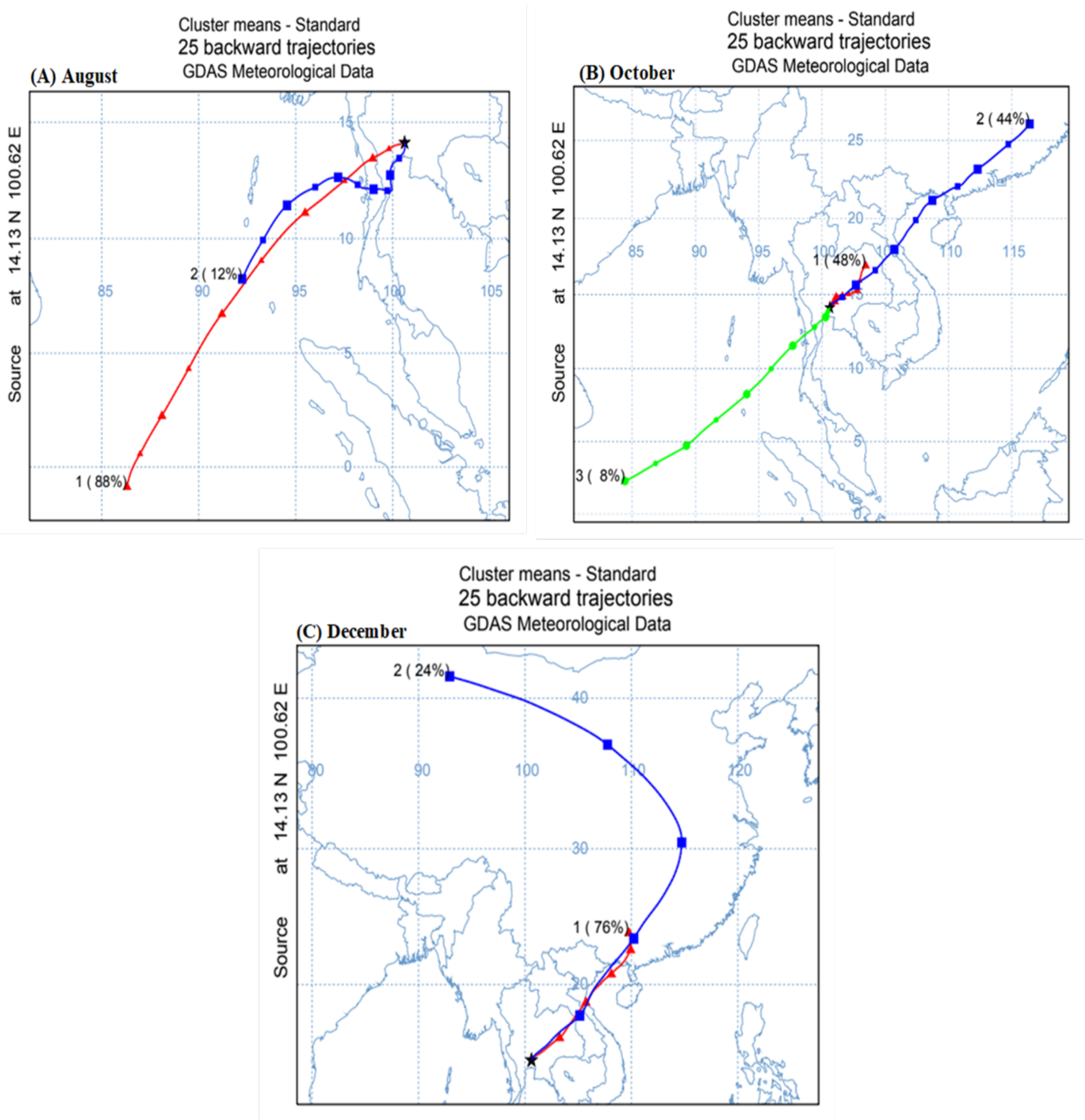

Figure 4.5. Air mass history during the aerosol sampling period at Bangkok; (A) August 2017, (B) October 2017 and (C) December 2017

4.3.7. Source identification and pattern recognition

4.3.7.1. HCA for Classification of Chemical Compounds during the Aerosol Sampling Period

The chemical components in $PM_{2.5}$ samples were classified by cluster analysis of carbonaceous compositions, WSIS and PAH profiles by the ward method with squared euclidean distance (see Fig. 4.6).

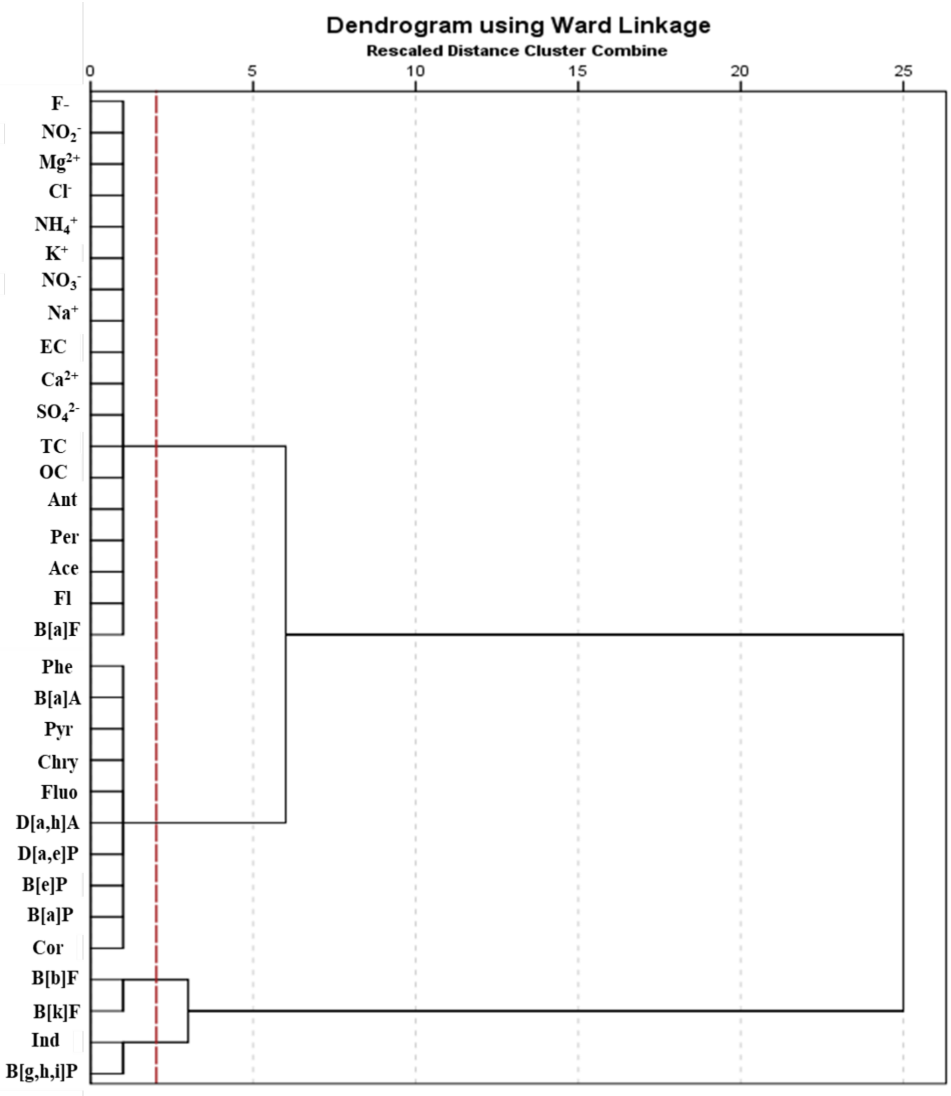

Figure 4.6. Dendrogram of $PM_{2.5}$-bounded chemical compounds in the ambient air of Bangkok

HCA was applied to separate the homogeneous clusters of individual carbonaceous component in $PM_{2.5}$ samples. The results indicated that the main components are separated into four clusters from the 32 individuals. The first cluster consists of F^-, NO_2^-, Mg^{2+}, Cl^-, NH_4^+, K^+, NO_3^-, Na^+, OC, Ca^{2+}, EC, TC, SO_4^{2-}, Ant, Per, Ace, Fl and B[a]F, which all OC, EC and WSIS were in this cluster. It indicated that the main source was mixture from combustion activities (e.g. biomass, fossil fuel, coal and industrial) (Long et al., 2014; Pani, et al., 2019).

The second cluster includes Phe, B[a]A, Pyr, Chry, Fluo, D[a,h]A, D[a,e]P, B[e]P, B[a]P and Cor. This cluster ordinarily initiates from pyrogenic sources that emitted from vehicular exhausts, diesel/gasoline engine, road carpeting asphalt, crude oil and tar (Ahrens and Depree, 2010) and dust from road site (Larsen and Baker, 2003). In agreement with previous studies reported, 3–4 ring PAHs have been related with vehicular exhausts and road dust in urban cities (Zakaria et al., 2002; Boonyatumanond et al., 2007).

The third cluster contains of B[b]F and B[k]F, which are the anthropogenic PAHs from petroleum products, vehicular exhausts, oil combustion and waste incinerators from industrial (Zhou et al., 1999; Ravindra et al. 2008). As B(k)F and B(b)F are classified as an indicator of fossil fuels combustion (Park et al., 2002). In summary, this cluster was assumed as vehicular exhausts contamination and petrogenic sources.

The last cluster encloses Ind and B[g,h,i]P, which are the anthropogenic PAHs from vehicular exhausts, industrial combustion (e.g. petroleum, oil and/or waste incinerators) (Zhou et al., 1999; Ravindra et al. 2008; Elghawi et al., 2010). A notable that Ind and B[g,h,i]P were found from both diesel and gasoline fuelled engines (Elghawi et al., 2010; Birgül et al., 2011).

4.3.7.2. Source estimations from PCA

The contaminations of carbonaceous aerosol compositions in fine particles have been analysed extensively in many countries (Lee et al., 2011). Thus, multivariate analysis including correlation coefficients and PCA have been applied to associate the source of carbonaceous compositions, WSIS and PAH profiles (Long et al., 2013).

Table 4.4. Rotated Component Matrix[a] of $PM_{2.5}$-bounded chemical compounds during the aerosol sampling period in Bangkok's atmosphere.

Compositions	**Principal components (PC)**				
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
TC	0.12	**0.97**	N.D.	0.09	0.04
OC	0.12	**0.96**	-0.05	0.11	0.09
EC	0.12	**0.93**	0.13	0.02	-0.09
F^-	-0.25	0.05	0.25	0.14	**0.88**
Cl^-	N.D.	0.04	**0.99**	N.D.	0.08
NO_2^-	-0.02	-0.12	0.06	-0.03	**0.92**
NO_3^-	0.13	**0.70**	**0.60**	0.09	0.09
SO_4^{2-}	0.04	**0.66**	**0.63**	-0.28	-0.04
Na^+	-0.18	**0.52**	**0.74**	0.01	0.23
NH_4^+	0.01	**0.89**	-0.02	-0.29	-0.03
K^+	0.06	**0.91**	0.31	-0.01	-0.03
Mg^{2+}	N.D.	0.11	**0.99**	-0.05	0.02
Ca^{2+}	0.02	0.11	**0.98**	-0.04	0.07
Ace	0.14	-0.57	-0.24	0.11	0.25
Fl	**0.60**	-0.42	-0.17	-0.04	0.23
Phe	**0.97**	-0.02	-0.02	0.04	0.01
Ant	**0.96**	0.01	N.D.	0.10	-0.10
Fluo	**0.88**	0.19	-0.02	-0.08	-0.06
Pyr	**0.97**	0.16	0.01	N.D.	-0.11
B[a]A	**0.91**	-0.04	0.05	0.21	0.11
Chry	**0.98**	0.04	N.D.	-0.08	-0.05
B[b]F	**0.92**	0.13	0.04	0.21	-0.11
B[k]F	**0.94**	0.08	-0.07	0.26	-0.06
B[a]F	**0.90**	0.04	-0.02	0.28	-0.07
B[e]P	**0.94**	0.04	-0.02	0.25	-0.08
B[a]P	**0.92**	0.06	0.03	0.27	-0.06
Per	**0.79**	-0.03	0.03	0.43	0.08
Ind	**0.74**	0.01	-0.04	**0.64**	-0.01
B[g,h,i]P	**0.68**	-0.07	-0.02	**0.67**	0.06
D[a,h]A	**0.73**	-0.04	-0.03	**0.51**	-0.07

Cor	0.36	N.D.	-0.04	**0.89**	0.06
D[a,e]P	**0.53**	-0.19	-0.15	**0.59**	0.10
Variance [%]	**43.7**	**24.0**	**10.5**	**6.48**	**4.46**
Estimated source	**Vehicular Exhaust**	**Biomass Burning**	**Sea-salt Aerosols**	**Power plants**	**Industrial Emission**

a Rotation Method: Varimax with Kaiser Normalization.

b Bold loading > 0.50

The concentrations of carbonaceous compositions, WSIS and PAH profiles were performed as the active variables for PCA analysis (see Table 4.4). The result presented 89.1% for the majority of the variance, which described by five principal components (PCs). The result showed 43.7% for the total variance in the PC1. Whereas the PC2 clarified for 24.0% of the total variance, followed by PC3, PC4, and PC5 explain for 10.5%, 6.48%, and 4.46% of the total variance, respectively.

PC1 contains high loading factors of Fl, Phe, Ant, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]F, B[e]P, B[a]P, Per, Ind, B[g,h,i]P, D[a,h]A and D[a,e]P, which can be explained as the results are correlated to the result that showed in the result of HCA. Therefore, the reasonable to explain PC1 might be delegate of pyrogenic sources that discharged from vehicular exhausts, diesel/gasoline engine, road carpeting asphalt, crude oil and tar (Smith and Harrison, 1998; Ravindra et al., 2008; Ahrens and Depree, 2010). Due to those congeners are profoundly related with vehicle exhaust, it is suitable to predicate that vehicle exhaust describe 43.7% of the total variance. While, B[k]F and B[g,h,i]P use as a marker of vehicle emissions (Miguel and Pereira, 1989; Harrison et al., 1996). Whilst B[a]P, B[k]F and B[g,h,i]P are a marker of diesel/gasoline emissions (Ravindra et al., 2008; Teixeira et al., 2013). In agreement with previous studies reported, 3–4 ring PAHs have been related with vehicular exhausts and road dust in urban cities (Zakaria et al., 2002; Boonyatumanond et al., 2007).

PC2 (24.0% of the total variance) was characterized by high loading of TC, OC, NO_3^-, SO_4^{2-}, Na^+, NH_4^+ and K^+. The result is related to biomass burning, which OC, EC and K^+ are assumed to be a tracer for biomass burning, which contain a significant amount of WSIS, such as NH_4^+, K^+, and NO_3^- (Pani et al., 2018). This result is related to the previous studies that conducted the particle in urban area and the major portion of OC released by biomass burning (de la Campa et al., 2009; Pirovano et al., 2015; Pani et al., 2019).

PC3 presented for 10.5% of the total variance, which the high loading of Cl^-, Na^+, SO_4^{2-}, NO_3^-, Mg^{2+} and Ca^{2+}. Thus, the significance of long-range transportation has been related to those components (Chan et al., 1997; Wang and Shooter., 2001), which affected by the plumes of smoke originating from long-range transport from surrounding provinces. This definition is in a good compliance with previous studies that the major elements came from sea salt aerosol, including Cl^-, Na^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} (Putaud et al., 2004; Radhi et al., 2010).

PC4 (6.48% of the total variance) displayed high loading values of Cor, B[g,h,i]P, Ind, D[a,h]A and D[a,e]P, in which Cor was highest correlation for this component (r=0.89). Accordingly, it seems suitable to conclude PC4 might be characteristic of the fuels combustion from power plants because the provinces nearby Bangkok such as Nonthaburi, Chachoengsao, Samut Prakan and Ayutthaya.

The last cluster PC5, (4.46% of the total variance) had high loading of F^- and NO_2^-, which showed a high correlation coefficient (r=86) and (r=89), respectively. Several studies emphasized that the importance of industrial activities as one of the major sources of F^- component in urban atmosphere (Haidouti et al., 1993; Mukherjee et al., 2003). Furthermore, F^- and NO_2^- are a typical pollutant of atmospheric aerosol in Bangkok, which could be from electrolytic aluminum enterprise (Zhou et al., 2018) and waste incineration (Wang et al., 2015) in industrial estate nearby the sampling area.

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Chapter-V

Results & Discussion

Long-Range Transboundary Atmospheric Transport of Polycyclic Aromatic Hydrocarbons, Carbonaceous Compositions, and Water-Soluble Ionic Species in Southern Thailand

Abstract

This study investigated atmospheric particulate matter (PM) with an aerodynamic diameter of <2.5 μm (PM$_{2.5}$) observed at the Prince of Songkla University (Phuket Campus) in southern Thailand. All samples (*n* = 75) were collected using MiniVol^{TM} portable air samplers from March 2017 to February 2018. Carbonaceous aerosol compositions, i.e., organic carbon (OC) and elemental carbon (EC), water-soluble ionic species, and polycyclic aromatic hydrocarbons (PAHs) in the PM$_{2.5}$ samples were identified and quantified. We found that the average PM$_{2.5}$ concentration was 42.26 ± 13.45 μg m^{-3}, the OC/EC ratio was in the range of 2.69–16.9 (mean: 6.05 ± 2.70), and the average concentration of 10 selected ions was 6.91 ± 3.54 μg m^{-3}. The average concentration of SO_4^{2-} was the highest throughout the entire study period (2.33 ± 1.73 μg m^{-3}); the average contribution of SO_4^{2-} to the major ionic components was 34%. Surprisingly, the average concentrations of NO_3^- and NH_4^+ were relatively low. The mean ratio of $[NO_3^-]/[SO_4^{2-}]$ was 0.33 ± 0.24. Strong positive correlation was found between K^+ and both OC and EC (r = 0.90 and r = 0.93, respectively). It is well known that K^+ is a marker of biomass burning (BB), whereas EC is a marker of both BB and fossil fuel combustion. Results showed that BB episodes might play a major role in producing the observed high levels of OC. The relatively high abundance of both B[g,h,i]P and Ind suggests that motor vehicles, petroleum/oil combustion, and industrial waste burning are the primary emission sources of PAHs in the ambient air of Phuket.

Interestingly, principal component analysis (PCA) indicated vehicular exhausts are the main source of carbonaceous aerosol compositions found in the ambient air of Phuket, whereas the contributions of marine aerosols and BB to secondary OC were also important.

Keywords: $PM_{2.5}$, PAHs, Carbonaceous Compositions, Water Soluble Ionic Species, Biomass Burning

5.1. Introduction

Although air pollution is primarily an urban phenomenon, it is an important problem globally. In population centres such as Thailand, large quantities of fuel are consumed in various economic sectors, for e.g., industry (Gocht et al., 2001), transportation (Silva, 2005), and electricity generation (Dung, 1996). Combustion of fossil fuels such as coal and petroleum is responsible for causing the majority of air pollution (Sookkai et al., 2000). Air pollution in the form of dust, especially particulate matter (PM) with an aerodynamic diameter of <2.5 μm ($PM_{2.5}$), is among the most dangerous. This is because it can affect the human respiratory system (Wheeler et al., 2006), exacerbating conditions such as bronchitis, influenza, pneumonia, tuberculosis, emphysema, and asthma, especially in children, the elderly, and people with underlying cardiopulmonary/respiratory diseases (Jinsart et al., 2002).

Carbonaceous aerosols have been studied thoroughly over recent decades because they can affect human health, ecosystems, and the climate system (Shih et al., 2008). Another major concern is that they are persistent organic pollutants that can remain in the environment for long periods (Jones and Voogt, 1999; Dachs and Eisenreich, 2000). Several studies have investigated the presence of carcinogenic and/or mutagenic substances in the atmosphere, derived via gas–particle partitioning, e.g., polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls, the origin of which is incomplete combustion attributable to both natural and anthropogenic sources. These substances, which are classified as semi-volatile compounds, can be released as solid material or vapour that can adhere to the surface of other particles (Smith and Harrison, 1998; Jones and Voogt, 1999; Dachs and Eisenreich, 2000; Schummer et al., 2010). Thus, they can spread from their source via many media, posing a danger to human health and the ecosystem. Therefore, measurement of the concentration of these carbonaceous aerosols is highly important.

In Thailand, information on PAHs, carbonaceous compositions, i.e., organic carbon (OC) and elemental carbon (EC), and water-soluble ionic species (WSIS) in the ambient air of southern parts of the country is rare. Previous study of carbonaceous aerosols in the coastal city of Hat-Yai (southern Thailand) found that aged marine aerosols from long-range transportation and/or particles from biomass burning (BB) made a major contribution to the carbonaceous aerosols measured at the top of a building in the study area (Pongpiachan et al., 2009, 2013b). Therefore, this study selected an observation site at the Prince of Songkla University (Phuket Campus) in southern Thailand to investigate atmospheric $PM_{2.5}$. Phuket is the largest island in Thailand. It is located in the south and encircled by the Andaman Sea. It has long slender shape with north–south orientation. In addition, Phuket has several other large and small satellite islands. Approximately 70% of the land area is mountainous, while the remaining 30% comprises plains. The climate of Phuket is warm and moist throughout the year.

The first unambiguous evidence that the air pollution seen frequently in fine atmospheric particles is caused by human activities became available several decades ago. Comprehension of the composition and major sources of carbonaceous aerosols is important for improving air quality. Therefore, the objective of this study was to determine the characteristics of OC, EC, WSIS, and PAHs in the $PM_{2.5}$ samples obtained at the study site. The analysis focused primarily on the following: (i) characterization of the chemical compounds detected in the $PM_{2.5}$ samples, (ii) statistical analysis of the chemical composition and its relation to source identification, and (iii) statistical source apportionment of the chemical composition, including OC, EC, WSIS, and PAHs.

5.2. Materials and Methods

5.2.1. Air Quality Observatory Sites

The aerosol sampling campaign was undertaken at Building 6 of the Prince of Songkla University (Phuket Campus) in Thailand (Fig. 5.1). Phuket, the largest island in Thailand, is in the south and surrounded by the Andaman Sea. The main island has long slender shape with north–south orientation and it has several other large and small satellite islands. Around 70% of the land area is mountainous, while the remaining 30% comprises plains. The climate of Phuket is warm and moist throughout the year. The MiniVol^{TM} air samplers were installed on the rooftop of Building 6 (4th Floor): 7.89318°N, 98.35209°E (GPS coordinates: 7°53’35.5”N, 98°21’07.5”E). The monitoring campaign was conducted from March 2017 to February 2018.

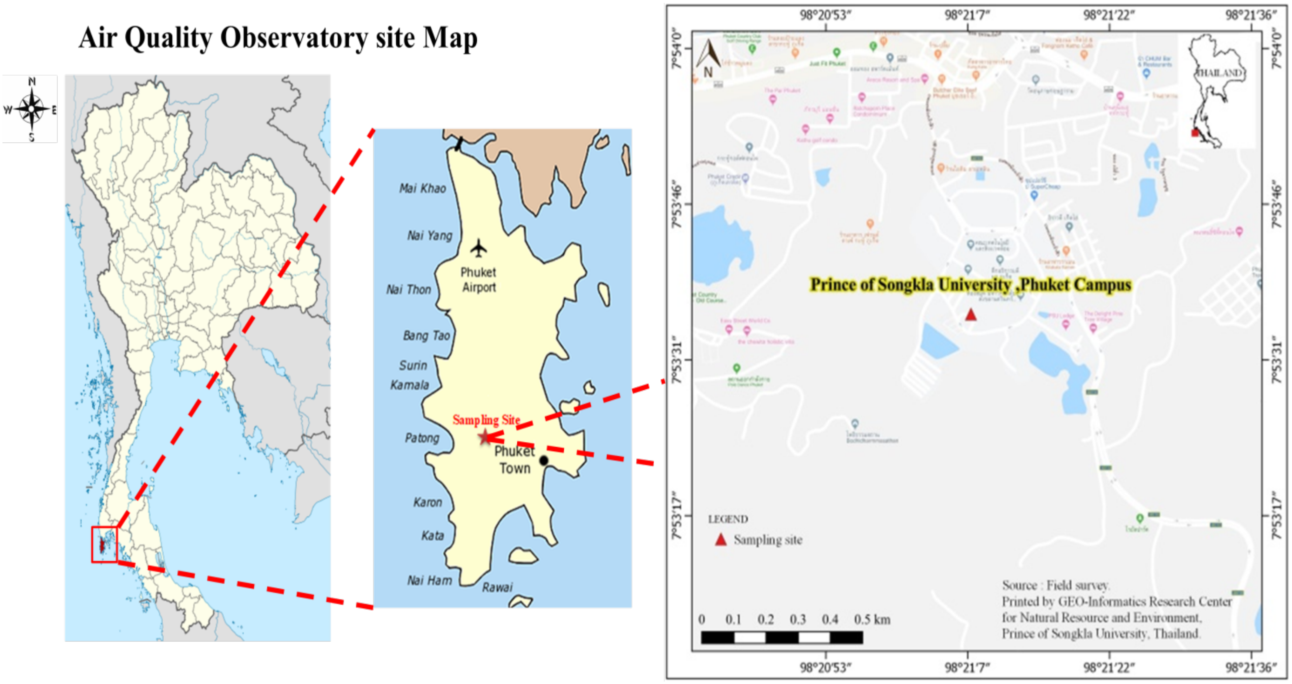

Figure 5.1. Location of the sampling site used in this study

Samples of $PM_{2.5}$ (n = 75) were obtained using MiniVol^{TM} portable air samplers (Airmetrics, USA) with 47-mm quartz filters and a flow rate of 5 L min^{-1}. All samples were collected over 72-h periods. All $PM_{2.5}$ samples were stored carefully in individual petri slide dishes and refrigerated to retain their chemical composition until required for further analysis. All $PM_{2.5}$ filter samples were analysed for PAHs, OC, EC, and WSIS.

5.2.2. Chemical Analysis

Carbonaceous aerosol analyses: organic carbon (OC) and elemental carbon (EC)

The measurements of carbonaceous aerosol compositions including calibration and quality assurance/quality control (QA/QC) processes were performed at the laboratory of the Institute of Earth Environment, Chinese Academy of Science (Xian, China). The protocols adopted were the same as reported previous by Chow et al. (2007a). Normally, the OC content was considered as the sum of individual OC fractions (i.e., OC1 + OC2 + OC3 + OC4) and the EC content was considered as the sum of individual EC fractions (i.e., EC1 + EC2 + EC3 + OP), based on the IMPROVE_A thermal optical reflectance protocol (Chow et al., 2007a; Fung et al., 2002).

Carbonate carbon was determined through assessment of CO_2 acidification from organic samples prior to the normal carbon analysis procedure. Seven temperatures were used for different fractions. The temperature protocol was applied to separate OC and EC in a process similar to the thermal optical reflectance and thermal optical transmittance pyrolysis correction. This protocol produces evaluations of total OC, total EC, and total carbon (TC), monitored by both reflectance and transmittance. For the QA/QC procedures that have been described elsewhere (Cao et al., 2003), the instrument was calibrated daily with known quantities of methane. Replicate analyses were performed for each group for 10 samples and the relative deviation of the replicate analyses was <5% for TC and <10% for both OC and EC.

Water-soluble ionic species (WSIS)

The concentrations of WSIS included five cations (i.e., Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and four anions (i.e., Cl^-, F^-, NO_3^-, and SO_4^{2-}). An ion chromatograph with a separation column was used for the extraction from all $PM_{2.5}$ samples. The QA/QC procedure for this analysis required all glassware to undergo ultrasonic cleaning and oven drying at 450 °C for approximately 6 h. All solvents used in the analysis procedure were pesticide residue grade (Wang et al., 2005).

Polycyclic aromatic hydrocarbons (PAHs)

The concentrations of PAHs in the $PM_{2.5}$ samples were measured using in-injection port thermal desorption coupled with gas chromatography/mass spectrometry, which quantified the concentration of 19 PAHs as non-polar organic compounds. This analytical procedure is similar to the alternative method of traditional solvent extraction followed by gas chromatography/mass spectrometry analysis. The analytical procedures have been described in previous studies (Ho and Yu, 2004; Chow et al., 2007b).

5.2.3. Statistical Analysis

This study used the SPSS System for Windows Version 22 to produce descriptive statistics (minimum, maximum, mean, and standard deviation) of the measured concentrations of PAHs, carbonaceous compositions, and WSIS. We also used PCA for identification of source appointment.

5.3. Results and Discussion

5.3.1. Concentrations of Total Carbon (TC), Organic Carbon (OC), and Elemental Carbon (EC)

The average concentrations of each carbon fraction for OC, EC, TC, and $PM_{2.5}$ in the samples from Phuket are presented in Table 5.1, and the concentrations of OC and EC in each individual sample are shown in Fig. 5.2.

Table 5.1. Concentrations of OC, EC, TC, and $PM_{2.5}$ samples from Phuket, Thailand

Species	**Minimum ($\mu g\ m^{-3}$)**	**Maximum ($\mu g\ m^{-3}$)**	**Mean ± SD ($n = 75$)**
OC1	0.00	0.22	0.04 ± 0.05
OC2	0.22	1.56	0.53 ± 0.23
OC3	0.73	5.34	1.57 ± 0.75
OC4	0.12	3.37	0.71 ± 0.62
OC	1.08	10.90	3.05 ± 1.70
EC1	0.10	3.74	0.70 ± 0.64
EC2	0.00	0.28	0.13 ± 0.06
EC3	0.00	0.00	0.00 ± 0.00
EC	0.09	3.90	0.63 ± 0.58
TC	1.17	14.80	3.67 ± 2.25

$PM_{2.5}$	20.07	91.02	42.26 ± 13.45

Seinfeld and Pandis (2006) reported that the highest carbonaceous fraction of fine atmospheric PM is OC at 70–80%, followed by EC and inorganic carbon at 5%. The average concentrations of carbonaceous chemical components found in our samples are listed in Table 1. It can be seen that of the OC fractions, OC3 was the highest, followed in descending order by OC4, OC2, and OC1. For the EC fractions, EC1 was the highest, followed by EC2 and EC3. In characterizing the chemical composition of aerosols in northern Indochina in March and April 2010, Chuang et al. (2013) found OC3 to be a reasonable tracer of BB, whereas OC2 is known as a tracer of both coal combustion (Chow et al., 2004) and vehicular exhausts (Cheng et al., 2015).

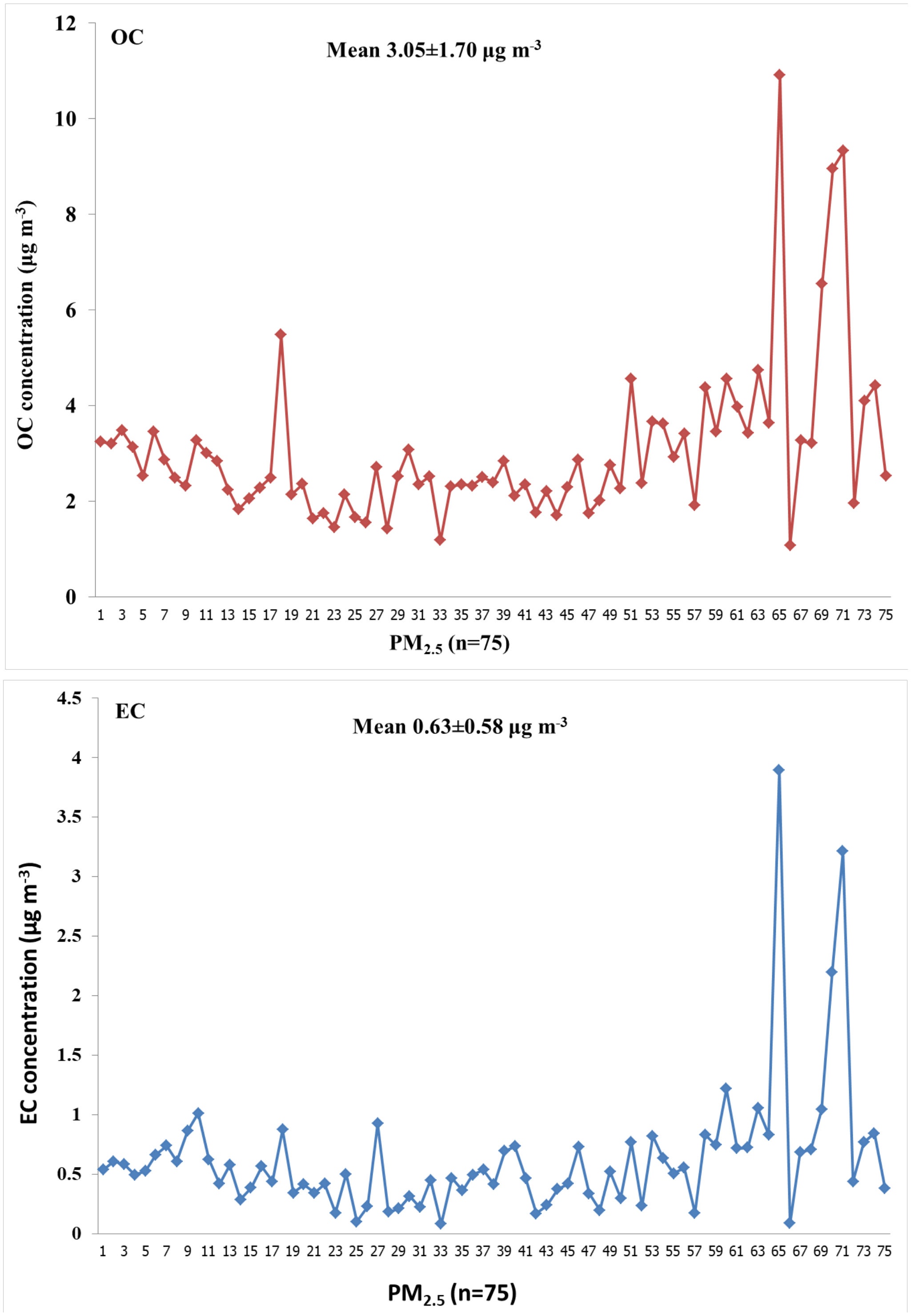

Figure 5.2. Concentrations of organic carbon (OC) and elemental carbon (EC) in individual $PM_{2.5}$ samples collected in Phuket during March 2017 to February 2018

In observations of ambient air throughout an entire year in Phuket, the OC fraction was found to be the major component because it is released directly into the ambient air following incomplete combustion of organic compounds (Jimenez et al., 2008). It can be emitted directly from various sources such as industrial processes and natural occurrences, e.g., BB (primary OC) or it can be formed from gas–particle partitioning in the air (secondary OC: SOC). It is well known that OC can have substantial impact on human health (Mauderly and Chow, 2008). Conversely, the EC fraction was found to be much lower than the OC fraction. As the chemical structure of EC is similar to that of impure graphite, it appears reasonable to assume that vehicular exhausts are a major source of EC. Consequently, the most important sources of EC are fossil fuel combustion and/or BB (Gelencsér, 2004).

The mean values of OC and EC in the $PM_{2.5}$ samples of this study were 3.05 ± 1.70 and 0.63 ± 0.58 $\mu g\ m^{-3}$, respectively. These values are much smaller in comparison with those from other areas. However, the average mean concentrations of OC and EC determined in this study are similar to those reported in autumn and winter in Cape Hedo, Okinawa (Kunwar and Kawamura, 2014). Generally, EC is released from any combustion source and it is usually used as a tracer of primary OC (Turpin and Huntzicker, 1995). Hence, the relationship between OC and EC can be used to estimate the source of carbonaceous particles. The relationship between OC and EC in the $PM_{2.5}$ samples obtained in Phuket in this study is illustrated in Fig. 5.3. The very strong correlation between OC and EC ($r = 0.93$) indicates they have similar sources in winter and spring, as reported by Kunwar and Kawamura (2014).

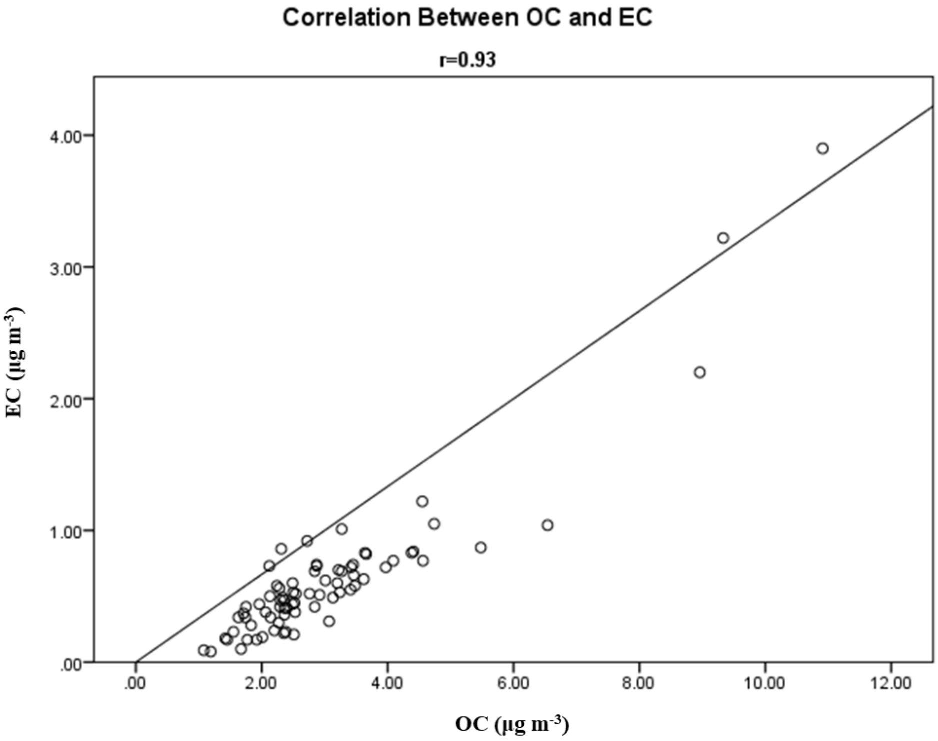

Figure 5.3. Correlation between organic carbon (OC) and elemental carbon (EC) in the $PM_{2.5}$ samples collected in Phuket during March 2017 to February 2018

5.3.2. OC/EC Ratios and Secondary Organic Carbon (SOC) Contributions

OC/EC ratios

Carbonaceous compounds represent a significant fraction of atmospheric aerosols, accounting for 20–35% of PM_{10} and 20–45% of $PM_{2.5}$ (Yttri et al., 2007; Putaud et al., 2010). The OC/EC ratio is applied frequently to explain the emission sources of carbonaceous aerosol compounds (Han et al., 2007, 2009b). The OC/EC ratios determined in this study were in the range of 2.69–16.9 with a mean value of 6.05 ± 2.70 (Fig. 5.4).

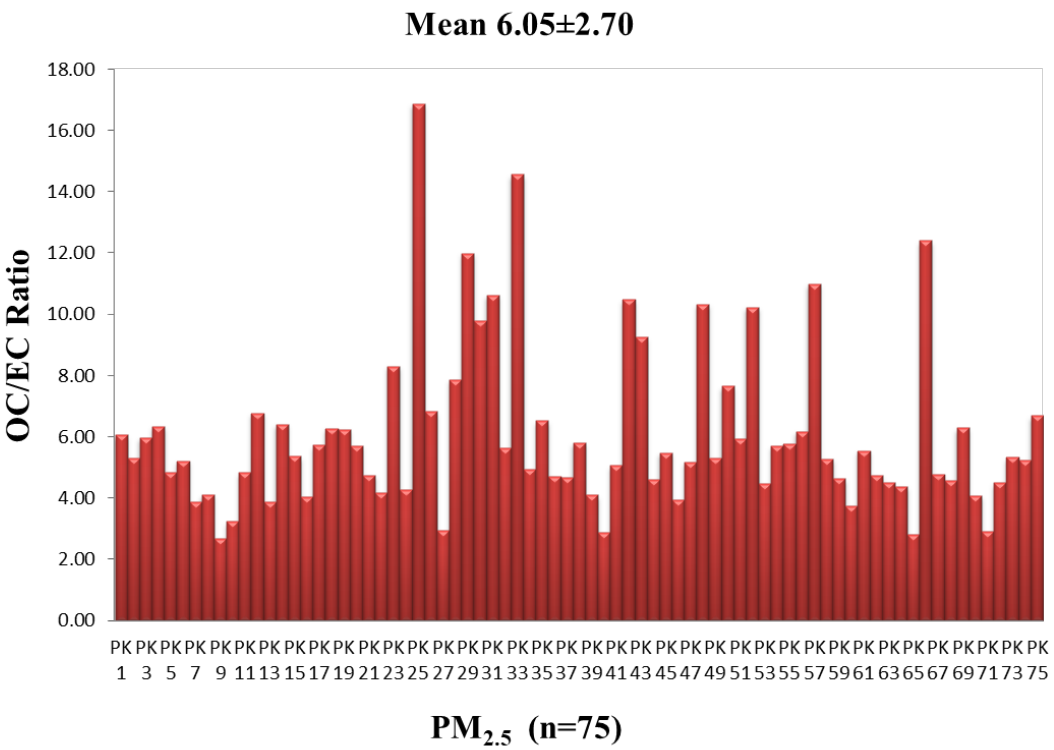

Figure 5.4. The OC/EC ratios of the 75 samples obtained in Phuket (Thailand) during March 2017 to February 2018

The value of the OC/EC ratio can indicate the primary source of pollution (Wang et al., 2015). Several previous studies have investigated carbonaceous PM in northern and central parts of Thailand (Chaiyo et al., 2011,13; Duangkaew et al., 2013; Pongpiachan et al., 2013a,b; 2014a,b; 2017; Tsai et al., 2013; Chaiyo and Garivait, 2014; Janta and Chantara, 2017; Pani et al., 2018; Thepnuan et al., 2019). However, the availability of data from southern Thailand is limited, especially from Phuket. This knowledge gap is of concern because Phuket is an important economic area; therefore, it is vital that the regional air pollution be investigated for PM_{10}, $PM_{2.5}$, and $PM_{2.5}$-bound carbonaceous compounds and PAHs.

The chemical characteristics of carbonaceous aerosols and PAHs of PM_{10} in the city of Hat-Yai in southern Thailand have been studied by Pongpiachan et al. (2014). Their study suggested that the persistence of high OC/EC ratios in December 2007 could have been attributable to contributions from marine aerosols, BB, and/or long-range transportation. The OC/EC ratio can be used to estimate the primary sources of pollution. Several studies on carbonaceous PM in different parts of the world have reported that high OC/EC ratios are related to SOC (Chow et al., 1993; Turpin and Huntzicker, 1995; Wang et al., 2015). Carbonaceous aerosols with OC/EC values >2 can be considered to contain significant quantities of SOC. In this study, the range of OC/EC ratios was 2.69–16.9 (mean: 6.05 ± 2.70). However, a high value of the OC/EC ratio (12) was reported by Cao et al. (2005) in aerosols derived from residential coal combustion. Therefore, the wide range of OC/EC ratios found in this study indicates that the emission sources of the $PM_{2.5}$ in the samples from Phuket were disparate in comparison with previous studies. The types of major pollution were found attributable to compound pollution under the combined effects of BB (Lee et al., 2016), SOC (Boreddy et al., 2018b), and cooking emissions (See and Balasubramanian. 2008). However, the concentrations of carbonaceous compounds vary inter-regionally in relation to local emissions and weather (Heald et al., 2008).

Secondary organic carbon (SOC) contributions

The measurement of SOC is moderately difficult because it does not have a direct analytical method. Many studies have used a widely accepted EC tracer method to measure SOC. Using this method, the contribution of SOC can be calculated based on the minimum values of OC/EC ratios, where EC is used as a measure of primary OC (Castro et al., 1999). In this study, SOC was estimated using the following equation:

$$SOC = OC_{total} - EC \times (OC/EC)_{pri} \qquad (1)$$

where OC_{total} represents the total OC and $(OC/EC)_{pri}$ is the mean of the three lowest OC/EC ratios.

The mean of the three lowest OC/EC ratios (2.79) was applied in this study to estimate the SOC content of the $PM_{2.5}$ samples from Phuket. Based on this technique, it was determined that the annual mean value of SOC was 1.30 ± 1.63 $\mu g\ m^{-3}$ and the highest value was 2.82 $\mu g\ m^{-3}$. The percentage contribution of SOC to OC_{total} was 42.6% in this study. This value is 1.4 times lower than the value (59.2%) detected in Okinawa, Japan (Kunwar and Kawamura, 2014) and 1.5 times lower than both the value (67.8%) reported for Hat-Yai, Thailand (Pongpiachan et al., 2014) and the value (65%) found in Claremont, USA (Na et al., 2004). Conversely, our value is 2.5 times higher than that observed in Birmingham, United Kingdom (Castro et al., 1999). Our result is close to that found by Li et al. (2009) in their study conducted at a coastal site (37.7%), and similar to values observed in northeastern China (42%) by Zhang et al. (2012) and in Kaohsiung in Taiwan (40%) by Lin and Tai (2001). Despite the relatively high OC/EC ratio (6.05 ± 2.70) observed in our study in Phuket, the SOC content (1.30 ± 1.63 μg m^{-3}) is relatively low, which indicates that marine aerosols in the Phuket region have comparatively low EC content.

5.3.3. Atmospheric Concentrations of Water-Soluble Ionic Species (WSIS) and PAHs in $PM_{2.5}$

Given that Phuket is the largest island in Thailand, it was considered important to examine the impact of marine aerosols on the characterization of carbonaceous compositions. The chemical characteristics of WSIS have been studied thoroughly in different areas of the world. Several studies have reported that SO_4^{2-} and Cl^- are the main contributors to WSIS found in marine aerosols, whereas NH_4^+ and K^+ are the main contributors to WSIS in aerosols attributable to BB (Kocaka et al., 2007; Park and Cho, 2011).

The individual and average concentrations of 10 selected ions (SO_4^{2-}, Na^+, Ca^{2+}, Cl^-, NO_3^-, NO_2^-, NH_4^+, K^+, Mg^{2+} and F^-) considered in this study are presented in Table 5.2.

Table 5.2. Concentrations of water-soluble ionic species (WSIS) observed in the $PM_{2.5}$ samples from Phuket, Thailand

Ionic Species	Mean (μg m^{-3})	Min. (μg m^{-3})	Max. (μg m^{-3})	% mass of total ion content
F^-	0.09 ± 0.01	0.07	0.12	1
Cl^-	0.53 ± 0.28	0.32	2.47	8

NO_2^-	0.30 ± 0.19	0.00	0.73	4
NO_3^-	0.53 ± 0.21	0.00	1.62	8
SO_4^{2-}	2.33 ± 1.73	0.33	9.21	34
Na^+	1.47 ± 0.39	0.65	3.04	21
NH_4^+	0.29 ± 0.32	0.00	2.38	4
K^+	0.28 ± 0.24	0.00	1.58	4
Mg^{2+}	0.13 ± 0.03	0.06	0.24	2
Ca^{2+}	0.96 ± 0.14	0.66	1.37	14
Total	6.91 ± 3.54	-	-	-

Several previous studies have used diagnostic ratios to analyse the sources of marine aerosols and non-marine aerosols or non-sea-salt for WSIS (Karthikeyan and Balasubramanian, 2006). Such work has determined that the sources of K^+, SO_4^{2-}, and Ca^{2+} are not solely from marine aerosols (Wang et al., 2001). Therefore, the contribution of each of these ions from non-sea-salt sources was calculated using the following equations (Hedge et al., 2007; George et al., 2008):

$$\text{nss-}SO_4^{2-} = (SO_4^{2-}) - 0.037*(Na^+) \qquad (2)$$

$$\text{nss-}Ca^{2+} = (Ca^{2+}) - 0.038*(Na^+) \qquad (3)$$

$$\text{nss-}K^+ = (K^+) - 0.25*(Na^+) \qquad (4)$$

*Note, nss-SO_4^{2-}, nss-Ca^{2+}, and (nss-K^+ can be used in the formulas above, assuming that marine aerosols are the same as sea-salt in terms of chemical composition. Meanwhile, Na^+ is used as a marker element to determine whether oceanic or continental concentrations have been calculated (George et al., 2008).

Based on the OC/EC ratios in this study, long-range atmospheric transport of BB plumes from nearby countries could represent one source. In this region, BB is a widespread activity and it is known that PM is transported from Indonesia (Southeast Asia) into southern Thailand (Phairuang et al., 2020). The OC/EC ratios in this study were in the range of 2.69–16.88. Moreover, strong correlation ($r = 0.80$) was found between nss-K^+ and OC, which was found related to long-range atmospheric transport and the influence of BB on organic aerosols during the study period.

Several studies have reported that Cl^- and SO_4^{2-} are the main components of WSIS found in marine aerosols, while K^+ and NH_4^+ represent the major contributors to other particles derived from BB and agricultural waste burning (Park and Cho, 2011; Pongpiachan et al., 2014). Generally, NO_3^- is considered a marker of particles derived from vehicular emissions and fossil fuel combustion. Therefore, based on the binary ratios between marine and BB components of WSIS and traffic emissions, NO_3^- can be used to identify aerosol types.

Normally, SO_4^{2-}, NO_3^-, and NH_4^+ are the major fractions in the form of secondary inorganic aerosols. In this study, they accounted for 46.0% of total ionic species concentrations. The average SO_4^{2-} concentration in Phuket was the highest throughout the entire study period (2.33 ± 1.73 μg m^{-3}); surprisingly, the average concentrations of NO_3^- and NH_4^+ were relatively low at 0.53 ± 0.21 and 0.29 ± 0.32 μg m^{-3}, respectively.

For the classification, $[NO_3^-]/[SO_4^{2-}]$ ratios were applied carefully to identify the incidence of stationary sources (e.g., boilers) and mobile sources (e.g., vehicular exhausts) of nitrogen and sulphur. They are generally formed via atmospheric reactions of their gaseous phase, e.g., NO_x and SO_2. Normally, SO_2 is released via coal combustion, whilst NO_x results from any type of combustion, e.g., coal power plants and vehicular emissions (Liu et al., 2011; Mkoma et al., 2014). Several previous studies have recommended the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ can be applied to estimate the relative contribution of stationary sources (e.g., BB, coal combustion) versus mobile sources (e.g., vehicular emissions) in aerosols (Javid et al., 2015; Park et al., 2015; Deng et al., 2016; Huang et al., 2016). A high $[NO_3^-]/[SO_4^{2-}]$ ratio was found in a region with high levels of vehicular emissions (Li et al., 2009). The mean $[NO_3^-]/[SO_4^{2-}]$ ratio found during this study was

0.33 ± 0.24. It is lower than that found in other areas in summer in China, e.g., Beijing (0.83), Tianjin (0.71), and Shijiazhuan (0.56) (Dao et al., 2014) because Phuket is in a tropical region. The high temperatures in Phuket modulate particulate nitrate into the gaseous phase, which reduces the $[NO_3^-]/[SO_4^{2-}]$ ratio. However, the ratio of 0.3–0.5 found in this study is also lower than that usually found in China because of the widespread use of sulphur-containing coal by the Chinese (Yao et al., 2002).

The ions SO_4^{2-} and NH_4^+ are secondary ions that have a complex reaction in that NH_4^+ responds rapidly with SO_4^{2-} to the constant form of ammonium salts (Lai et al., 2007; Li et al., 2012; Wang et al., 2013). The gas/aerosol distribution of precursor gases in terms of temperature and humidity affect the reaction of NH_4^+ and NO_3^- (Han et al., 2014). Generally, SO_4^{2-} is influenced by anthropogenic sources in industrial areas. The concentration of SO_4^{2-} was significantly higher than that of Na^+ and Cl^-, whereas nss-SO_4^{2-} was the primary species for acid replacement (Zhang et al., 2010). Similar to other ions with anthropogenic sources (e.g., NO_3^-), the correlation with those of nss-SO_4^{2-} was reasonable (Zhang et al., 2010).

In general, Na^+ and Cl^- are the sea salt ions that form the largest fractions in marine aerosols. In this study, the highest concentrations of Na^+ and Cl^- were 1.47 ± 0.39 and 0.53 ± 0.28 $\mu g\ m^{-3}$, which accounted for 21.0% and 8.0% of the total ionic species, respectively. For marine aerosols, Zhang et al. (2010) reported that sea salt aerosols (i.e., NaCl) can emit HCl via exchange with sulphuric acid and nitric acid, which results in a shortage of Cl^- relative to Na^+. The annual average equivalent ratios of Cl^-/Na^+ in the aerosols from Phuket were 3.4 and 3.2 times lower than those on Yongxing Island and those of seawater, respectively (see Table 5.3). This assumes that Cl^- enrichment had a high-temperature pyrogenic source, e.g., vehicular exhausts, power plants, and BB (Stogiannidis and Laane, 2015)

Table 5.3. Comparison of equivalent ratios of ionic species in aerosols observed in Phuket, on Yongxing Island (Xiao et al., 2017), and those in seawater (Keene et al., 1986)

Ion ratios	**Phuket Island**	**Yongxing Island**	**Seawater**
Cl^-/Na^+	0.37	1.25	1.17
Mg^{2+}/Na^+	0.09	0.21	0.22
K^+/Na^+	0.19	0.048	0.021
Ca^{2+}/Na^+	0.68	0.62	0.044
SO_4^{2-}/Na^+	1.54	0.66	0.12
nss-SO_4^{2-}/Na^+	1.51	0.54	-
NO_3^-/Na^+	0.37	0.18	-
NH_4^+/Na^+	0.20	0.022	-
NO_3^-/nss-SO_4^{2-}	0.35	0.34	-
NH_4^+/nss-Ca^{2+}	0.33	0.038	-

Correlations of chemical composition of $PM_{2.5}$ and its relation to source identification

Some ions in carbonaceous aerosol composition such as K^+, SO_4^{2-}, and Ca^{2+} have multiple sources, e.g., ocean and land surfaces. Additionally, nss-SO_4^{2-} in the atmosphere can be derived from various sources. It originates from the combustion of fossil fuels such as coal, oil, and natural gas (Kunwar and Kawamura, 2014). In Phuket, we found the highest concentrations of carbonaceous aerosols found in OC and nss-SO_4^{2-} were 3.05 and 2.28 μg m^{-3}, respectively. Several previous studies reported that SO_4^{2-} and Cl^- are the principal supporters of WSIS normally found in marine aerosols, whereas K^+ and NH_4^+ are the primary supporters of particles initiated from BB and agricultural waste burning (Matsumoto et al., 1998; Kocaka et al., 2007; Park and Cho, 2011; Pongpiachan et al., 2014).The correlations of OC, EC, and WSIS found in this study are shown in Table 5.4. The results showed strong correlation between K^+ and both OC ($r = 0.90$) and EC ($r = 0.93$). It is well known that K^+ is a marker of BB (Kundu et al., 2010), whereas EC is a marker of incomplete combustion of biomass and/or fossil fuel. We also found strong correlation between nss-K^+ and both EC ($r = 0.86$) and OC (0.80); therefore, BB episodes might also play a major role in generating the higher OC concentrations. Previous analysis of satellite imagery revealed evidence of frequent BB episodes in southern Thailand, e.g., in preparation for agriculture, agricultural produce burning, and forest fires.

Table 5.4. Pearson correlation analysis of OC, EC, and WSIS in $PM_{2.5}$ samples obtained from Phuket during March 2017 to February 2018

Correlation coefficients (r) of Carbonaceous Compositions in $PM_{2.5}$ from Phuket, Thailand.

	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	nss-SO_4^{2-}	nss-Ca^{2+}	nss-K^+	OC	EC
F^-	1														
Cl^-	0.13	1													
NO_2^-	.24*	0.003	1												
NO_3^-	0.17	0.15	.51**	1											
SO_4^{2-}	-0.16	-0.07	-0.02	.55**	1										
Na^+	-0.01	.58**	-0.05	.4**	.61**	1									
NH_4^+	0.07	-0.11	0.2	.67**	**.73****	.27*	1								
K^+	-0.05	-0.08	0.14	.50**	**.79****	.39**	**.81****	1							
Mg^{2+}	0.13	.33**	0.03	.47**	.46**	**.71****	.37**	.32**	1						
Ca^{2+}	0.001	0.15	0.02	.34**	**.71****	.60**	.52**	.65**	.50**	1					
nss-SO_4^{2-}	-0.16	-0.08	-0.02	.55**	1.0**	.61**	**.73****	**.79****	.46**	**.71****	1				
nss-Ca^{2+}	0.006	0.1	0.03	.32**	.69**	.53**	.53**	.65**	.45**	1.0**	.69**	1			
nss-K^+	-0.04	-0.35	0.17	.37**	.58**	-0.02	**.76****	**.91****	0.03	.44**	.59**	.47**	1		
OC	-0.07	-0.12	0.06	.41**	**.73****	.40**	**.72****	**.90****	.27*	.59**	**.73****	.58**	**.80****	1	
EC	-0.04	-0.15	0.1	.46**	**.77****	.36**	**.78****	**.93****	.25*	.58**	**.77****	.57**	**.86****	**.93****	1

t test is $<$ 0.01 for the correlation where r is is $>$ 0.70

Among the major ions measured in marine aerosols in this study, the concentration of NH_4^+ was low. It might mean that little ammonia is transported to Phuket; however, surprisingly, NH_4^+ was strongly correlated with K^+ (r = 0.81). It is assumed that one effect of BB was significant enrichment of OC in $PM_{2.5}$. Previous studies related that fertilizer use as well as agriculture waste and related domestic activities are sources of gaseous ammonia emissions (Thepanondh et al., 2005). Reasonable correlation was found between Mg^{2+} and Na^+ (r = 0.71) in our Phuket samples. Moreover, the ratio of Mg^{2+} to Na^+ was 0.09, which is 2.3 and 2.4 times lower in comparison with the values from Yongxing Island and of seawater, suggesting that the main source of Mg^{2+} might be airborne dust rather than sea salt aerosols (Goddard et al., 2007).

Air mass back trajectories

To elucidate potential transport pathways and potential source regions of the aerosols sampled in this study, we applied the Hybrid Single-Particle Lagrangian Integrated Trajectory model of the Air Resources Laboratory of the National Oceanic and Atmospheric Administration. This model has been used for similar purposes in many previous studies (Tiwari et al., 2010; Zhao et al., 2011; Chen et al., 2015; Cong et al., 2015). The transport pathways of air masses reaching Phuket are shown in Fig. 5.5. It can be seen that the majority of air masses during March–May (Fig. 5.5A) and June–August (Fig. 5.5B) originate over the sea. Of the air masses that reach Phuket during March–May, 10% pass over northern Sumatra. Hence, these air masses might carry aerosols associated with BB, forest fires, and peat fires in Kalimantan and Sumatra in Indonesia (See et al., 2007). During September–November (Fig. 5.5C), a significant proportion (33%) of air masses originates from areas to the northeast of Phuket, e.g., Cambodia, Laos, and Vietnam. From December 2017 to February 2018 (Fig. 5.5D), all the air masses that passed over Phuket also passed over Cambodia, Laos, and China. Thus, these air masses might have contained pollutants released through BB, agricultural waste burning, fossil fuel combustion, and vehicular exhausts.

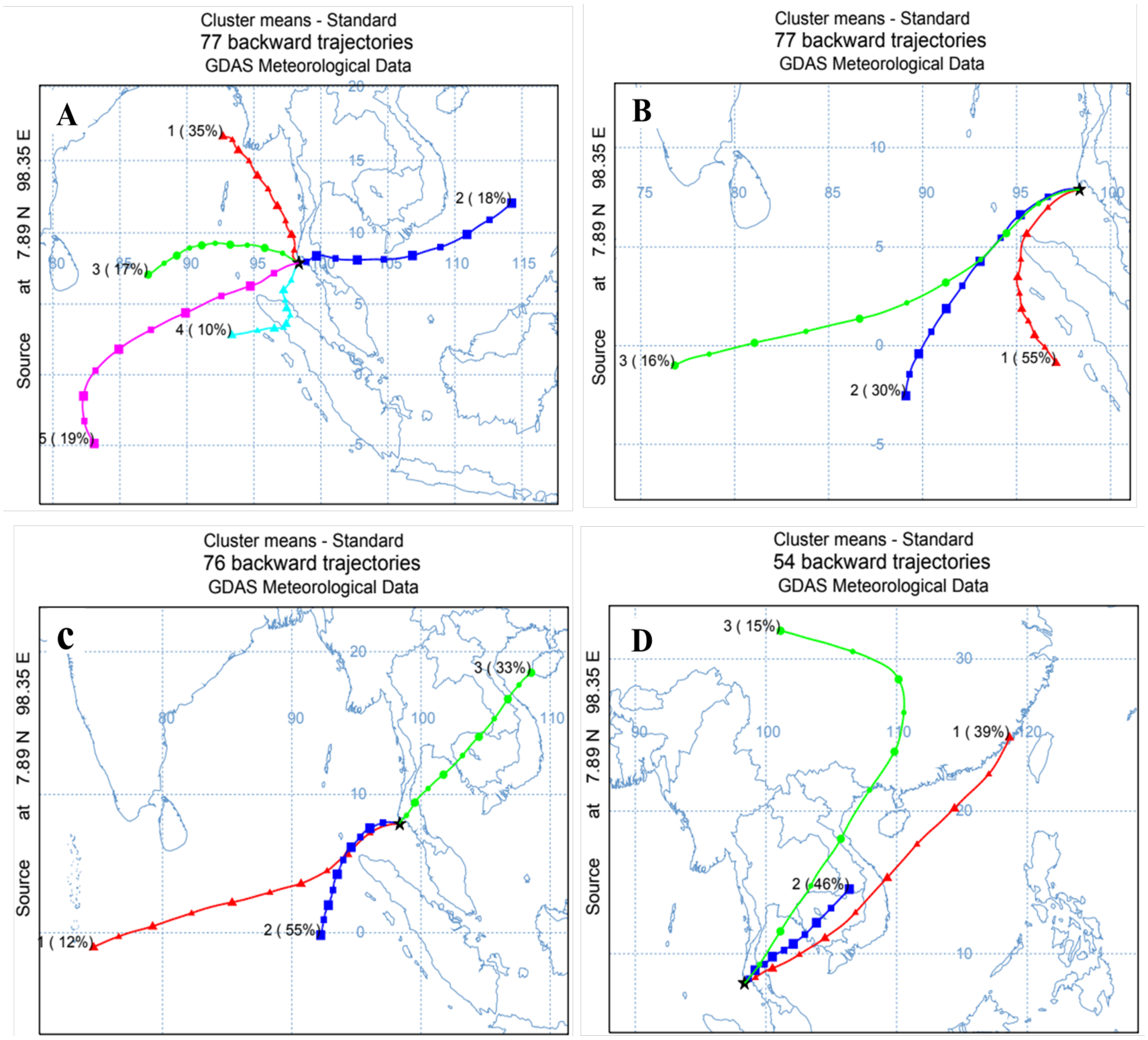

Figure 5.5. Air mass back trajectories during March 2017 to February 2018 in Phuket, Thailand: (A) March–May 2017, (B) June–August 2017, (C) September–November 2017, and (D) December 2017 to February 2018

Concentrations of polycyclic aromatic hydrocarbons (PAHs)

The concentrations of PAHs are summarized in Table 5.5. The total concentration of all 19 PAHs was 0.3780 ± 0.3480 µg m^{-3}. The values determined in this study are lower than those measured in other areas of Thailand such as Chiang-Mai and Bangkok, which are known as heavily polluted areas (Pongpiachan, 2013a,b; Pongpiachan et al., 2014a,b).

Table 5.5. Summary of PAH concentrations in Phuket, Thailand

PAH (μg m^{-3})	Mean	SD	Min.	Max.
Ace	0.0140	0.0096	0.0015	0.0507
Fl	0.0112	0.0079	0.0082	0.0270
Phe	0.0409	0.0411	0.0261	0.0711
Ant	0.0067	0.0045	0.0059	0.0160
Fluo	0.0120	0.0120	0.0070	0.0221
Pyr	0.0110	0.0127	0.0062	0.0160
B[a]A	0.0340	0.0163	0.0206	0.0581
Chry	0.0067	0.0070	0.0028	0.0099
B[b]F	0.0239	0.0220	0.0228	0.0464
B[k]F	0.0238	0.0229	0.0086	0.0340
B[a]F	0.0032	0.0030	0.0025	0.0057
B[e]P	0.0144	0.0134	0.0056	0.0169
B[a]P	0.0174	0.0190	0.0072	0.0224
Per	0.0048	0.0058	0.0029	0.0061
Ind	0.0507	0.0500	0.0359	0.0652
B[g,h,i]P	0.0575	0.0590	0.0348	0.0709
D[a,h]A	0.0133	0.0118	0.0243	0.0032
Cor	0.0239	0.0208	0.0185	0.0356
D[a,e]P	0.0085	0.0091	0.0069	0.0129
ΣPAHs*	0.3780	0.3480	-	-

*ΣPAHs is the sum of Ace, Fl, Phe, Ant, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]F, B[e]P, B[a]P, Per, Ind, B[g,h,i]P, D[a,h]A, Cor, and D[a,e]P

Several previous studies have investigated the environmental cycle of PAHs in different environmental situations in Thailand (Pongpiachan, 2013a,b; Pongpiachan et al., 2014, 2015a). In northern Thailand, BB, forest fires, and agricultural waste burning during winter emit large quantities of PM into the atmosphere, especially ultra-fine particles that include PM$_{2.5}$-bound PAHs. In central Thailand, vehicular emissions represent a major contributor to atmospheric PM. However, in southern Thailand, especially Phuket, the limited availability of PAH data makes it difficult to identify the sources of the pollution emitted into the atmosphere.

The concentrations of the individual PAHs in the PM$_{2.5}$ samples obtained in Phuket during March 2017 to February 2018 decreased in the following order: B[g,h,i]P > Ind > Phe > B[a]A > Cor > B[b]F > B[k]F > B[a]P > B[e]P > Ace > D[a,h]A > Fluo > Fl > Pyr > D[a,e]P > Chry > Ant > Per > B[a]F. Of the 16 priority PAHs identified by the United States Environmental Protection

Agency, 9 are emitted via combustion processes such as those involving coal, diesel, and petroleum. Ravindra et al. (2008) reported that Flu, Pry, B[a]A, Chry, B[b]F, B[k]F, B[a]P, B[g,h,i]P, and Ind are combustion PAHs. The ratios of the concentrations of these combustion PAHs have been analysed in many studies to identify the sources of the PAHs in aerosols (Manoli et al., 2004). In this study, high abundances of B[g,h,i]P and Ind were detected, indicating that motor vehicles, petroleum/oil combustion, and industrial waste burning are emission sources of the PAHs found in the ambient air of Phuket (Zhou et al., 1999; Ravindra et al., 2008).

5.3.4. Principal Component Analysis (PCA)

We used PCA to identify potential sources of the carbonaceous aerosol compositions of the $PM_{2.5}$ samples (OC, EC, WSIS, and PAHs). The PCA method is a multivariate procedure that links multivariate data reduction by transforming the data into rectangular components. Hence, PCA reduces multidimensional data into smaller dimensions (Wold et al., 1987). The strong correlation between nss-K^+ and both OC and EC, discussed in section 3.3, demonstrates that BB is the main contributor to carbonaceous aerosols. Moreover, the relatively high abundances of B[g,h,i]P and Ind suggest that vehicular exhausts should be investigated as a potential major emission source of PAHs in the southern region of Thailand. In this section, source identification coupled with quantitative source apportionment of targeted chemical species is considered using PCA.

In this study, the concentrations of OC, EC, WSIS, and 19 individual PAHs from 75 samples were collected as active variables. The majority of the variance (82.8%) of the scaled data was explained by five eigenvectors/principal components (PCs) (Table 5.6). The first PC (PC1) accounts for 55.5% of the total variance, while the second PC (PC2) explains 10.9% of the total variance, followed by PC3–PC5 that describe 10.6%, 5.2%, and 3.7% of the total variance, respectively.

Table 5.6. Rotated component matrix[a] of carbonaceous compounds, WSIS, and 19 individual PAHs in the $PM_{2.5}$ samples from Phuket, Thailand

Compositions	**Principal Component (PC)**				
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
TC	0.423	**0.854**	0.139	0.033	−0.005
OC	0.441	**0.824**	0.157	0.041	−0.023
EC	0.345	**0.895**	0.080	0.007	0.050
F^-	−0.225	−0.002	−0.038	0.052	**0.618**
Cl^-	−0.050	−0.218	−0.015	**0.810**	0.060
NO_2^-	0.229	−0.050	−0.014	−0.055	**0.774**
NO_3^-	0.191	0.387	0.215	0.284	**0.694**
SO_4^{2-}	0.315	**0.754**	0.198	0.297	−0.020
Na^+	0.155	0.308	0.101	**0.883**	−0.043
NH_4^+	0.312	**0.734**	0.265	0.022	0.345
K^+	0.424	**0.845**	0.127	0.090	0.077
Mg^{2+}	−0.013	0.299	0.154	**0.718**	0.211
Ca^{2+}	0.130	**0.625**	0.291	0.452	−0.071
Ace	0.259	0.092	**0.838**	0.053	0.011
Fl	0.119	0.486	**0.663**	0.017	0.287
Phe	0.408	0.478	**0.614**	0.075	0.212
Ant	**0.623**	0.336	**0.595**	0.079	0.069
Fluo	**0.795**	0.465	0.324	0.030	0.041
Pyr	**0.850**	0.436	0.218	0.014	0.046
B[a]A	0.257	0.187	**0.780**	0.178	−0.127
Chry	**0.774**	**0.571**	0.202	0.015	0.026
B[b]F	**0.886**	0.322	0.171	−0.013	0.014
B[k]F	**0.835**	0.379	0.176	0.018	−0.021
B[a]F	**0.852**	0.290	0.233	0.007	0.114
B[e]P	**0.893**	0.328	0.231	0.032	0.008
B[a]P	**0.849**	0.399	0.244	0.061	0.015
Per	0.373	−0.021	0.069	0.000	−0.208
Ind	**0.936**	0.255	0.133	0.047	−0.005
B[g,h,i]P	**0.946**	0.200	0.149	0.050	−0.005
D[a,h]A	**0.874**	0.109	0.069	0.057	0.031
Cor	**0.938**	0.163	0.090	0.037	0.018
D[a,e]P	**0.761**	0.095	0.045	0.099	−0.046
Variance [%]	**55.5**	**10.9**	**6.1**	**5.2**	**5.1**
Estimated source	**Vehicular Exhausts**	**Biomass Burning**	**Diesel Emissions**	**Sea Salt Aerosols**	**Industrial Emissions**

^{a}Rotation Method: Varimax with Kaiser Normalization.
Bold: loading > 0.5

In accounting for 55.5% of the total variance, PC1 showed high loading of B[g,h,i]P, Cor, Ind, B[e]P, B[b]F, D[a,h]A, B[a]F, Pyr, B[a]P, B[k]F, Fluo, Chry, D[a,e]P, and Ant with corresponding correlation coefficients of 0.946, 0.938, 0.936, 0.893, 0.886, 0.874, 0.852, 0.850, 0.849, 0.835, 0.795, 0.774 0.761, and 0.623, respectively. Anthropogenic activity is concentrated in urban areas; therefore, these positive loadings in PC1 could be attributed to anthropogenic activities involving combustion of coal, diesel, and petroleum. In particular, the high levels of molecular 4–6 ring PAHs found in PC1 could be related to vehicular exhausts (Miguel and Pereira, 1989; Harrison et al., 1996) and/or gasoline vehicles (Schauer et al., 2002, Teixeira et al., 2013).

Significant correlations of EC, TC, K^+, OC, SO_4^{2-}, NH_4^+, Ca^{2+}, and Chry were found in PC2 with correlation coefficients of 0.895, 0.854, 0.845, 0.824, 0.754, 0.734, 0.625, and 0.571, respectively, accounting for 10.9% of the total variance. It is related to biomass burning coupled with a high loading on OC, EC and WSIS which K^+ is a marker of biomass burning which generated from biomass burning (Lee et al., 2016; Pani et al., 2018). However, OC and EC can be related to biomass burning as well (Mkoma et al., 2013).

As illustrated in Table 5.6, PC3 represented 6.1% of the total variance. Several studies reported that Phe and Ant could be used as geochemical tracers of PM released from diesel engine exhausts and coal combustion (Fang et al., 2006). Findings of a previous study that analysed air samples collected at the Central Bus Station of Londrina (Brazil) suggested that PAH congeners with two and three rings were responsible by 90.2% of the total PAHs (Tavares Jr. et al., 2004). In this study, Phe exhibited the highest atmospheric concentrations with an average value of 0.0409 ± 0.0411 $\mu g\ m^{-3}$.

PC4 represented 5.2% of the total variance. The comparatively high loadings of Na^+ (r = 0.883), Cl^- (r = 0.810), and Mg^{2+} (r = 0.718) underline the importance of marine aerosols, which can be attributed to long-range transportation across the ocean from nearby countries (Chan et al., 1997; Wang and Shooter, 2001).

PC5 represented 5.1% of the total variance. Moderately high loadings of NO_2^- (r = 0.774) and NO_3^- (r = 0.694) were detected together with F^- (r = 0.618). Over recent decades, numerous studies have underlined the importance of industrial activities as one of the major sources of particulate F^- in the urban atmosphere (Haidouti et al., 1993; Lovelock, 1971; Mukherjee et al., 2003). For instance, hydrofluoric acid is used widely in the manufacture of chemicals and plastics and in laundries (WHO, 2000). The relatively low percentage contribution of industrial emissions was found in reasonable accord with the fact that the factories in Phuket account for only 0.31% of total number of factories in Thailand, based on a statistical survey conducted by the Department of Industrial Works of the Ministry of Industry in 2019. Consequently, it appears plausible that "industrial emissions" represented by PC5 account for only 5.1% of the total variance.

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Chapter-VI

Results & Discussion

Black carbon, char, soot and polycyclic aromatic compounds records in northwestern Thailand: connections to climate change and human activities

6.1. Introduction

Black carbon (BC) is a kind of particle with highly refractory characteristics uniquely originating from incomplete combustion of biomass vegetations and fossil fuels [1, 2]. It is ubiquitous in the environment including the atmosphere, soil, sediments, ice cores, and waters due to the transport by the atmosphere and riverine. BC has received extensive attentions in recent decades because as a unique light-absorbing aerosol it has an important role in the Earth's climate system [3, 4]. Especially, in atmosphere science BC is regarded as the specific part of aerosol with a strongly visible light-absorbing property [3], that is, soot, and for the weak light-absorbing part it is regarded as brown carbon [5]. However, this was not supported by the present BC aerosol measurement [6] since the most popular methods such as the thermal optical [7] and optical [8] methods such as the athelometer are not based on its strongly light absorbing characteristics at different visible wavelengths. These methods very likely report BC concentrations far beyond the soot part but including char part [6, 9]. Soil and sediment science that mainly focuses on the study of the geochemical cycles of BC regards BC as the combustion continuum [2], ranging from slightly charred, degradable biomass to highly condensed, refractory soot, and it is better to be regarded as two subtypes, the combustion residues namely char and the combustion condensates namely soot [6, 10].

BC has both biomass burning and fossil fuel combustion sources, and thus its climatic properties can be impacted by the transition from the nature biofuel combustion processes to the human industrial activities. The study of the historical variations of the transition processes, such as from the pre-industrial to industrial period, is thus meaningful. Previous studies focused mainly on the developed countries [11-14] and some quick developing countries such as in China [15-17], and found that BC, char, and soot records can varied with the different timing of industrialization and a rapid increase in BC records occurred during the industrial periods. It seems that, from these studies, human activities contributions to BC emissions have far surpassed those from natural biomass burning. However, it is still unknown at the global scale whether this is true. Especially, in the southeastern Asia, where the largest atmospheric brown clouds (ABCs) due to mixing of human emissions such as fossil fuel sulfates, nitrates, BC, and fly ash, and natural emissions of organic carbon and BC from biomass burning [18] contributes to atmospheric solar heating and global warming, whether the human emitted BC has far more than those from biomass burning. In addition, when and how these processes happened are still unknown. These limit us understand the relationship between BC records and natural climate processes and human emissions.

Some studies have used the statistic data of human energy usages and reconstructed BC history over the past 150 years globally and in south Asia [19]. However, these findings cannot answer the variations of BC contributions from natural biomass burning. Lake sediments provide an important medium to records both human emissions and natural inputs. But most of these studies also emphasized the contributions of fossil fuel emissions to BC records [12, 20], while seldom studies investigated the relationship between BC emissions and climate change such as the precipitation and temperature variations for the past several hundred years. Studies that differentiate between the human contributions and natural processes are still sparse. The clear interpret of BC emissions from natural climate influence and human activities would help us understand the processes that control BC emissions and facilitate our predictions on future interactions among human emissions, climate change, biomass burning, and soil nutrients storage.

In this study, we selected the Phayao Lake of northwestern Thailand to investigate the BC, char, and soot records over the past ~150 years. The objectives of this study are to: (1) reconstruct the history of BC, char, and soot emissions; (2) identify the dominant factor that influences natural biomass burning and BC, char, and soot emissions during the pre-industrial periods; (3) find out the real industrialization time and the sources for BC, char, and soot using the variations of the polycyclic aromatic compounds; (4) discuss the potential impact of human activities and biomass burning on lake water and the surrounding soils.

6.2. Sampling and methodology

6.2.1. Study site and sampling

The Phayao Lake (N 19°09'-19°13', E 99°51'-99°56'; Fig. 6.1), is located at the southern tips of two mountains, Doi San Klang and Doi Huai Nam Khao, nourished by the Ing River, and it is the third largest fresh water resource with a pan basin area of 20.5 km^2 [21]. It has an average depth of 1.9 m, and consists of average water volume of 33.84 Mm^3 drained from 11 canals into the basin [21]. It is the main water supply for the domestic and agricultural activities in this area, and the major pollution of this lake is caused by the urban run-off and draining of the agricultural activities from the surrounding area.

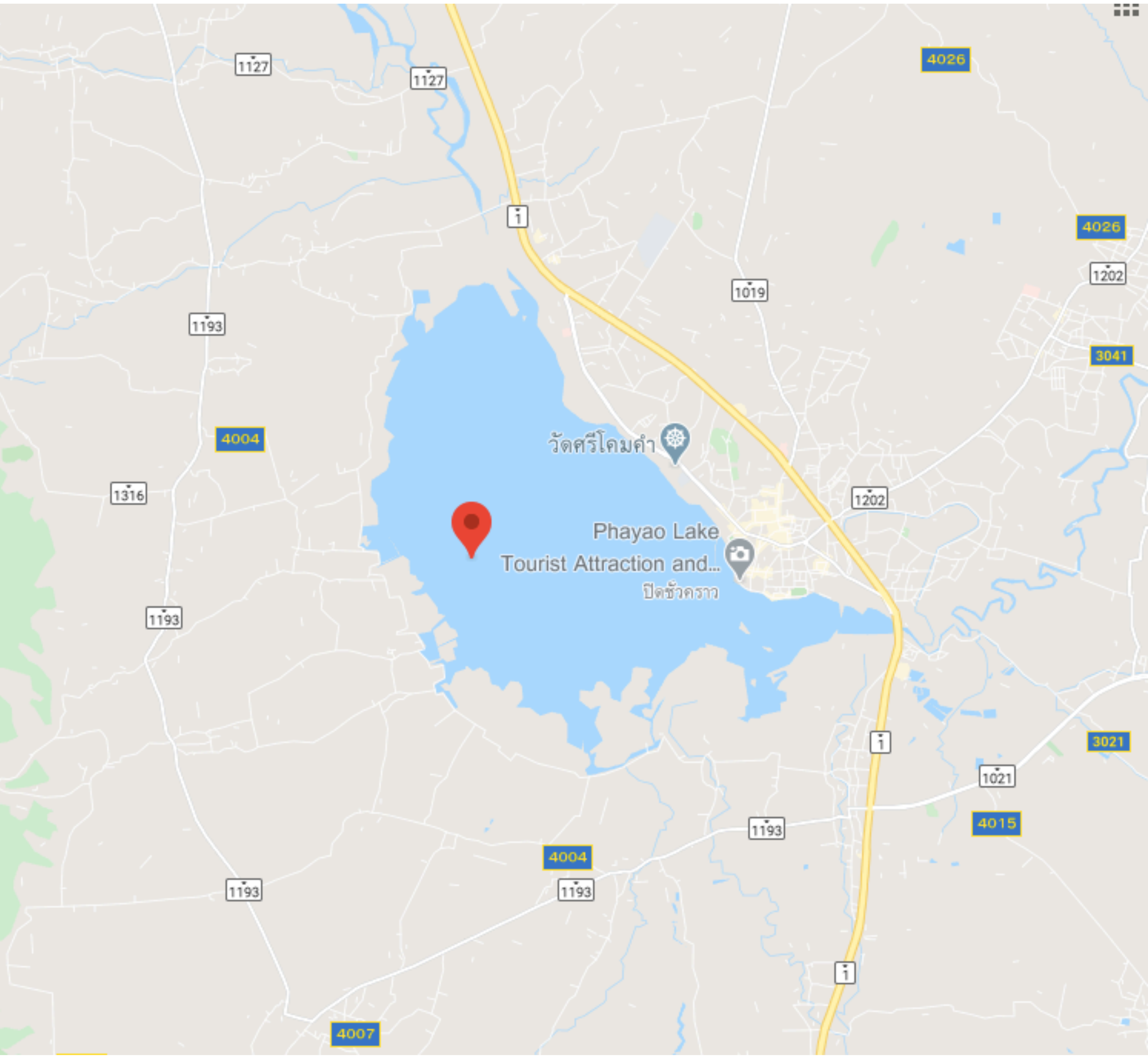

Figure 6.1. Sample location of Phayao Lake in northeastern Thailand. (A) Phayao Lake in southeastern Asia with climatic system in this region; (B) Sampling in Phayao Lake

The climate in the Phayao region is influenced by the south Asian monsoon system, the southwest summer monsoon and the northeast winter monsoon. Three main seasons are identified: 1) summer (March-May) with the maximum temperature of 39.5°C; 2) rainy (May-October) with the average of 1,043.9 mm; and 3) winter (November-February) with the minimum temperature of 10.8 °C.

In March, 2016 two parallel sediment cores (PY-1 and PY-2) with lengths of 61 and 50 cm, respectively, were taken from the centre of the Phayao Lake (Fig. 1) with a water depth of ~3 m using a gravity corer (Uwitec, Austria; Fig. S1C). Distinct water-sediment interface and discernible laminations were observed, indicating a lack of post-depositional disturbance. The cores were sliced on the site continuously at 0.5 cm intervals for the upper 20 cm and at 1 cm interval for the lower part. All samples were taken back to the Institute of Earth Environment, Chinese Academy of Science, and freeze-dried, agate mortar ground, and frozen at -20°C until further analysis. The water content and dry density data were estimated from the mass of samples before and after freeze-drying.

6.2.2. Chronology dating

The PY-2 sediment core was selected for chronology dating. The activities of ^{137}Cs, ^{210}Pb, and ^{226}Ra were analyzed by direct gamma counting of 3-6 g of dried sediments using a multi-channel γ-ray spectrometer (PerkinElmer, GWL-120-15) [22, 23]. The constant rate of ^{210}Pb supply (CRS) model[24-26], which is not influenced by the sediment fluxes, was applied for chronology reconstruction. The reconstructed dates and their corresponding mass accumulation rates (MARs) were presented in Fig. 6.2. ^{137}Cs activities presented their values at depths of 9-29 cm, corresponding the CRS ages of 2003.4-1976.8. However, all these ^{137}Cs activities are all lower than 10 Bq kg^{-1}, close to their limit of detection, and thus not used as the independent marker in this study.

6.2.3. Carbon fractions and polycyclic aromatic compounds measurement

The sediment core of PY-1 was selected for chemical analyses. The OC and total nitrogen (TN) concentrations were directly measured using a CHNOS elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Langenselbold, Germany). The comparison of with and without acid pretreatments showed very similar OC and TN concentrations, which is in agreement with the fact that the study site has very small influences from mineral dust. We also conducted duplicate analyses at the rate of one for each batch of 10 samples. The relative standard deviation was less than 2% for OC and less than 3% for TN.

BC, char, and soot concentrations are determined using the IMPROVE (Interagency Monitoring of Protected Visual Environments) method with a commercial DRI Thermal/Optical Carbon Analyzer (Model 2001, Atmoslytic Inc. Calabasas, CA, USA) after chemical pretreatment. The detailed method can be referred to Han et al. [15, 27].

PACs, including 26 parent- and alkyl-PAHs (∑26PAHs, and ∑25PAHs for those excluding perylene, which is mainly of in-situ biogenic diagenesis origin [26]), 13 oxygenated-PAHs (∑13OPAHs) and 3 azaarenes (nitrogen heterocyclic polycyclic aromatic compounds, ∑3AZAs) were measured by 7890A gas chromatograph coupled to a 5975C mass spectrometer (GC/MS, Agilent, Santa Clara, CA, U.S.A.), with extraction by accelerated solvent extractor (ASE 200: Dionex, Sunnyvale, CA, USA) followed by clean-up/fractionation using column chromatography (10 % deactivated silica gel). Detailed description of the method please refer to [16, 28].

Mass accumulation rates (MARs) of BC, char, and soot were calculated using the CRS-reported MARs for each measured sample multiplied by the corresponding concentrations of BC, char, and soot.

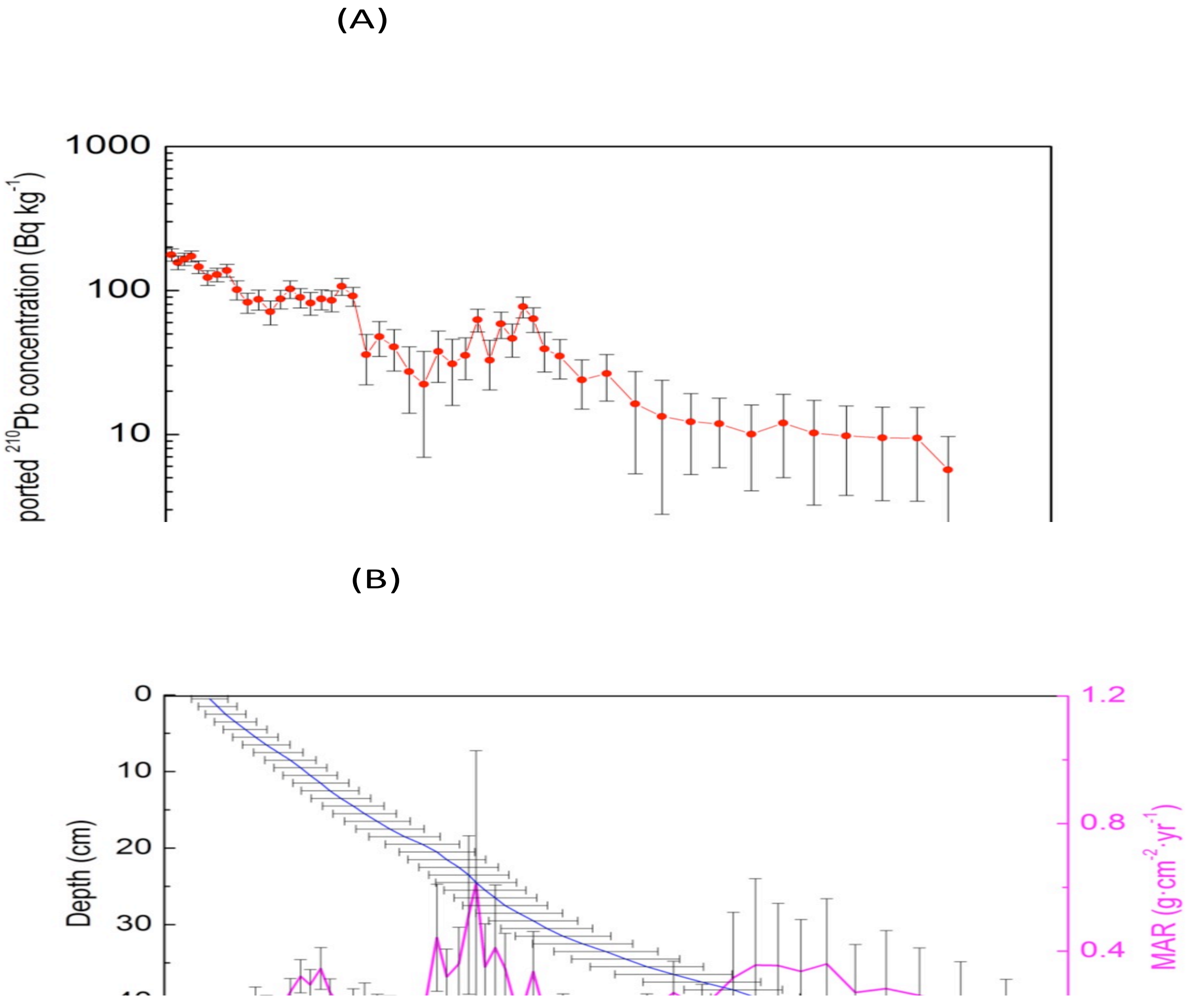

Figure 6.2. Chronology reconstruction for sediment core PY-2 using the constant rate of supply (CRS) ^{210}Pb model. (A) Excess ^{210}Pb activities against cumulative dry mass; (B) Chronology reconstruction using the constant rate of supply (CRS) model (upper blue line with uncertainties) and the calculated mass accumulation rates (MARs, magenta line with uncertainties)

6.3. Results

Similar variations of OC and TN concentrations were observed, which showed an increasing trend from 1868 to 1950 and fluctuations thereafter at relatively high values (Fig. 6.3). OC/TN ratios presented two distinguish parts, with relatively high values before 1980 in spite of fluctuation and low values after 1980.

BC and char concentrations, with similar variations, presented an overall decreasing trend from 1868 to present. Highest concentrations of BC and char happened at the bottom of the sediment core corresponding to 1868-1874. Also, distinct low BC and char concentrations occurred since 1980. However, for soot, its concentrations presented an opposite trend to BC and char and showed an roughly overall increasing trend in spite of fluctuations. Although post-1980 soot concentrations were not the highest, they have overall relatively high values than before. The MARs of BC, char, and soot showed similar profiles with their corresponding concentrations. Char/soot ratios presented an overall decreasing trend. Similarly, two distinct groups for char/soot ratios were observed, with lower values (in general lower than 5.0) after 1980 and relatively higher values (in general higher than 5.0 and highest value reaching over 40.0) before that time.

The concentrations of PAHs, LMW-PAHs, HMW-PAHs, OPAHs, and Az all presented increasing trends, with abrupt increase occurring at 1980. LMW-/HMW-PAHs presented an roughly overall decreasing trend.

6.4. Discussion

6.4.1. Distinct increase in fossil fuel contributions since 1980

From the results of concentrations variations of BC, char, soot, PAHs, HMW-PAHs, and LMW-PAHs, as well OC/TN, char/soot, and LMW-/HMW-PAHs ratios, a clear separation time of 1980 can be observed, which corresponds well with the beginning operation of the Mae Moh coal plant [29] and suggests the industrial period starting here.

MARs of BC and char showed vary similar variations due to much high proportion of char in BC in this core, and both presented an overall decreasing trends. However, for soot, its MARs presented an overall increasing trend. Although BC including char and soot originate from both biomass burning and fossil fuel combustions [1], due to their different formation pathways for char and soot, with char being combustion residues produced in relatively low temperature, while soot as combustion condensates produced via gas-to-particle conversion in relatively high temperature, high proportions of char can produced in biomass burning while more proportions of soot can be emitted from fossil fuel combustions. This suggests that the increasing trend in soot MARs is likely associated with the industrialization. Especially after 1980 a fast increase in soot MARs happened, while for char MAR it presented a relatively stable level.

Soot, as its ultrafine particle size and regional atmospheric transport [2, 10, 30], has been suggested to be used to reflect atmospheric soot deposition from its sediment records [16]. Previous studies have reconstructed soot emission history in southeastern Asia using the statistic data of human activities, and it presents an emissions growth rapidly in the latter half of the twentieth century [19]. However, it does not include a emissions from biomass burning. Previous studies have found a quick increase in soot MARs occurring at ~1950 in eastern China [16], due to the industrialization of China, with the post-1980 soot MARs being about 6.7-7.7 times of those for pre-1950 period. However, in this study although soot MARs present an increasing trend at 1980, the extent looks not as big as that occurring in China. Soot MARs during post-1980 period were lower than those during the pre-1980 period in some cases. This may suggest that fossil fuel emissions in this region are not as big as those occurring in eastern China, the intensive developed region. In some cases when an intensive biomass burning occurred such as the periods 1911-1921 and 1942-1954 (see Sec. 4.2), the emitted soot concentrations may be higher than those from industrial emissions. This suggests that in southeastern Asia the soot emissions of biomass burning and its potential climatic implications cannot be overlooked when we estimate the human influences [19]. This is consistent with the global estimate on BC sources [31], which estimated that ~42% BC aerosol originated from forest open burning in 1996.

The comparison of soot MARs from Phayao Lake sediments with those in China lake sediments (Table 6.1) showed a lower values than those from the industrialized regions such as Chaohu and Taihu regions, while they are comparable with those in rural areas such as Daihai region and higher than those from relatively remote areas such as Qinghaihu region. Char/soot ratio has been used as an useful indicator to differentiate fossil fuel combustion from biomass burning emissions [10]. It showed a clear decreasing trend for char/soot ratios in the studied sediment core, consistent with the increasing fossil fuel combustion contributions in this region. A pronounced decrease in char/soot ratios happened in ~1980, with the ratios in general lower than 5.0 compared with those higher than 5.0 for pre-1980 period, which further supports the industrialization in this region due to the beginning operation of the Mae Moh coal plant [29], which is located approximately 93 km away in the northern part from the Phayao Lake. The highest post-1980 soot MARs happened at the year of 2000, which corresponds to the expansion of the Mae Moh Coal plant, reaching 13 units and producing 2,625 Megawatts electricity [29].

Table 6.1. Comparison of the concentrations and mass accumulation rates (MARs) of BC, char, and soot, as well as char/soot ratios in Phayao Lake, northern Thailand with those around the world in the literature (For the different methods used here please refer to Han et al. [15])

Areas	Description	Concentration ($mg\ g^{-1}$)			Deposition flux ($mg\ cm^{-2}\ yr^{-1}$)			Char/soot	Methods	Refs.
		BC	Char	Soot	BC	Char	Soot			
Lake Phayao, Thailand	Northern Thailand	0.38-2.87 (0.80)	0.28-2.8 (0.66)	0.01-0.30 (0.14)	0.06-0.72 (0.21)	0.05-0.7 (0.17)	0.01-0.08 (0.04)	1.9-41.2 (5.6)	IMPROVE-A	This study
Qinghai Lake (North)	edge of north Tibetan Plateau	0.40-1.45 (0.57)	0.18-1.09 (0.31)	0.22-0.35 (0.26)	0.028-0.101 (0.040)	0.013-0.076 (0.022)	0.015-0.025 (0.018)	0.63-3.30 (1.16)		26
Qinghai Lake (South)		0.39-0.61 (0.46)	0.07-0.36 (0.19)	0.22-0.38 (0.27)	0.028-0.044 (0.033)	0.005-0.026 (0.014)	0.016-0.027 (0.019)	0.18-1.43 (0.73)		
Nam Co Lake	Central Tibeten Plateau	0.49-1.09 (0.74)			0.012-0.044 (0.026)					17
Daihai Lake	Rural mountain, North China	0.52-4.90 (2.26)	0.37-4.69 (2.05)	0.12-0.35 (0.21)	0.06-0.7 (0.31)	0.045-0.67 (0.27)	0.014-0.043 (0.03)	2.09-21.64 (9.76)		53
Taihu Lake	urban, Eastern China	0.41-1.95 (1.01)	0.01-1.43 (0.60)	0.31-1.09 (0.42)	0.115-0.689 (0.33)	0.003-0.555 (0.20)	0.086-0.312 (0.13)	0.03-4.21 (1.51)		
Chaohu Lake	sub-urban, Eastern China	0.61-2.03 (1.13)	0.48-1.58 (0.93)	0.08-0.47 (0.20)	0.170-0.567 (0.316)	0.135-0.443 (0.259)	0.023-0.131 (0.057)	2.82-8.02 (5.14)		16
Huguangyan Maar Lake	Southeastern China	0.26-1.73 (0.58)	0.15-0.82 (0.36)	0.06-0.98 (0.22)	0.008-0.068 (0.023)	0.005-0.032 (0.014)	0.002-0.038 (0.009)	0.77-4.62 (2.31)		
Aspvreten, Sweden	background area				0.0071-0.04				CTO-375	54
Pan-Arctic	Arctic	0.17-1.5			0.00013-0.0036					55
Slovenian Lakes	Alps	0.09-1.93			0.03-1.10					56
West Pine Pond	New York state	0.6-8			0.0026-0.077				STN	14

6.4.2. Dryness controls biomass burning in southeastern Asia

MARs of BC, char, and soot, and sometimes their concentrations as well, are traditionally used as indicators of biomass burning (BB) in wildfire reconstruction [27]. Before the industrialization period, BC, char, and soot originated mainly from biomass burning. Due to their different formation pathways, i.e. char being combustion residues formed in smoldering fires and soot via gas-to-particle conversion in flame [10, 32], soot and char have been used to indicate regional high intensity flaming fires and local smoldering fires, respectively [33]. Overall, similar profiles char and soot MARs were observed, indicating both high intensity and smoldering combustion can occur simultaneously in a single fire. However, discrepancies still existed for char and soot MARs. For example, at the bottom of the sediment core, it presented very high char MARs while low soot MARs, which is likely associated with the local and regional contribution of char and soot, respectively, or the different transport ways, with char mainly from riverine inputs while soot mainly from distant atmospheric deposition [10].

Although there is no consensus regarding the dominant factor that determines BB occurrences because both dry and wet climate and both high and low temperature from local BB records have been linked with high BB activities in paleowildfire studies [34, 35], dryness is accepted to be the key factor controlling BB activities in modern global biomass burning observation [36]. Palmer Drought Severity Index (PDSI) is a traditional proxy for soil moisture availability. The comparison of the MARs of BC, char, and soot with the southeastern Asia PDSI reconstructed from tree ring records in southeastern Asia [37], presented a good coupling between the BB activities and PDSI. For example, before 1980 there are three main drought periods: before 1868-1886, and 1911-1921, and 1942-1954, all of which time correspond with peaks of BC, char, and soot MARs (Fig. 6.4). Especially, although the 1868-1886 drought event is relatively moderate indicated by the reconstructed southeastern Asia PDSI by Sano et al. [37], it corresponds the late Victorian Great

Drought [38], and thus presents a very high BC and char MARs but with a relatively low soot MARs, an indicator of regional flaming fires [33]. This also suggests that this drought event had likely different manners in different locations, and in some southeastern Asia regions the intensity of this drought may be low. This may be also true for the period of 1876-1886, when there were relatively moderate BC and char MARs. Apparently, the 1942-1954 drought event lasted a long time and had a relatively high intensity, leading to a very high biomass burning indicated by BC, char, and soot MARs.

Previous studies [37, 39] observed that warm sea surface temperature (SST) anomalies in the tropical Pacific El Niño-like (warm) phases and regional climate forcing over the Indian Ocean and western Pacific sectors are these important factors contributing to the drought in this region. This confirms that in this region ENSO-modulated dryness is the dominant factor controlling BB occurrences and thus their emissions of BC, char, and soot during the pre-industrialization period. In southeastern Asia, the PDSI has been found to be positively related to temperature while negatively correlated to precipitation [40], suggesting that temperature and precipitation may influence biomass burning and BC, char, and soot emissions in this region. The similar timing of decrease of temperature and BC, char, and soot MARs from 1950 to 1975 (Fig. 6.5C) may imply the temperature effect on the drought and biomass burning.

After 1980, the relationship between the drought indicated by the PDSI and the biomass burning indicated by BC, char, and especially soot MARs, seems weak. This confirms that the dominant factors controlling on soot MARs variation originated from industrial activities in the Industrial period. The drought event influences on biomass burning seems weak; for example, the most pronounced El Niño event that resulted in the extensive drought in southeastern Asia during 1997-1998 [41] just caused a relatively small increase in BC and char MARs, which are even lower than most of their corresponding values during pre-1950 period. However, the increase of temperature in northwestern Thailand at 1980 may also contribute to drought and biomass burning, and such effect cannot be totally overlooked.

6.4.3. Polycyclic aromatic compounds associated with different sources contributions and atmospheric transport

PACs are important pollutants in the environment and mainly originate from human activities, and especially similar to BC, char, and soot from combustions, in modern time. A quick increase in PACs concentrations including ∑25PAHs, HMW-PAHs, LMW-PAHs, ∑13OPAHs, and ∑3AZAs occurred at ~1980 (Fig. 6.5), which is in well agreement with our demonstration that industrialization occurred in this region at that time.

Although PAC compounds ratios have been widely used for source identification [42, 43], the method is limited by availability of local emission data. LMW-/HMW-PAHs ratio seems the valuable method in historical PACs source identifications [16], which is seldom impacted by the local specific emission characteristics. An overall decreasing trend of LMW-/HMW-PAHs ratio suggests an increase in fossil fuel emissions in this region. Especially, the lowest ratios (lower than 1.0) occurred at ~1980s, which is in well agreement with the local Mae Moh Coal plant with little emission reduction measures at that time [29]. The comparison of the LMW-/HMW-PAHs ratio in this study with those from our previous works in Chaohu and Taihu Lakes, an industrialized region in eastern China with LMW-/HMW-PAHs ratios generally lower than 1.5, and from Qinghai Lake, a relatively rural area at the edge of Tibetan Plateau with LMW-/HMW-PAHs ratios ranging between 0.76 and 2.17, indicates that the Phayao region is a relatively less human influenced region.

As soot is sub-micron sized particles and comes mainly from atmospheric deposition in sediments [16, 26], the ratios of other pollutants to soot would reflect the transport pathways for other pollutants. For example, in this study the ratios of ∑25PAHs/soot, ∑13OPAHs/soot, and ∑3AZAs/soot all present a sharp increase since ~1980. This suggests that the local emissions and contributions of PAHs, OPAHs, and AZAs increased after 1980 and this is consistent with the increase of local coal plant emissions. However, considering that the transition from biomass burning to fossil fuel emissions happened at 1980 (see section 4.1), the differences in emissions of soot and PACs from biomass burning and fossil fuel combustion cannot be overlooked. As some of HMW-PACs can perform as the precursors of soot [44], it may suggest more PACs emitted from fossil fuel combustions than the proportions of soot. For example, much higher ∑25PAHs/soot ratios happened during the 1980s and at the early of 1990s, while thereafter the ratios of ∑25PAHs/soot decreased to the same level as the pre-industrial biomass burning period. This suggests that, on the one hand, the main local fossil fuel emissions from the Mae Moh coal-fired plant, which mainly occurred during the 1980s and at the early of 1990s, and on the other hand, there may be a transition of coal burning emissions to vehicle emissions since 2000, which is supported by the sharp increase in vehicle amounts in Thailand over the past few years. As a consequence of first-car buyer scheme (Noparumpa and Saengchote, 2017), the total automotive production in Thailand increased from 1.65 million cars in 2010 to 2.46 million cars in 2013 (http://www.boi.go.th/upload/content/BOI-brochure%202015-automotive-20150325_70298.pdf). There were also 1.8 million motorcycles produced, with domestic sales of 1.6 million and exports of 350,000 units. In addition, the monthly sold car numbers in Thailand are clearly reported by the Thai Automotive Industry Association (http://www.taia.or.th/Statistics/).

Noparumpa, T. and Saengchote, K., 2017. The impact of tax rebate on used car market: Evidence from Thailand. International Review of Finance, 17(1), pp.147-154.

The ratios of ∑13OPAHs/∑25PAHs also support the potential variations of the transition from coal burning to gasoline emissions since the late of 1990s, when it presents a quick increase in the ∑13OPAHs/∑25PAHs. As gasoline emissions contain more oxygen-contain species [45], more OPAHs could be emitted from vehicle emissions than coal combustion.

BeP/BaP ratio is a commonly use indicator for atmospheric process as BaP is more vulnerable to atmospheric degradation than BeP [46, 47] and long-term exposure to atmosphere ultra-violet (UV) would lead to high BeP/BaP ratios. The historical variation of BeP/BaP ratios presents a decreasing trend, but with small fluctuations since 1900. Especially, since 1980 the BeP/BaP ratios had just small increased. This suggests that although atmospheric processes would influence on the PAC variations in the studied region, the sources transformed from biomass burning via coal combustion to vehicle emissions may be the main reason for the historical variation of PACs. This may be also true for soot variations in this region. For more details of PAC variations, please see the supplementary materials.

6.4.4. Potential influences of biomass burning and human activities on lake sediments and surrounding soil quality

Sedimentary organic matter can mainly from surrounding soil inputs and in-lake production [48]. OC/TN ratio has been suggested to indicate the relative in-lake production, with low values indicating a high in-lake production [48, 49]. The concentrations of OC and TN in lake sediments present an overall increasing trend until ~1950s and fluctuations occurred thereafter (Fig. 6.3-6.4). During the pre-industrial period the highest OC and TN concentrations happened at ~1950, while the lowest OC and TN concentrations happened at the bottom of the sediment core (before 1880). Both of them correspond to a drought climate with high SE Asia PDSI [37]. So, it is hard to say that climate is the key factor that controls soil quality. However, the lowest OC and TN concentrations for pre-1880 period corresponding a long-term drought climate and an extremely high local low intensity biomass burning indicated by the char-MARs, suggesting that extensive biomass burning likely decreased OC and TN concentrations in surrounding soils. Thereafter, in the natural processes until 1950 moderate or low biomass burning that can also produce biochar to keep soil nutrients [50] and thus may restore soil quality. The 1950 drought event may be another extensive climate event that may result in the reduce in soil organic matter in following years.

Distinct decrease in OC/TN ratios occurred at ~1980, which corresponds well with the industrialization in this region [29]. Also, this is consistent with the fact that industrial and human agricultural activities would result in enhanced in-lake production [51, 52] and promote the eutrophication. After the industrialization in 1980, the whole variation of OC and TN concentrations seems similar with that soot MAR fluctuation, with the two peaks of soot MARs during 1980-1985 (in association with coal plant emissions) and 2000-2007 (in association with vehicle emissions) corresponding to the high OC and TN concentrations. This may suggest that the industrial activities may mainly influence OC and TN concentrations in lake sediments, while whether such effects can also reach the surrounding soil is unknown since the in-lake production may cause the increase in OC and TN concentrations in lake. In recent year, the OC and TN concentrations in lake sediments reached their highest, which corresponds to the enhanced in-lake productions indicated by the reduced OC/TN ratios, suggesting the extensive industrial activities or fertilizer usage in this region. The most recent study showed that both Nitrogen and Phosphorus balances in the agricultural system of Phayao Province were negative because of the large amount of nutrient loss through numerous ways such as nutrient leaching into water systems (Jakrawatana et al., 2017). Also, the ∑3AZAs, an indication of unique human products, and ∑13OPAHs also reached their highest values in the upmost sediments (Fig. 6.5), supporting the human contributions to water quality.

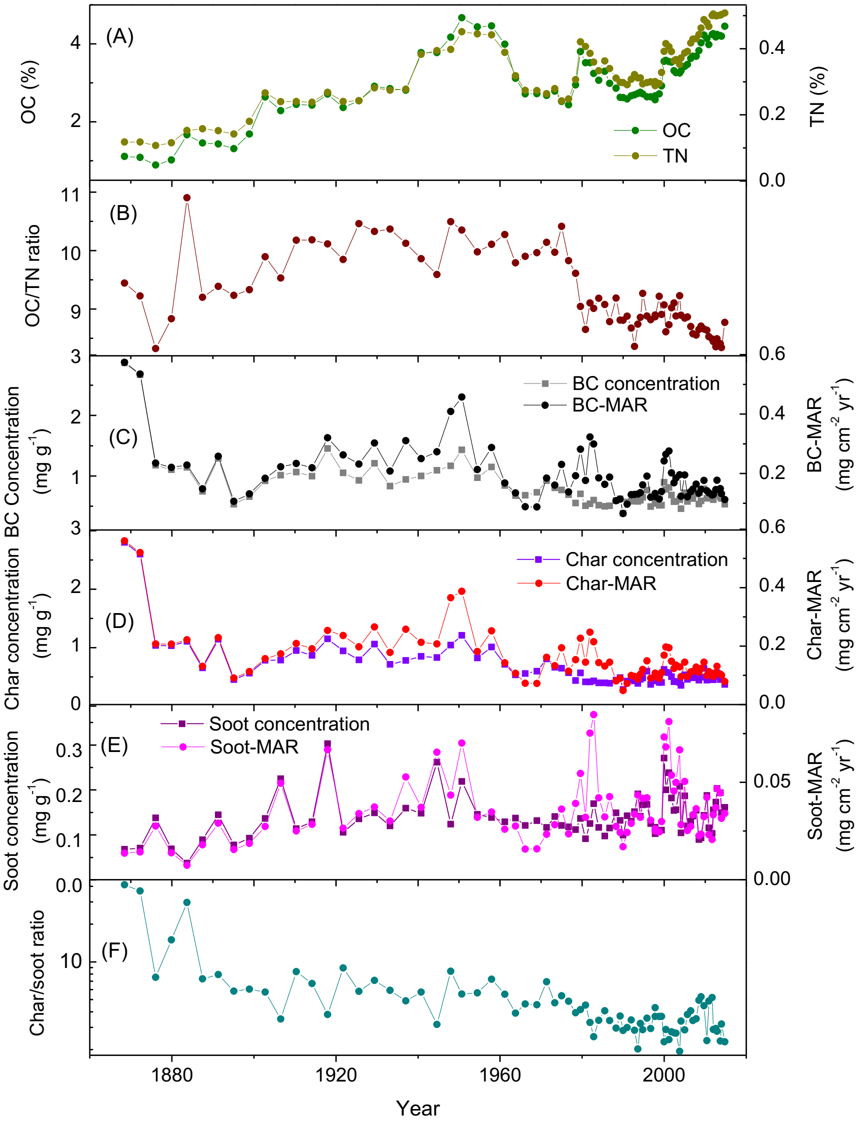

Figure 6.3. Historical variations of different carbon fractions (concentration and mass accumulation rate, MAR) and TN concentrations, as well as some of their ratios from sediments of Phayao Lake, northern Thailand

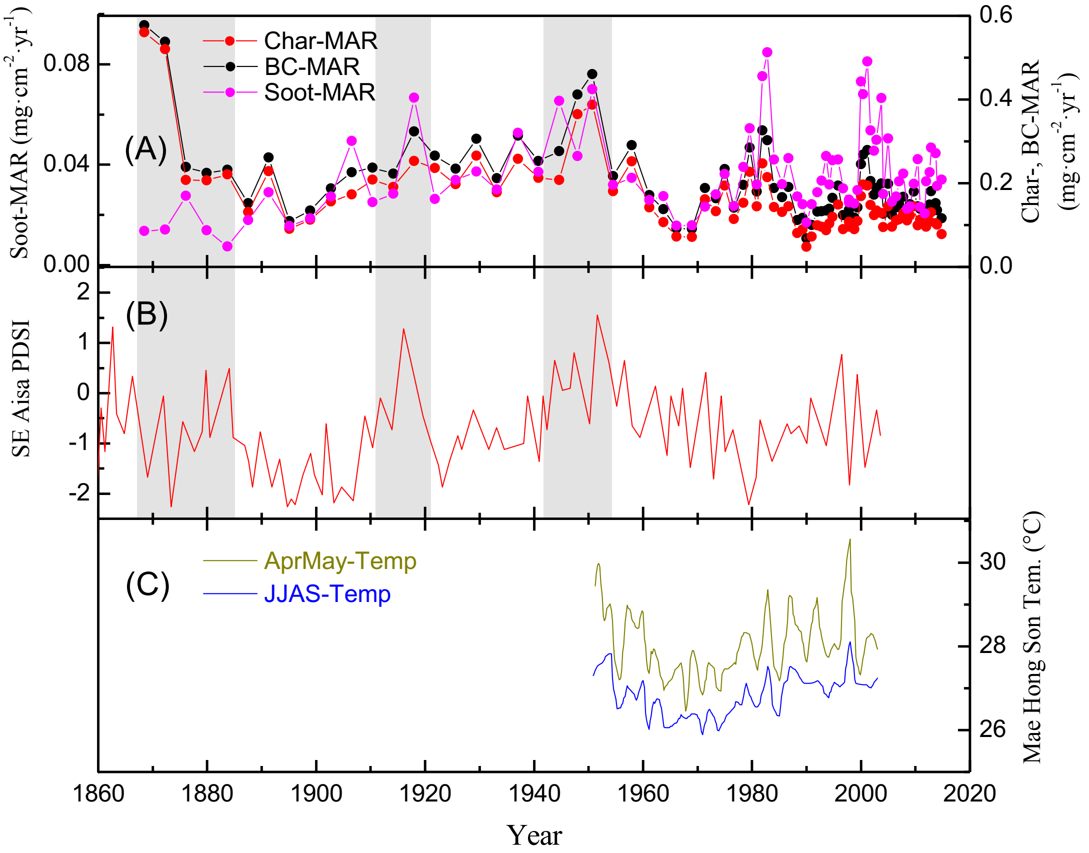

Figure 6.4. Variations of mass accumulation rate (MAR) of BC, char, and soot of Phayao sediments in comparison of the PDSI (Palmer Drought Severity Index) of southeastern Asia reconstructed from tree ring record [37] and the historical temperature variations in Mae Hong Son of northern Thailand [39]

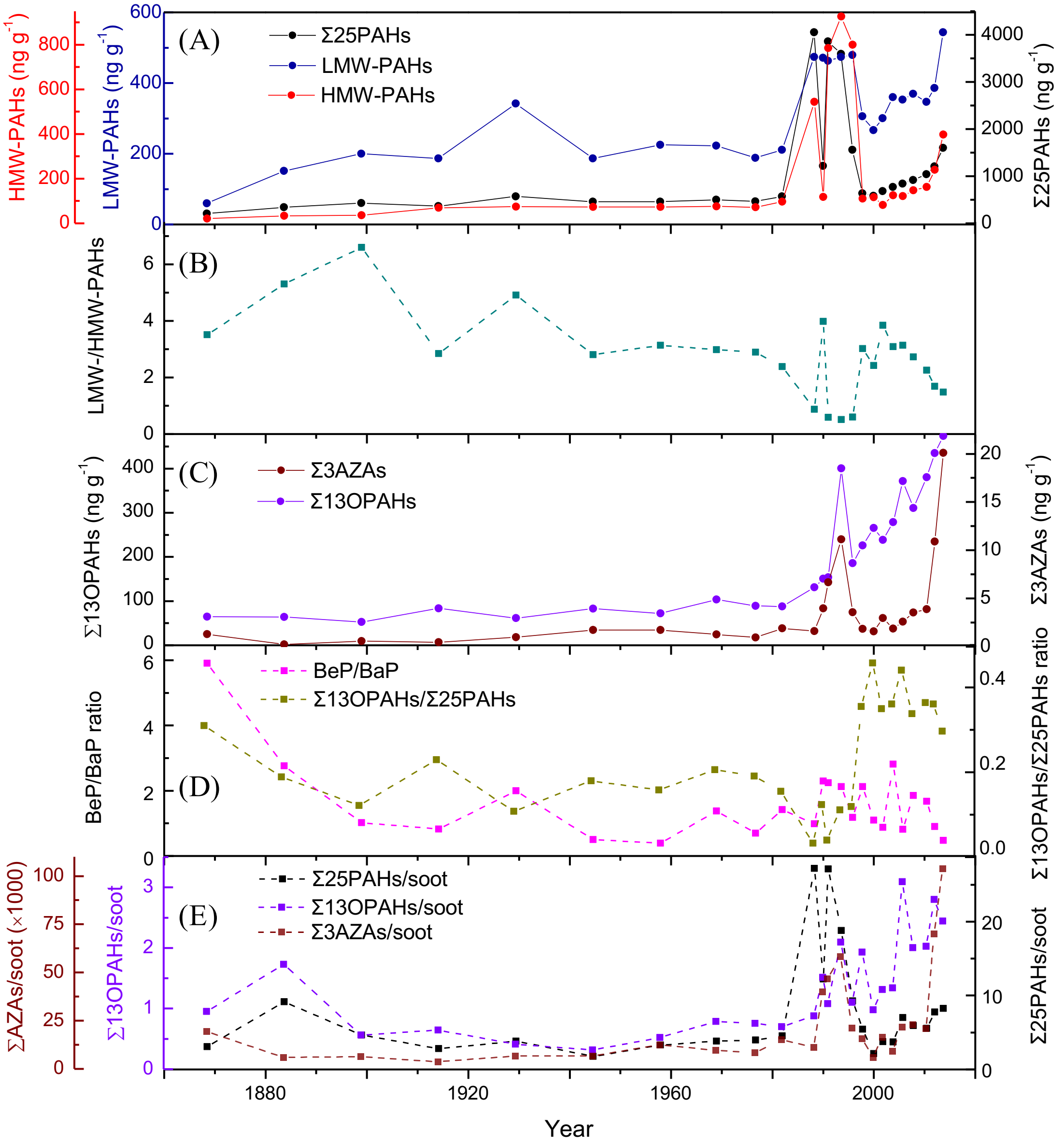

Figure 6.5. Historical variations of concentrations of polycyclic aromatic compounds (PACs) and their concentration ratios in Phayao Lake, northern Thailand

6.5. Reference

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Chapter-VII
Results & Discussion

Vertical Profile of Organic and Elemental Carbon in Sediments of Songkhla Lake, Thailand

Abstract

In this study, a historical record of atmospheric deposition in the sediment cores from Songkhla Lake, the second largest lake in Southeast Asia, located in the southern part of Thailand is reported. It is well known that lake sediments, including spheroidal carbonaceous particles generated by both anthropogenic and natural emissions, contain records of lake, catchment, and atmospheric deposition histories. Vertical profiles of these carbonaceous particles can be used to investigate enormously influential disturbances, particularly those triggered by extreme paleo events, over large spatial areas. In this study, organic carbon/elemental carbon (OC/EC) ratios displayed unusually high values of 3.07 and 4.02 for depths 240 and 340 mm, respectively. Previous studies have attributed remarkably high values of OC/EC ratios to both biomass burnings and volcanic eruptions. Although anthropogenic emissions (e.g. fossil fuel combustions) can be responsible for relatively high levels of contamination, as expected, the existence of relatively low OC/EC ratios (i.e. 1.43 ± 0.30) for all sediment samples (except those collected at 240 and 340 mm depths) suggests a tropical background of these particles.

7.1. Introduction

Numerous studies have extensively investigated the physicochemical properties of organic carbon (OC) and elemental carbon (EC) in aerosols (Huang et al. 2013; Li et al. 2006; Pongpiachan et al. 2013; Pongpiachan et al. 2014a, 2014b; Srivastava et al. 2014; Zhang et al. 2009, 2011), soils (Lal 2006; Möller et al. 2005; Raich and Schlesinger 1992), and sediments (Gacia et al. 2003; Hung et al. 2006; McCourt et al. 1996) especially, in Asian countries over the past few years. Although previous reports have highlighted the importance of anthropogenic emissions of carbonaceous aerosols in different environmental compartments (Chen et al. 2005; Ito and Penner 2005), the influences of biomass burning, forest fires, and volcanic eruptions also play a major role in governing OC and EC contents (Birch and Cary 1996; Cachier et al. 1989; Ito and Penner 2005; Martinsson et al. 2009; Szidat et al. 2006). Recent studies suggest that there has been a tendency toward enhanced summer floods in south China, increased droughts in north China, and moderate cooling in China and India, despite the ambient air warming trends in other parts of the world (Menon et al. 2002; Ramanathan and Carmichael 2008; Yihui et al. 2007). Since heat-absorbing carbonaceous aerosols increase the air temperature and influence both regional atmospheric stability and vertical movements, the investigation of OC/EC ratios can assist the understanding of regional-scale circulation and hydrologic cycles with significant regional climate impacts for many reasons.

Firstly, OC/EC ratios have been used as chemical tracers for characterizing emission sources from vehicle exhausts. According to a busy roadway tunnel experiment in central Lisbon, OC/EC ratios in aerosol components were in the range of 0.3-0.4 (Pio et al., 2011). Similar OC/EC ratios were detected at the road side of Birmingham, UK (Pio et al., 2011). The average OC/EC ratios in PM_{10}

(i.e. particulate matter less than 10 microns) collected from seven air quality observatory sites in heavily polluted road sides of Bangkok was 0.99±0.63, indicating that traffic emissions responsible for relatively low OC/EC ratios (Pongpiachan et al., 2014b). Secondly, biomass and agricultural waste combustions play a crucial role in elevating the OC/EC ratios as earlier discussed in numerous studies (Cao et al., 2007; Gonçalves et al., 2011; Pongpiachan et al., 2009). For instance, the generated smoke aerosols were characterized by relatively high OC/EC ratios detected from controlled field burning of rice straw (10) and wood combustions (7.8) (Engling et al., 2009; Ram and Sarin, 2010). Since OC/EC and Char/Soot ratios provide valuable insights for source identifications, many scientific reports have focussed on the chemical characterisation of carbonaceous compounds, particularly in lake sediments, which is exceedingly advantageous for deciphering historical trends related with biomass burnings/forest fires (Cong et al., 2013; Han et al., 2011). During the El Niño-Southern Oscillation (ENSO) year, severe droughts provoke forest leaf-shedding and greater flammability and thus forests became vulnerable to fire. Since numerous studies underline the strong correlation between the frequency of forest fires and ENSO (Nepstad et al., 1999; Schoennagel et al., 2005; Siegert et al., 2001), it appears reasonable to apply OC/EC ratios for reconstructing historical trends of forest fires in Southeast Asian regions.

A previous study also highlighted the importance of dissolved organic carbon (DOC) (i.e. water soluble organic carbon in aquatic ecosystem) as a key indicator for predicting and understanding the response of lake ecosystems to multiple threats such as acid rain, toxic heavy metal and hazardous persistent organic pollutants, enhancement in UV radiation, and climate change (Williamson et al., 1999). As a consequence of 20 year global warming, drought and enhanced biomass burnings between 1970 and 1990 appears to be responsible for the DOC reduction by 15-

25% in lakes of North-western Ontario, Canada (Schindler et al., 1997). It is also crucial to note that DOC is deeply connected with microbial metabolism, light climate, acidity, and primary production in lakes (Sobek et al., 2007). While the altitude, mean annual runoff, and precipitation were negatively correlated with lake DOC, the conductivity, soil carbon density, and soil C:N ratio were positively associated with lake DOC (Sobek et al., 2007). It has been suggested that increasing trends in DOC in the surface waters of glaciated landscapes across eastern North America and northern and central Europe between 1990 and 2004 can be briefly described by an elementary simulation based solely on variations in atmospheric deposition chemistry and catchment acid-sensitivity (Monteith et al., 2007). A similar rising trend of DOC contents in streams and lakes of UK within a range of 8 to 42 years was also detected with the average annual enhancement in DOC content of 0.17 mg C l^{-1} year^{-1}(Worrall et al., 2004). Overall, it appears reasonable to assume that carbonaceous aerosols are deeply connected with those of DOC contents in lakes and reservoirs and thus underlining the impacts of particulate OC-EC on numerous stressors over aquatic ecosystems.

Despite a large number of research studies focusing on the computation of emission factors of carbonaceous particles released from different fuel and vehicle types (Alves et al. 2015; Shen et al. 2014; Wei et al. 2014), little is known about their past records in tropical sediments. To the best of our knowledge, there is no information available on the vertical profile of OC/EC ratio distributions in the lake sediments of Thailand. Overall, the main objectives of this study are to (*i*) generate novel insights into the nature of complex climate systems in Southeast Asian countries with some assistances from OC/EC ratio data; (*ii*) obtain a vertical profile of total carbon (TC), OC, and EC for the Songkhla Lake sediments; and (*iii*) quantify the OC/EC ratios and compare their values with previous combustion source studies.

7.2. Materials & methods

7.2.1. Study site

The Thale Noi Lake (TNL) is located at 7° 46′ 00″ N 100° 09′ 11″ E, which is the largest lagoon lake in Thailand, is a protected freshwater wetland situated in Phatthalung Province and covers an area of over 460 km^2. TNL became regionally acknowledged as an ecosystem dynamic hotspot in 1975 when the Ministry of National Resources and Environment and in conjunction with the International Union for Conservation of Nature (IUCN) declared it a Protected Area Category III (Natural Monuments). TNL can be further separated into four subareas namely Melaleuca forests (170 km^2), Rice Paddies (153 km^2), Swamp (109 km^2), and Open Water (28 km^2). It is also important to highlight that TNL is positioned in the northern part of Thale Luang, Thale Sap, and Songkhla Lake. The area around the lake consists of farmland, forests, and swamps. There is no main river flowing through this area, but sediment loads from many small man-made canals as well as run-off water from the high steep mountains is observed (VKI, 1997). The sediment core samples of TNL were collected from three sites (Fig. S1 and Table S1) and Fig. S2 shows the sampling method and collected sediment cores.

7.2.2. Sediment collection

Three uninterrupted sediment cores were obtained from the northern, central, and southern parts of the TNL in August 2017 when the water level ranged between 150 and 170 cm (see Fig. S1–S2). A gravity corer was lowered from a speedboat equipped with a transparent PVC plastic tube 12 cm in diameter 1.2 m in length. All materials used for core sectioning were washed carefully with detergent and water, and rinsed successively with methanol and dichloromethane prior to removing the frozen core from the freezer. The putty knife and spatulas were properly cleaned with tap water, methanol, and then dichloromethane. More information associated with QA/QC considerations were strictly followed the standard operating procedure for the USGS Reston, Virginia Environmental Organic Geochemistry Laboratory Appendix 3 (https://water.usgs.gov/nrp/biogeochemical-processes-in-groundwater/forms/SOP_LMWOA_05272015_FINAL_Website.pdf).

For this study, as displayed in Fig. S1, only No. 1 sediment core was selected for the chemical analysis of OC/EC ratios. The retrieved sediment columns were subsequently maintained in the vertical position to avoid disturbance or damage to sediments during transport to the laboratory. In this study, no physical evidence of bioturbation was detected in the retrieved sediment columns, indicating biological limitations in the TNL. In this project, the No.1 sediment core (580 mm) was precisely subdivided into a series of slices in 20 mm intervals. The 29 sediment sections (i.e. 580/20) were subsequently freeze-dried in order to remove the water content without greatly altering the physicochemical properties of the lake sediment. The samples were then passed through a 0.15 mm mesh sieve and kept in a refrigerator at - 20 °C in labelled zip lock bags for further OC/EC ratio analysis.

7.2.3. Analysis of OC & EC

The dried sediment samples were ground and homogenised with an agate mortar and sieved though a 200-mesh sieve. The sample pre-treatment procedure has been clearly described in previous studies (Han et al. 2007a, 2007b) and will not be discussed here (see Table S2 for more details). Entire sediment samples were quantitatively identified employing a DRI Model 2001

Thermal/Optical Carbon Analyser (Desert Research Institute, Division of Atmospheric Sciences 2215 Raggio Parkway Reno, NV 89506) (Chow et al. 1993, 2001). The employment of an analytical instrument is depended on the advantageous oxidation of OC and EC components at various heating conditions. Its operation depends on the truth that OC can be evaporated from the filter in a non-oxidising helium (He) atmosphere while EC has to be ignited by an oxidiser. The degree of decomposition brought by high temperature can be calculated by repeatedly observing the filter reflectance and/or transmittance throughout an analysis cycle. The reflectance and transmittance, mainly occupied by the existence of light absorbing EC, reduces as pyrolysis occur and enhance as light-absorbing carbon is liberated over the subsequent process of the determination. By observing the amount of light transmitted by a sample (i.e. transmittance) and the amount of light that reflects from the surface of a sample (i.e. reflectance), the EC peak area is theoretically positively correlated with pyrolysed OC, which can be precisely converted to the OC fraction. The computation for the charring conversion of OC to EC is important for eliminating the bias in the detection of carbon components (Johnson et al. 1981). The charring corrections of thermal optical reflectance (TOR) and thermal optical transmittance (TOT) are not essentially identical, owing to charring of organic vapours adsorbed within the quartz fibre filter (Chow et al. 2004; Chen et al. 2004). All samples were analysed by a DRI Model 2001 Thermal/Optical Carbon Analyser (Atmoslytic Inc. Calabasas, CA). The operation of the DRI Model 2001 Thermal/Optical Carbon Analyser is based on the preferential oxidation of OC compounds and EC at different temperatures. Its function relies on the fact that organic compounds can be volatilised from the sample deposit in a non-oxidising He atmosphere while EC must be combusted by an oxidiser.

7.2.4. Probability distribution function (PDF) of carbonaceous sediments

The PDF was applied to TC, OC, and EC of sediments collected at the TNL. Normally, a PDF is an equation that explains the relative probability of a random parameter to take a given value. The probability for the random parameter to fall within a specific area is given by the Gaussian distribution, which can be described as follows:

$$y = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x-\mu)^2}{2\sigma^2} \right) \quad \textbf{(1)}$$

Where y, σ, σ^2, μ and x symbolise PDF, standard deviation, variance, arithmetic mean, and contents of carbonaceous compositions in lake sediments, respectively. In addition, Statistical Program for Social Sciences (SPSS) version 13 was used for simple linear regression analysis (SLRA), analysis of variance (ANOVA), and Pearson correlation analysis.

7.2.5. Estimation of secondary organic carbon (SOC) in PM_{10} collected at Hat-Yai City

Since numerous constraints can cause comparatively high OC/EC ratios in atmospheric deposits, it is important to perform further evaluation of SOC, which is generally related to the atmospheric long-range transportation (ALRT) process (Wang et al. 2012; Zhou et al. 2012). Secondary Organic Carbons (SOCs) are carbonaceous pollutants released from both natural and anthropogenic sources. SOCs are formed through a complex interaction of photo-oxidation, aqueous phase reaction, biogenic volatile organic compounds (BVOCs) from forests, plants, vehicles or imperfect combustions from industrial activities, and other particulate pollutants (Bessagnet et al., 2008; Claeys et al., 2004; Sartelet et al., 2018; Zhang et al., 2018). It is well known that SOCs can play a major role in governing gas-particle partitioning of persistent organic pollutants (POPs), which has been detected to cause lung cancers, respiratory problems and other adverse health impacts (Cocker et al., 2001; Odum et al., 1996; Pongpiachan et al., 2009, 2013). In this study, particulate carbonaceous contents were cited from a previous study that collected PM_{10} at two air quality observatory stations, namely Novotel Centara Hat-Yai Hotel (7°00′20.65″ N 100°28′15.65″ E) and Lee Gardens Plaza Hotel (7°00′21.39″ N 100°28′15.94″ E), which were situated at the centre of Hat-Yai city, Songkla province (Pongpiachan et al., 2014a). The computation of SOC was conducted by applying the protocol proposed by Na et al. (2004). This method is based on the hypothesis that atmospheric deposits possessing the smallest OC/EC ratios constitute essentially primary carbonaceous compositions (Castro et al. 1999). For the atmospheric deposits observed at Hat-Yai city, the arithmetic mean of the three lowest OC/EC ratios was 8.47 and hence, these could be employed for the calculation of the SOC. It is also crucial to highlight that the three lowest OC/EC ratios were assumed to have solely primary OC and the impacts of small proportions of SOC was ignored. The content of SOC was estimated as follows:

$$OC_{\sec} = OC_{tot} - EC \times (OC / EC)_{primary}$$

(2)

Where OC_{sec}, OC_{tot}, and $(OC/EC)_{primary}$ are SOC, TOC, and the arithmetic mean of the three lowest *OC/EC* ratios, respectively.

7.3. Results & Discussion

Statistical descriptions of TC, OC, EC, and SOC detected during the sampling interval in the TNL are shown in Table 7.1. The arithmetic mean contents of TC, OC, EC, and SOC ranged from 178 to 1,136 mg g^{-1}, 142 to 636 mg g^{-1}, 35 to 555 mg g^{-1}, and 27 to 520 mg g^{-1}, respectively. For percent contributions relative to TC mass, OC varied from 51 to 80 % with an arithmetic mean of 60 ± 6.9 %, whilst EC ranged from 20 to 49 % with an arithmetic mean of 40 ± 6.9 %. SOC differed from 15 to 46 % contributing on average of 37 ± 7.3 %. In addition, the ANOVA test revealed a statistical difference between the mean values of OC (396 ± 126 mg g^{-1}) and EC (284 ± 125 mg g^{-1}). These results indicate that OC is the major chemical composition of the TC mass concentration. It is worth mentioning that three main features for the vertical profile of OC/EC ratio in the sediment core were observed. Firstly, three maximum peaks of TC were observed at sediment layer depths of 160–180 mm, 260-300 mm, and 500–520 mm, which were in good agreement with those of OC (see Fig. 7.1). Secondly, two maximum peaks of EC and SOC were detected at the same sediment layer depths of 480–500 mm and 500–520 mm. Thirdly, two maximum peaks of OC/EC ratios were measured at sediment layer depths of 320–340 mm and 220–240 mm.

7.3.1. OC/EC ratios and estimation of SOC

In this study, TC, OC and EC contents are assumed to be random parameters and remain unchanged during early diagenesis in sediments for numerous reasons. Diagenesis is the alteration of deposits or existing sedimentary rocks into a various sedimentary rock in the middle and after rock formation (i.e. lithification), at temperatures and pressures less than that necessary for the creation of metamorphic rocks (Berner, 1980). Since there are no hydrothermal vent and/or hot springs exist in the study sites, it appears reasonable to consider that diagenesis can take place at Songkla Lake sediments. However, it is crucial to note that diagenesis excludes surface alteration and metamorphism. In other words, diagenesis does not include any changes from physical, chemical and biological weathering. As a consequence, it seems rationale to conclude that diagenesis plays a minor role in governing physicochemical properties of Songkla lake deposits and thus TC, OC and EC concentrations should theoretically remain unchanged at the early stage of diagenesis in lacustrine deposits. One of the major factors associated with variations of carbonaceous contents in sediments is simply the chemical compositions of TC, OC, and EC contents originally contained in aerosols prior to its wet and/or dry depositions into Songkla Lake. In spite of the possible impacts of atmospheric depositions, biota living in the lake and in its watershed can be considered as the crucial sources of the organic compounds initially contributed to the lake system. Microbial reprocessing in the middle of sinking and early sedimentation noticeably reduce the total amount of organic matter while substituting many of the primary organic matters with secondary ones (Meyers and Ishiwatari, 1993). Therefore, much of the organic matter content of lacustrine sediments is the product of this microbiological decomposition. Numerous carbonaceous compounds of lake sediments still reserve source information and by that assist for better understanding of regional paleolimnological conditions.

Over the last few years, OC/EC ratios have been comprehensively employed for interpreting the photo-oxidation process of carbonaceous compositions, formation of secondary organic aerosols (SOA), and quantification of its potential sources (Gray 1986; Turpin and Huntzicker 1995; Strader et al. 1999). In this study, as displayed in Table 7.1 and Fig. 3, OC/EC ratios ranged from 1.02 to 4.02 with an arithmetic mean of 1.59 ± 0.65. In order to categorise any plausible contributors of carbonaceous compositions, the average OC/EC ratio in the sediment core of the TNL was compared with a previous study on emission sources of carbonaceous aerosols as illustrated in Fig. 7.3 (Pongpiachan et al. 2013). It should be noted that the average OC/EC ratio of the TNL sediments was similar to those of Rubber Factory and Traffic Emissions (see Table 7.2 and Fig. 7.3), but lower than those of $PM_{2.5}$ collected at Chaumont, Switzerland (2.8), Guangzhou, China (2.8 ± 2.8), and Xi'an, China (2.9 ± 2.7) (Cao et al. 2003, 2005; Hueglin et al. 2005). The comparatively low average OC/EC ratio observed in the sediment core of the TNL reflects the impacts of agricultural waste burnings coupled with local vehicle releases in this area.

However, it is crucial to note that two maximum peaks of OC/EC ratios, detected at 320 ~ 340 mm and 220 ~ 240 mm sediment layers, were 4.02 and 3.07, respectively. The relatively high OC/EC ratios measured at these two peaks could be attributed to numerous causes. First, earlier investigations underline the significance of the generation of SOC via ALRT (Wang et al. 2012; Zhou et al. 2012). For example, the considerably high $PM_{2.5}$-bound OC/EC ratios (range: 1.6–10.4; average: 5.2 ± 1.8) detected at Mount Heng, China were attributed to in-cloud SOA creation coupled with ALRT (Zhou et al. 2012). Second, both heterogeneous and homogeneous photochemical reactions of carbonaceous particles enhance dramatically during spring and summer, which were responsible for the comparatively high OC/EC ratios observed in the North China Plain (Wang et al. 2012). Since the TNL is located adjacent to the equator, it is reasonable to assume that the seasonal effect over the fluctuations of OC/EC ratios is of minor importance. Third, the unusually high OC/EC ratios can be ascribed as to extremely low EC value during the observatory period. Unfortunately, this interpretation cannot be used to explain the relatively low OC/EC ratios (i.e. comparatively high EC) found in other sediment layers.

Further investigations on the formation of SOC were conducted by applying the Eq. 2. OC_{sec} concentrations and its percentage contributions of PM_{10} collected at the Hat-Yai city, the nearest city to sediment sampling sites, were detected as 3.96 ± 2.18 $\mu g\ m^{-3}$ and 63 ± 25 %, respectively. This arithmetic mean percentage contribution is considerably higher than that of Kaohsiung (40.0 %, Lin and Tai 2001) and almost 3.7 times higher than that of Birmingham, United Kingdom (17 %, Castro et al. 1999). This underlines the considerable impacts of atmospheric depositions from Hat-Yai city as the potential mechanism responsible for relatively high OC/EC ratios observed in the sediment layers at 320–340 mm and 220–240 mm depths. In spite of the overwhelming impacts from Hat-Yai city, it is also crucial to underline other plausible influences such as local biomass burnings and ALRT as alternative causes for comparatively high OC/EC ratios detected in the lake deposits. A previous study detected the radioactivity of isotope ^{137}Cs using gamma-ray spectrometer in the Songkhla Lake sediments (Chittrakarn et al. 1996). Results of the analysis for ^{137}Cs in all 20 sediment cores show that the average sedimentation rate in Songkhla Lake, determined from each core, ranged from 0.0 to 8.7 mm y^{-1} with an arithmetic mean of 5.4 ± 0.2 mm y^{-1}. By using this sedimentation rate, the age of the two maximum peaks of OC/EC ratios could be indirectly quantified as 59–63 y and 41–44 y for the sediment layers at 320–340 mm and 220–240 mm depths, respectively.

7.3.2. SLRA

As described in section 3.1, the relatively high OC/EC ratios observed for the sediment layer depths of 320–340 mm and 220–240 mm are probably related to high OC rather than low EC values. There are three possible causes for this, i.e. human activities (e.g. traffic releases and factory emissions), biogenic emissions (e.g. forest fires, agricultural waste burnings, and plant wax), and ALRT of carbonaceous particles from outside of the TNL. Relative contribution of ALRT and local biogenic emissions can be evaluated by applying the SLRA for OC and EC concentrations in the lake sediments. If a larger part of OC in the atmospheric deposits of the TNL sediments were governed by local biomass burnings, the R-value of OC and EC should be low since EC is principally emitted from vehicular exhausts. On the contrary, if R-values of OC and EC are high, it appears reasonable to assume that both were released instantly from a single source, namely traffic emissions (Chen et al. 2012).

In order to test this hypothesis and to evaluate the influence of ALRT on maximum peaks of OC/EC ratios observed in the TNL, linear regression between OC and EC concentrations in each sediment layer was performed. As indicated in Figs. 7.4–7.6, the SLRA of TC vs. OC, TC vs. EC, and OC vs. EC were plotted along with their respective slopes and intercepts. Generally, a comparatively high R-value (R = 0.81) coupled with a lower p-value ($p < 0.0001$) was detected in the SLRA of OC vs. EC in all sediment layers indicating a single dominant contributor (plausibly traffic-associated emissions). On the contrary, the lowest R-value (R = 0.79, $p < 0.0001$) was observed in the SLRA of TC vs. OC while the highest R-value (R = 0.95, $p < 0.0001$) was detected in the SLRA of TC vs. EC. These findings highlight the importance of vehicular exhausts, which are predominantly connected with EC emissions, as one of the main contributors of carbonaceous particles in the TNL sediments. These results also indicate that the unusually high OC/EC ratios measured at sediment layer depths of 320–340 mm and 220–240 mm are probably associated with non-traffic emissions, namely ALRT, rather than the impacts of local biomass burnings.

7.3.3. PDF

The PDF was applied to all TC, OC, and EC contents at 29 sediment sections as explained in section 7.2.2. PDF is a function that describes the relative probability for a random parameter to assume a given value. The probability for the random variable to fall within a particular region is given by the Gaussian distribution as explained by Eq. 1. PDF will give an idea of vertical spatial distribution pattern of target compounds. It is important to underline that “vertical spatial distribution” indicates the distribution of target compounds along with numerous sediment depths not in the sense of distribution among several sampling sites. For instance, if PDF is normally distributed, this indicates an homogeneous distribution of chemical substances in Songkla Lake sediments. In the case of right skewness, this implies comparatively high inputs of chemical species in the study area. On the contrary, if PDF is left skewness, this underlines potential decaying mechanism (e.g. micro-biodegradation) of chemical species in the observatory site. As shown in Figs. 7.7–7.9, symmetrical bell-shape curves were observed for all carbonaceous compositions. Since the detected values of the PDF are more concentrated in the middle than in the tails, it seems rational to attribute it to moderately homogeneous spatial distribution of carbonaceous compositions in the background lake sediments that were less likely to be influenced by extreme events (e.g. forest fires and volcanic eruptions). Previous studies have highlighted the significance of large scale of forest fires and volcanic eruptions on fluctuations of carbonaceous compositions in atmospheric deposits (Bhugwant et al. 2000; Cachier et al. 1989; Lavoué et al. 2000; Martinsson et al. 2009; Pio et al. 2008). A previous study suggested that volcanic eruptions (Piton de la Fournaise, 2632 m above sea level) do not emit EC directly and during the air quality observation period from 10 to 28 March 1998, no significant vegetation fires ignited by the lava were observed (Bhugwant et al. 2000). The exceedingly high OC/EC ratio of 5.08 was also observed during the intense forest fire episode that occurred during the summer of 2003 in the Aveiro region, Portugal (Pio et al. 2003). Since no asymmetrical distribution curves for the carbonaceous compositions were observed in the sediment cores of the TNL, it appears reasonable to assume that atmospheric deposits in the TNL were mainly released from a single dominant source, probably vehicular exhaust. Nevertheless, it is safe to mention that the exceedingly high OC/EC ratios detected at the sediment layer depths of 320–340 mm and 220–240 mm are plausibly related to some extreme episodes such as forest fires and/or volcanic eruptions.

7.4. Reference

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Table 7.1 Statistical descriptions of TC, OC, EC, SOC, and OC/EC ratios in sediment samples collected from the TNL

	TC [mg g^{-1}]	**OC [mg g^{-1}]**	**EC [mg g^{-1}]**	**SOC [mg g^{-1}]**	**OC/EC**
Aver	679	396	284	260	1.59
Stdev	245	126	125	118	0.65
Min	178	142	35	27	1.02
Max	1136	636	555	520	4.02

Table 7.2 Statistical descriptions of TC, OC, EC, and OC/EC ratios in PM_{10} samples collected from various emission sources (Pongpiachan et al. 2013)

	PM_{10} [µg m^{-3}]	**TC [µg m^{-3}]**	**OC [µg m^{-3}]**	**EC [µg m^{-3}]**	**OC/EC**
PSU Campus1	35.7 ± 10.3	6.671 ± 8.391	4.838 ± 5.650	1.833 ± 0.856	2.639
PSU Campus2	27.9 ± 8.7	4.897 ± 3.640	3.573 ± 1.937	1.324 ± 0.673	2.699
Traffic Intersection	46.9 ± 30.6	14.831 ± 37.439	8.572 ± 10.572	6.259 ± 13.786	1.370
Corpse Incinerator	35.9 ± 28.7	7.485 ± 15.925	5.230 ± 5.854	2.254 ± 4.079	2.320
CPF	24.5 ± 5.4	7.385 ± 15.428	5.168 ± 4.448	2.217 ± 4.221	2.331
Songkla Lake1	13.8 ± 2.9	4.296 ± 2.000	3.063 ± 1.426	1.232 ± 0.268	2.486
Songkla Lake2	11.6 ± 3.7	0.977 ± 1.849	0.757 ± 0.397	0.221 ± 0.401	3.425
Rubber Factory1	34.4 ± 8.6	15.829 ± 31.658	10.852 ± 17.158	4.977 ± 6.096	2.180

Rubber Factory2	36.7 ± 15.7	11.022 ± 24.784	6.922 ± 10.449	4.100 ± 6.833	1.688
Bus terminal	42.8 ± 24.9	14.112 ± 29.391	8.062 ± 8.154	6.050 ± 11.015	1.333
Garbage burner	86.6 ± 65.4	24.449 ± 64.879	5.427 ± 11.266	19.023 ± 31.442	0.286
Barbeque Festival	30.2 ± 14.1	6.280 ± 8.799	4.850 ± 2.611	1.430 ± 1.849	3.392
Petkrasem Road	25.1 ± 9.2	9.650 ± 22.896	5.438 ± 8.693	4.212 ± 7.385	1.291
Kor Hong Mountain	9.6 ± 4.0	1.850 ± 1.224	1.352 ± 0.894	0.499 ± 0.055	2.709
Straw Burning	217.8 ± 96.1	80.362 ± 91.936	64.992 ± 51.974	15.370 ± 12.574	4.229
Bush Burning	25.5 ± 2.3	11.106 ± 10.069	7.980 ± 2.234	3.126 ± 2.696	2.553
Para Rubber Tree Burning	83.7 ± 23.2	48.390 ± 66.486	38.578 ± 35.154	9.812 ± 10.090	3.931

Prince of Songkla University (**PSU**): The sampling station is positioned at approximately 3 m above the basement of the Faculty of Environmental Management, Prince of Songkla University. This location is about 3 km far from city centre and thus can be acknowledged as an urban residential zone.

Traffic Intersection (**TI**): This monitoring site is situated at the traffic intersection adjacent to Tesco Lotus department store in Hat-Yai city. TI can be considered as a representative of vehicular exhausts.

Corpse Incinerator (**CI**): The monitoring site is located at crematory of Kor-Hong Buddhist monastery adjacent to PSU and approximately 1.5 km away from TI. CI can be considered as a representative of both timber and tire-combustions.

Charoen Phokphand Factory (**CPF**): CPF is located inside the facility of fish can producing factory owned by Charoen Phokphand group. This site can be considered as a representative of crude oil combustion.

Songkhla Lake (**SL**): SL is positioned at the coastal area of Songkhla Lake and is roughly 13 km away from Hat-Yai city. SL is also located approximately 14 km away from the western side of the Gulf of Thailand. This sampling site can be acknowledged as a representative of rural background monitoring site.

Rubber Sheet Manufacturing Factory 1 (**RMF1**): RMF1 can be considered as a mixture of Para rubber trees combustions coupled with emissions of latex fragments and sulphuric acid particles. This sampling stations is situated at Tumbol Tungwan, Hat-Yai district, Songkla province.

Rubber Sheet Manufacturing Factory 2 (**RMF2**): RMF2 can be considered as a mixture of Para rubber trees combustions coupled with emissions of latex fragments and sulphuric acid particles. This sampling stations is situated at Tumbol Tachang, Banglum district, Songkla province.

Bus Terminal (**BT**): This monitoring site is positioned at bus terminal about 1.4 km away from PSU. BT was carefully chosen as a representative of diesel emissions since most of the buses are diesel-fuelled.

Waste Incinerator (**WI**): WI is a facility which is a part of the municipality of Hat-Yai city. This sampling station can be acknowledged as a mixture of solid wastes and diesel oil combustions.

Barbeque Festival (**BF**): BF is positioned at the centre of PSU campus on the rooftop of Faculty of Natural Resources. PM_{10} samples was collected during the barbeque festival which is an annual tradition normally occurred in the second week of August. BF can be acknowledged as an representative of charcoal combustion.

Petkrasem Road (**PR**): PR is situated close to Petkrasem Road at the city centre of Hat-Yai. This site can be considered as the most congested area of Songkla province. As a consequence, PR can be considered as a representative of a mixture of diesel and benzene combustions.

Kor-Hong Hill (**KHH**): KHH is located on the top of Kor-Hong hill with a height of 356 m. KHH can be regarded as a mixture of anthropogenic emissions from Hat-Yai city.

Rice Straw Burning (**RSB**): RSB can be regarded as a representative of rice straw combustion. This sampling site is positioned at rice paddy field in Satingpra district, Songkla province.

Biomass Burning (**BB**): BB can be considered as a mixture of agricultural waste burnings at the planting areas of Namon district, Songkhla province.

Para Rubber Tree Burning (**PTB**): PTB can be regarded as an emission source of Para rubber tree combustion.

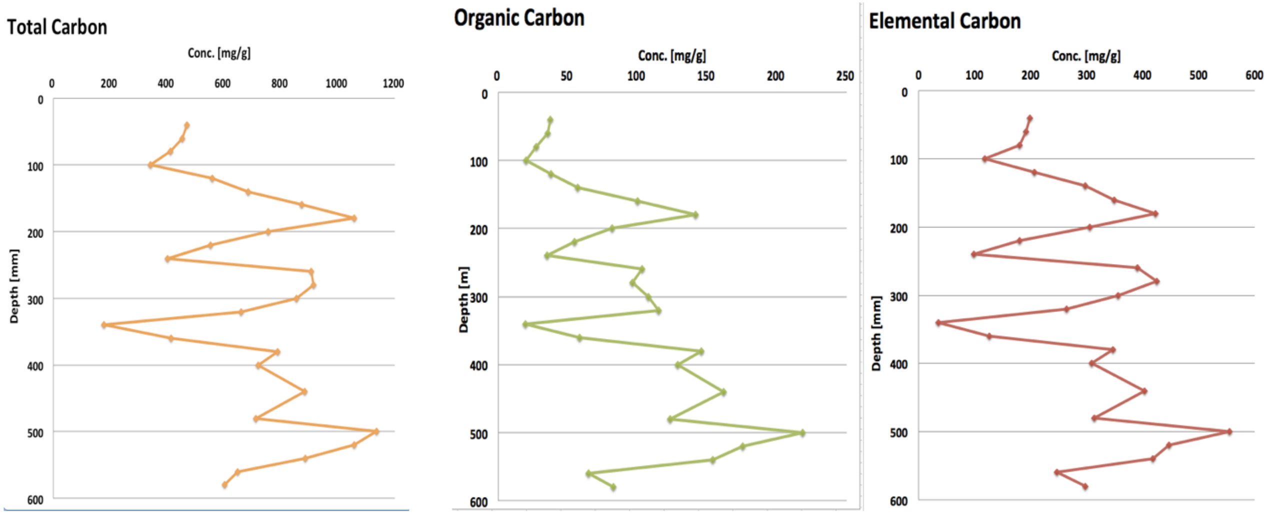


Figure 7.1. Vertical profile of TC, OC, and EC in sediments collected from the TNL

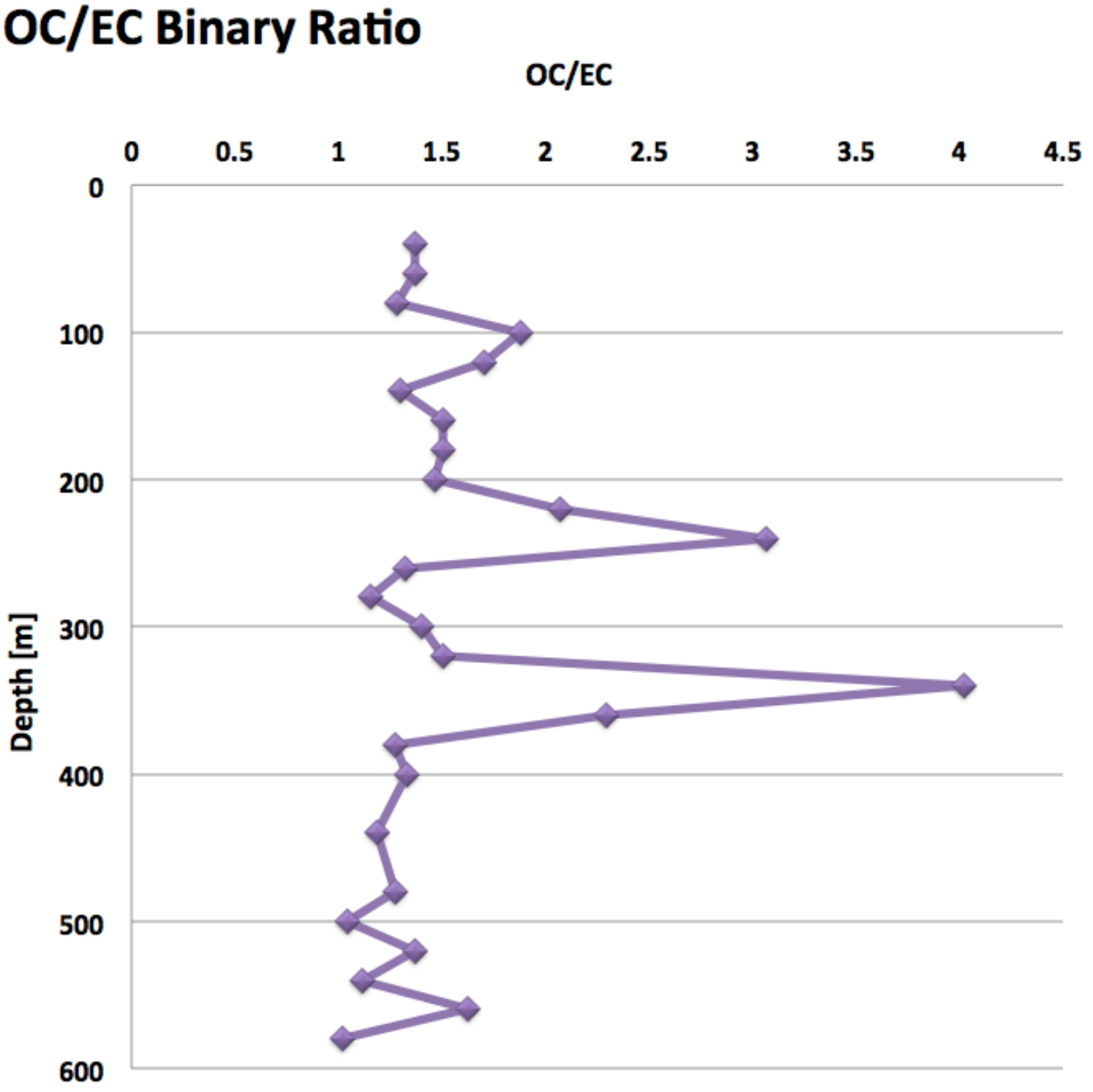


Figure 7.2. Vertical profile of OC/EC ratios in sediments collected from the TNL

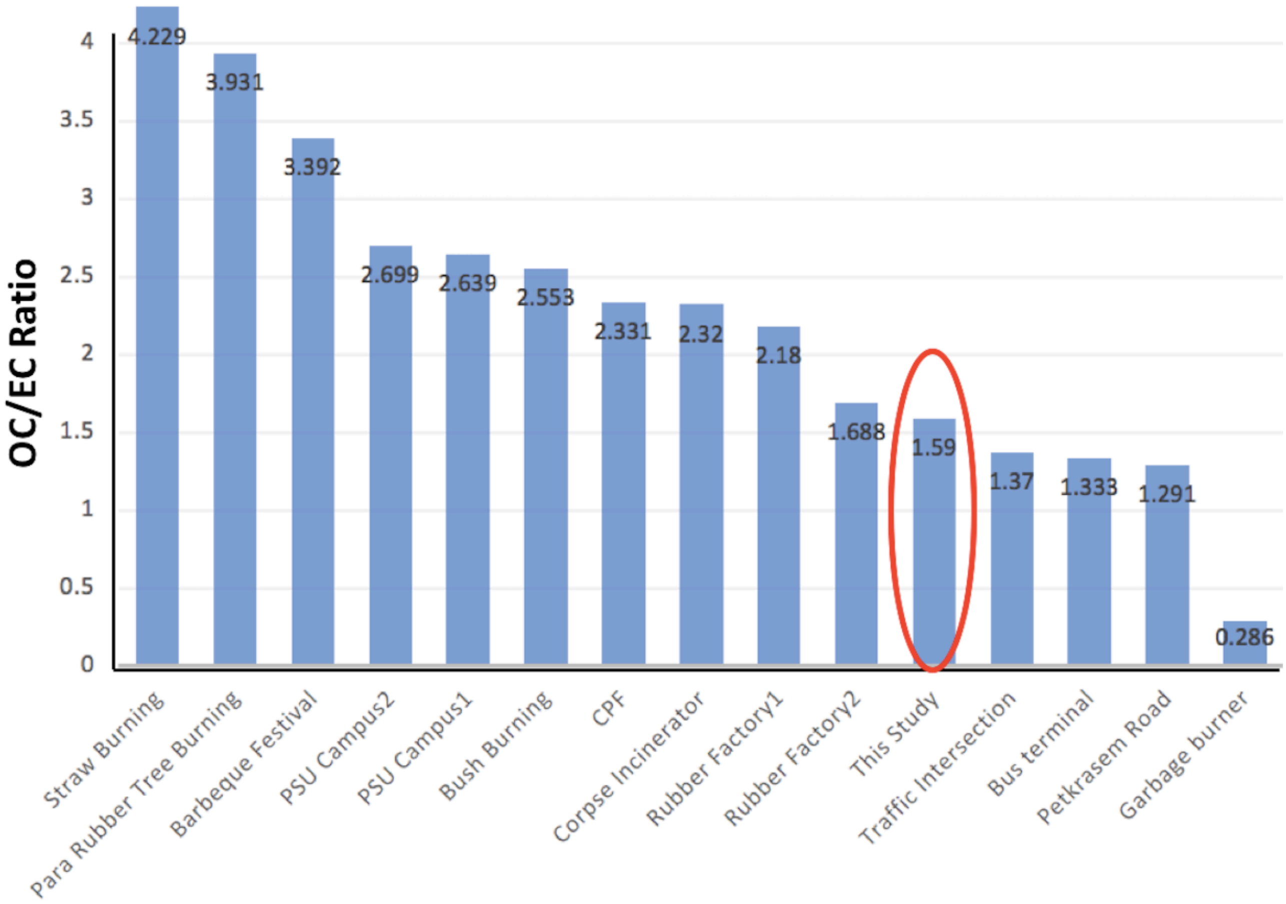


Figure 7.3. OC/EC ratios in sediments collected from the TNL in comparison with those of various emission sources

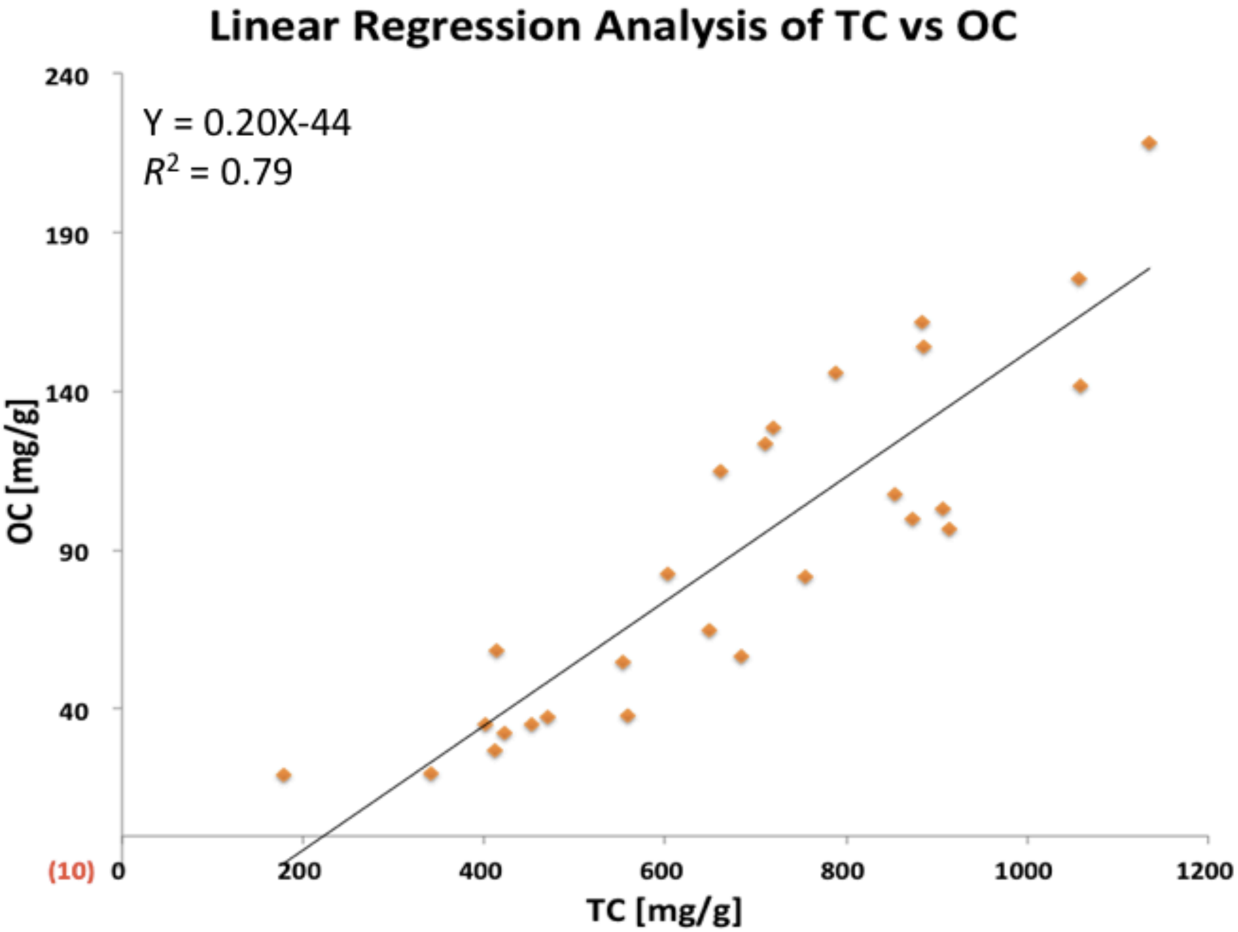


Figure 7.4. Linear regression analysis of TC *vs.* OC in sediments collected from the TNL

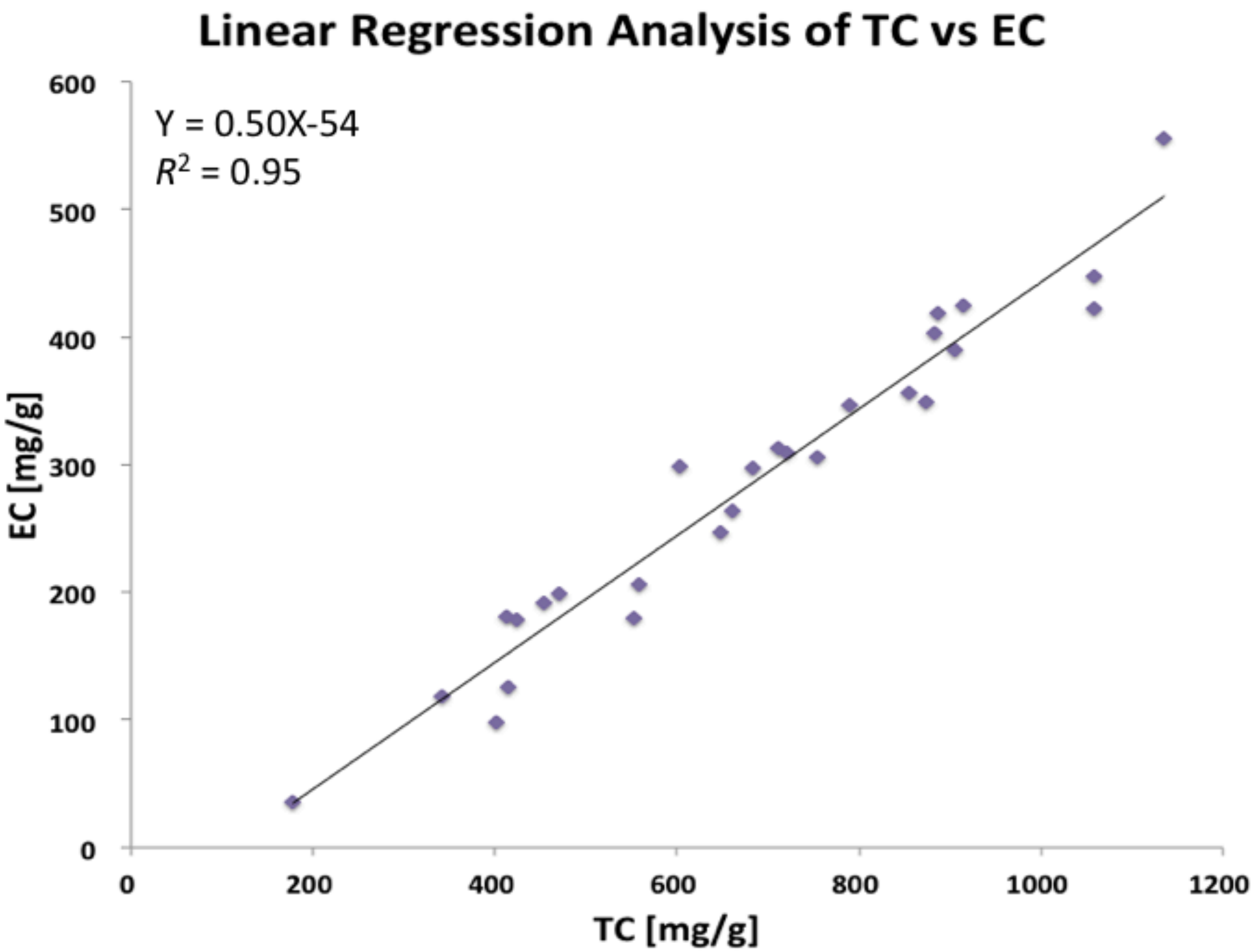


Figure 7.5. Linear regression analysis of TC *vs.* EC in sediments collected from the TNL

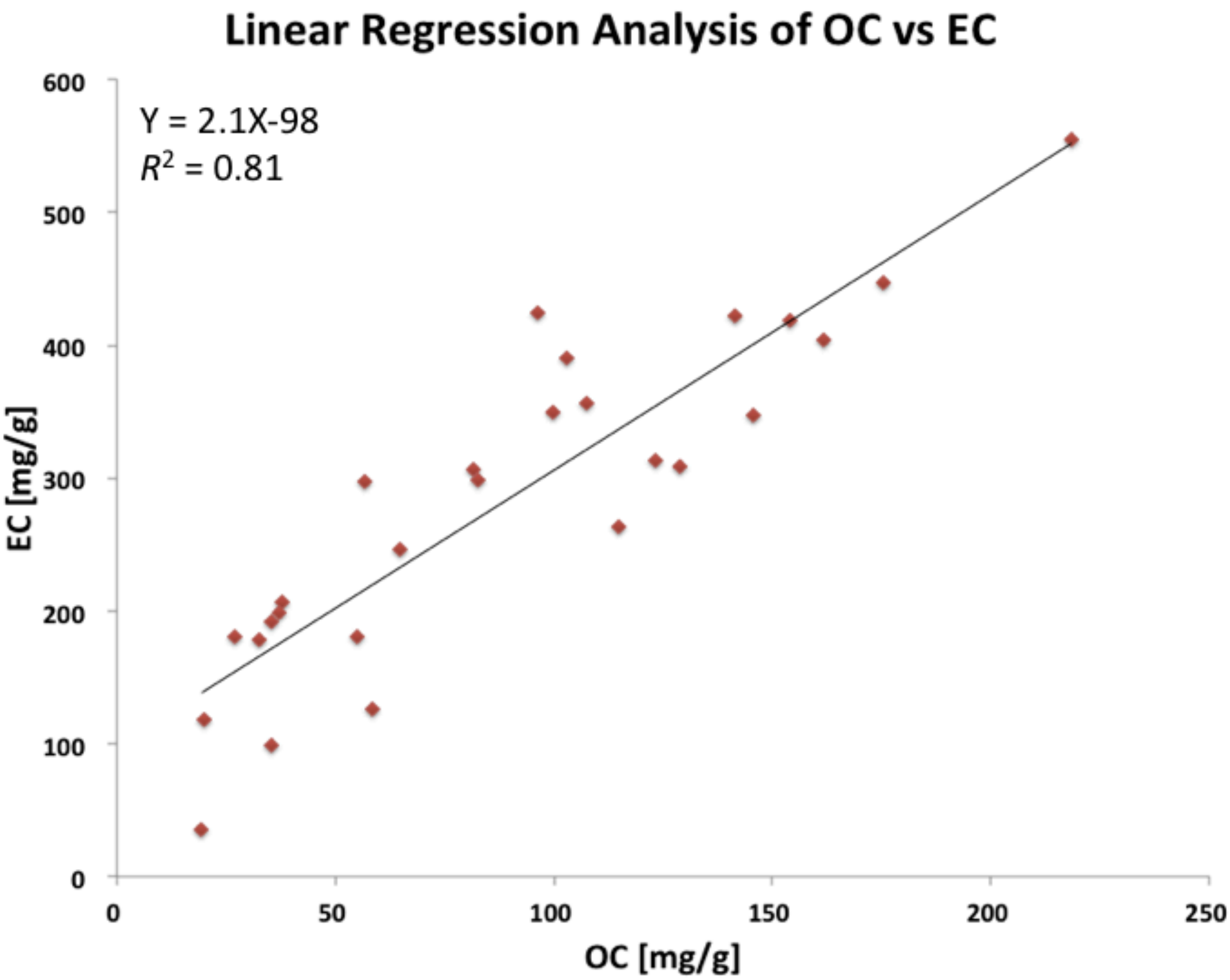


Figure 7.6. Linear regression analysis of OC *vs.* EC in sediments collected from the TNL

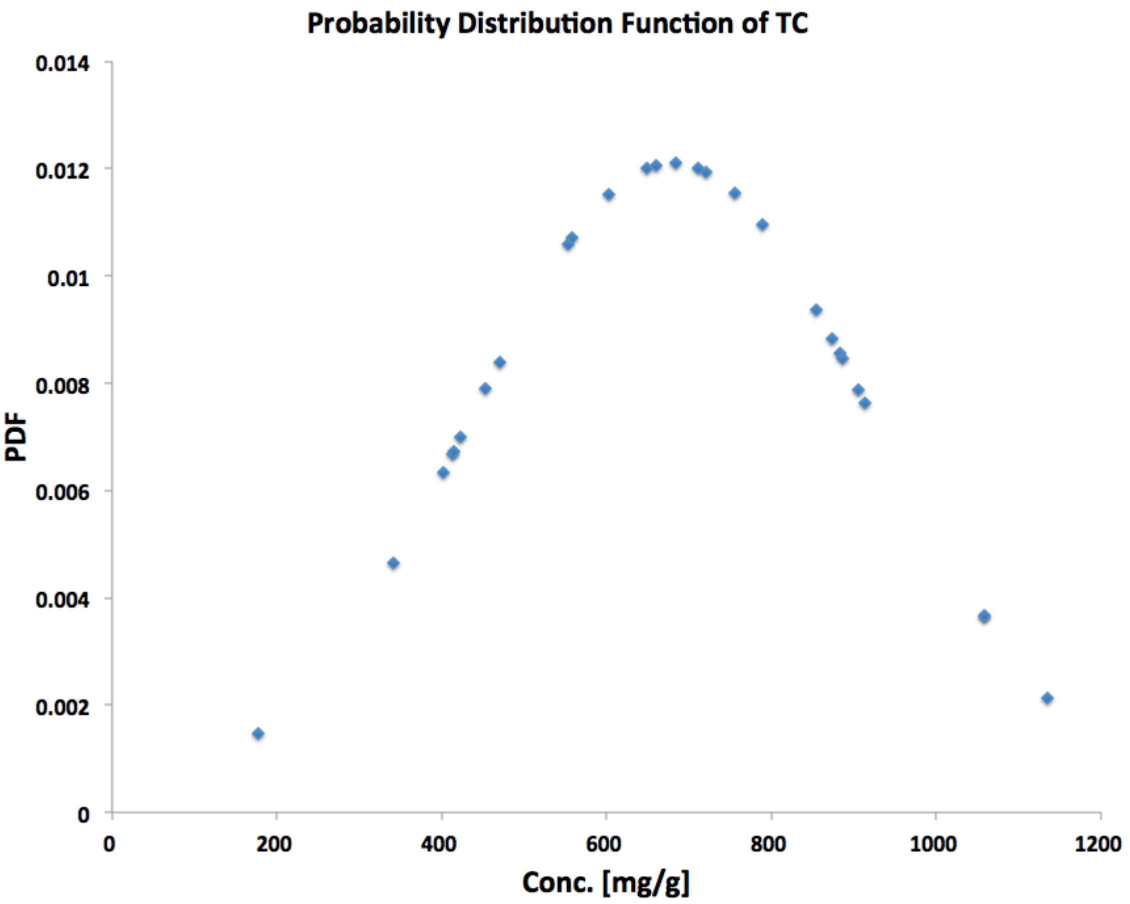


Figure 7.7. PDF of TC in sediments collected from the TNL

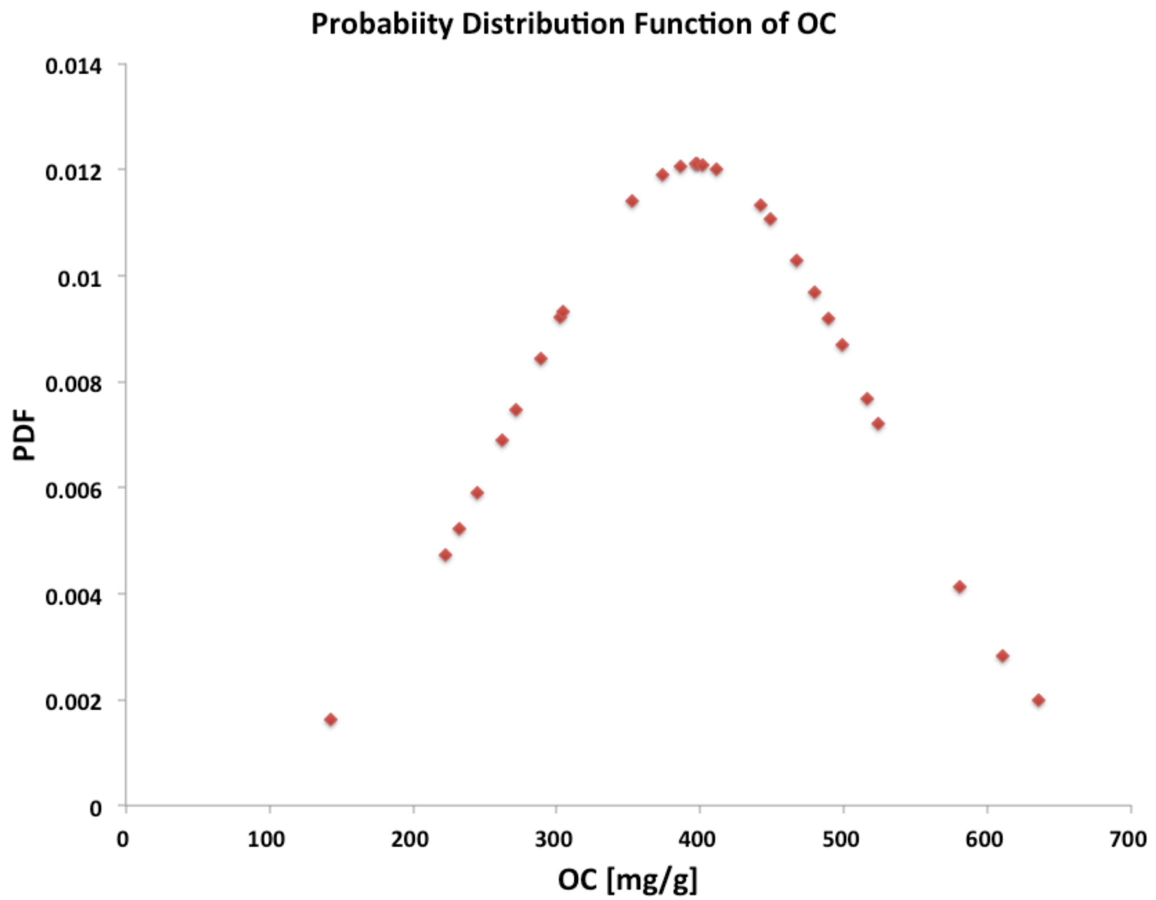


Figure 7.8. PDF of OC in sediments collected from the TNL

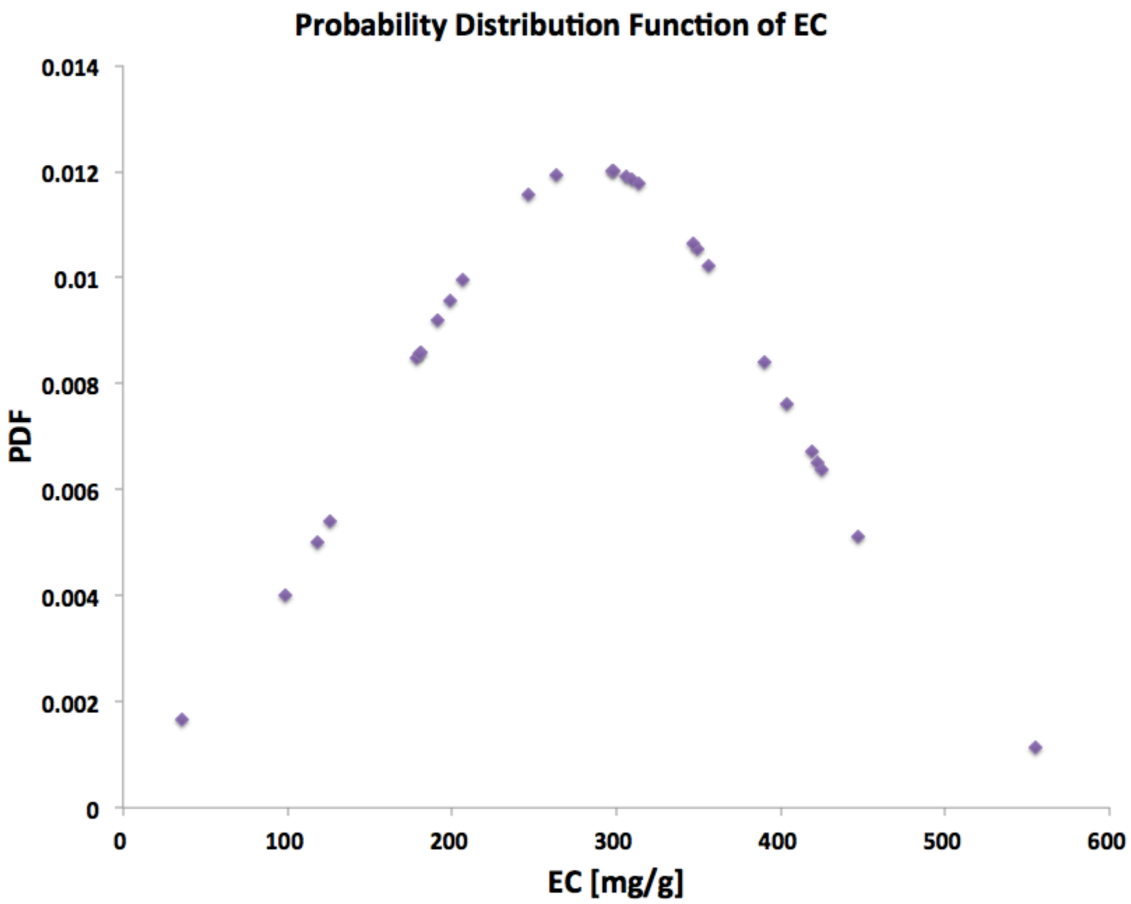


Figure 7.9. PDF of EC in sediments collected from the TNL

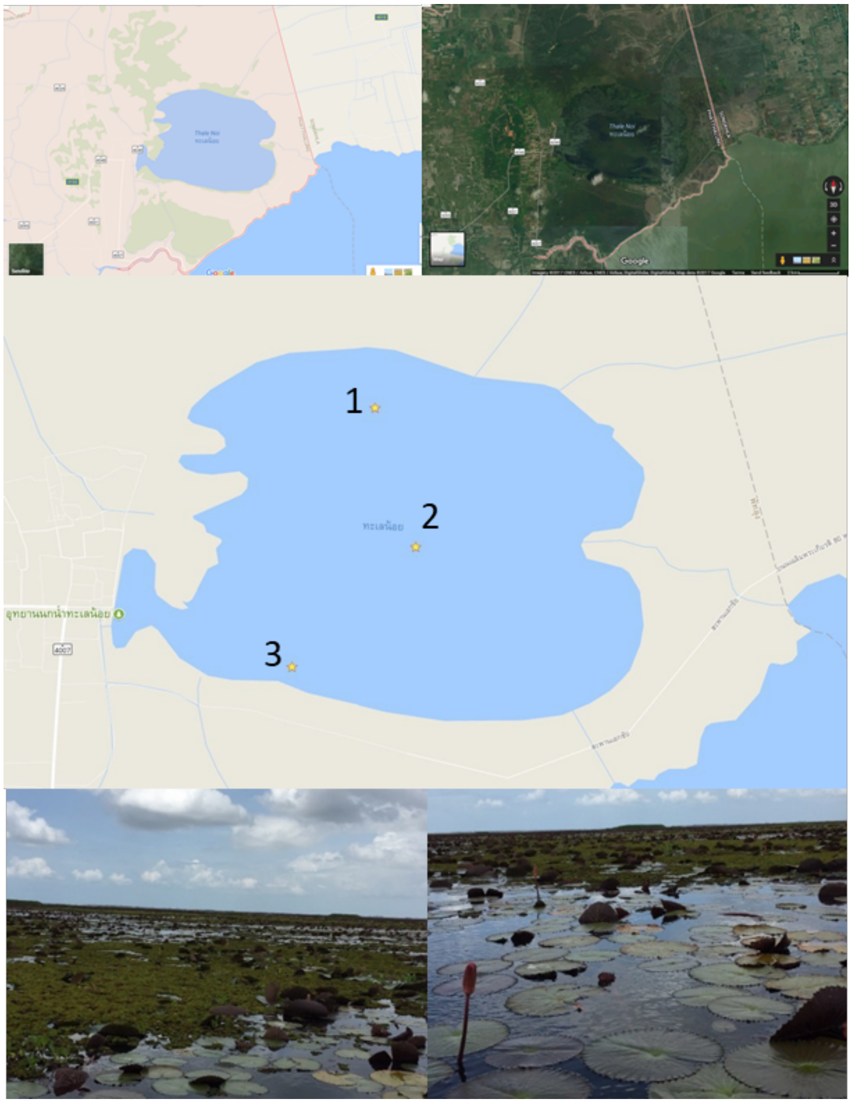


Figure S1 Sampling site locations at the TNL

Figure S2. Sampling method and sediment cores at the TNL

Table S1. Locations of sediment cores sampled form the TNL

Sample	Location		Sub-sample (2 cm)	Site-Description
	lat	long		
1	7.7703	100.1436	29 samples	Up-stream mud / black Thale Noi is a protected fresh water wetland situated in Phatthalung province,

				southern part of Thailand. Covering an area of 460 km^2, the wetlands are positioned roughly 20 km inland from the east coast peninsula of the Gulf of Thailand and 115 km north of the Malaysian border in Satun province. Thale Noi Non-Hunting Area is one of the largest natural freshwater lakes in South East Asia. It is the smallest, northernmost basin in the chain of lagoons that form Songkhla Lake, spreading across three provincial boundaries into Nakhon Si Thammarat, Phatthalung and Songkhla provinces and is home to the critically endangered Irrawaddy dolphin (Orcaella brevirostris)

Chapter-VIII
Conclusions & Future Works & National Policy

Conclusion 8.1

The results of the one-year monitoring campaign highlight the importance of biomass burning as one of the main contributors of carbonaceous particles in the ambient air of Chiang-Mai, Thailand. The comparatively high OC/EC ratios (e.g. 6.8±3.0), coupled with the high SOC contents (e.g., 8.12±0.26 μg m^{-3}) detected at Chiang-Mai, emphasize the dominant effects of biomass/agricultural waste burning in northern Thailand. HCA illustrates that mixtures of biomass burning, fossil fuel, coal combustion, and industrial emissions are major sources of $PM_{2.5}$. It is also to interesting to note that PCA successfully identified five major sources of $PM_{2.5}$, namely, vehicular exhaust, biomass burning, diesel emissions, sea-salt aerosols and agricultural emissions, which accounted for 51.6%, 16.2%, 10.6%, 5.20% and 3.70%, respectively. Overall, this study provides compelling evidence for adopting a zero-burning farming policy as a priority for national clean air act policies, strategies and plans.

Conclusion 8.2

In this project, the result presents the mean of $PM_{2.5}$ was three times higher than the annual average concentration of Thai National Ambient standard (25 μg m^{-3}) as well as USEPA standard. The OC/EC ratios suggested that the source was gasoline and LPG exhausts, while the comparatively high Char-EC/Soot-EC ratio coupled with a strong correlation between K^+ with OC (r=0.86) and Char-EC (r=0.82), respectively, so it guided that the ambient aerosol was emerging from biomass burning activity. Interestingly, a strong correlation between K^+ with NO_3^- (r=0.81) was also found in Bangkok area, as the major source of NO_3^- is originated from incomplete combustion, including traffic emissions and industrial emission. Thus, the result underlined that vehicular exhausts and biomass burning played a significant role in the Bangkok's atmosphere.

HCA indicated that the main source was mixture from combustion activities (e.g. biomass burning, vehicular exhausts, fossil fuel, coal and industrial). It is remarkable to notice that PCA efficiently separated five important sources of $PM_{2.5}$ samples, including vehicular exhaust, biomass burning, sea salt aerosols, power plants and industrial emission, which clarified for 43.7%, 24.0%, 10.5%, 6.48% and 4.46%, respectively. Overall, the results from this study emphasized that the effect of both local (vehicular exhausts) and regional (biomass burning) sources on the level of $PM_{2.5}$. Hence this data can be significance for potential manage plans for decreasing exposure at Bangkok's atmosphere such as policy as a priority for national clean air act.

Conclusion 8.3

This study investigated the carbonaceous aerosol compositions (OC, EC, WSIS, and PAHs) of $PM_{2.5}$ samples obtained in Phuket during March 2017 to February 2018. The main findings are as follows. The average $PM_{2.5}$ concentration was 42.26 ± 13.45 $\mu g\ m^{-3}$. Of the OC fraction, OC3 was the highest, followed in descending order by OC4, OC2, and OC1. Of the EC fraction, EC1 was the highest, followed by EC2 and EC3. Despite the relatively high OC/EC ratio (6.05 ± 2.70), the SOC content (1.30 ± 1.63 $\mu g\ m^{-3}$) was relatively low, reflecting the comparatively low EC content in marine aerosols. Strong correlation (r = 0.80) was found between nss-K^+ and OC, which was also shown to be affected significantly by long-range atmospheric transport of organic aerosols associated with BB. The concentrations in the $PM_{2.5}$ samples of 10 selected WSIS, i.e., SO_4^{2-}, Na^+, Ca^{2+}, Cl^-, NO_3^-, NO_2^-, NH_4^+, K^+, Mg^{2+}, and F^- accounted for 34%, 21%, 14%, 8%, 8%, 4%, 4%, 4%, 2%, and 1% of the total mass of ions, respectively. The average SO_4^{2-} concentration in Phuket was the highest throughout the entire study period (2.33 ± 1.73 $\mu g\ m^{-3}$). The average contribution of SO_4^{2-} to the major ionic component was 34%. It was surprising that NO_3^- and NH_4^+ had relatively low concentrations, i.e., 0.53 ± 0.21 and 0.29 ± 0.32 $\mu g\ m^{-3}$, respectively. The mean $[NO_3^-]/[SO_4^{2-}]$ ratio found during this study was 0.33 ± 0.24. The concentration of individual PAHs in the $PM_{2.5}$ samples decreased in the following order: B[g,h,i]P > Ind > Phe > B[a]A > Cor > B[b]F > B[k]F > B[a]P > B[e]P > Ace > D[a,h]A > Fluo > Fl > Pyr > D[a,e]P > Chry > Ant > Per > B[a]F. In this study, relatively high abundances of B[g,h,i]P and Ind were detected, indicating that motor vehicles, petroleum/oil combustion, and industrial waste burning are emission sources of the PAHs found in the ambient air of Phuket. Source identification of the chemical species by PCA revealed that five sources of carbonaceous composition observed in the $PM_{2.5}$ samples of ambient air in Phuket explained 82.8% of the total variance. The highlight showed that vehicular exhausts, BB, diesel emissions, sea salt aerosols, and industrial emissions accounted for 55.5%, 10.9%, 6.1%, 5.20%, and 5.1% of the total variance, respectively. Interestingly, the PCA result showed vehicular exhausts as the main source. However, the contributions of both marine aerosols and BB to SOC also played a major role. Overall, 17.2% of the variance could not be attributed to the five primary local and/or regional sources; this proportion was considered to originate from other combustion activities such as incinerators, incense burning, and cooking.

Conclusion 8.4

Long-term pollutants history from pre-industrial to industrial period would tell us the interactions between natural processes and human activities, advancing our prediction of future climate and environment. Previous studies emphasized more about human influences on pollutions, while less discussed about the natural impact. It is still unknown that in the less industrialized regions of southeastern Asia, human emissions or natural processes, which, play a key role in the emissions of light-absorbing carbon fractions of black carbon (BC), char, and soot. In this study, we determined historical variations of organic carbon (OC), total nitrogen (TN), BC, char, soot, and polycyclic aromatic compounds (PACs including 26 PAHs, 13 OPAHs, and 3 azaarenes) over the past 150 years from sediments of Phayao Lake, northern Thailand. We observed a clear transition from pre-industrial to industrial processes occurring at ~1980. However, the mass accumulation rates (MARs) of soot, the key atmospheric light-absorbing aerosol, after 1980 did not fully exceed their pre-industrial period, indicating that in rural and remote regions natural biomass burning emission is still a main contributor for soot. Well correlations of BC, char, and soot MARs with the reconstructed regional Palmer Drought Severity Index (PDSI) were observed for the pre-industrial period, suggesting that drought is the dominant factor controlling biomass burning. PACs source identification indicates two sub-stages of the industrial period: the transition from coal burning to vehicle emissions since ~2000. From natural processes to industrial activities, the surrounding soil and the lake water quality have been impacted, and notably more in-lake production associated with the eutrophication occurred during the industrial period.

Conclusion 8.5

The analyses of OC/EC ratios, OC_{soc}, SLRA, and PDF reveal that traffic emissions are the most influential factor controlling the atmospheric deposits of carbonaceous compositions observed in the TNL core sediments. Although vehicular exhausts play an important role in governing carbonaceous compositions of most sedimentary samples, multiple types of extreme events, including the ALRT of forest fire particulate matter and smoke from volcanic eruptions, seem to be the principal contributors detected at 320–340 mm and 220–240 mm sediment layers. By applying a sedimentation rate of 5.4 ± 0.2 mm y^{-1}, the age of the two extreme events could be roughly estimated as 59–63 y and 41–44 y, respectively. Irrespective of some degree of uncertainty resulting from sediment age dating techniques, the overwhelming contribution of traffic releases to carbonaceous deposits is unquestionably evident. These findings also provide evidence for considerable concerns regarding ecotoxicology and environmental safety of communities surrounding the Songkhla Lake and thus, are likely to encourage policy makers to develop realistic plans for the reduction of traffic related pollutants, especially under the context of sustainable development.

Futureworks

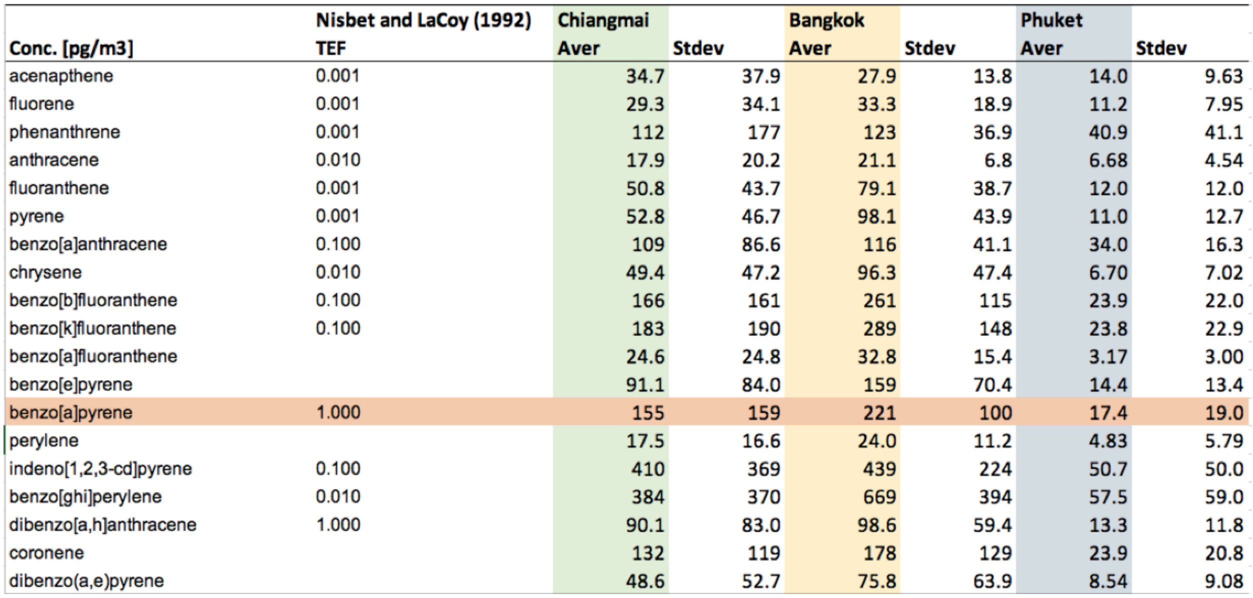
In the interest of public health, the risks *vs.* benefits of the possible alternatives must be carefully considered. For instance, it might well be that the traffic emissions result in a certain number of patients suffering from lung cancer per year. However, this risk must be balanced against the available alternatives of no vehicles or even no long distance transportation. Unless or until the creativity and technological developments offer superior methods for trapping those carcinogens, the policy makers have to make decision based on risk assessment. Since PAHs are continuously released into the atmosphere, raising concerns over the safety of urban residents and those who are living at countryside, it is therefore crucial to continue monitoring PAHs at the three air quality observatory sites. This will expand the database, and thus amend the scope of long term temporal trend analysis of PAHs in both urban and rural atmosphere.

Moreover, one should keep in mind that air quality compliance measurements should be conducted at multiple monitoring sites within the city. Therefore, a more comprehensive air monitoring network requires to be developed in order to provide a more precise risk assessment of human exposures in cities of Thailand. The combination of PAHs, WSIS, and OC/EC provides useful information to enable better source characterisation. However, the greater difficulty lies in proper source identification during the agricultural waste burning episodes (e.g. sugar cane burnings). Therefore, future work and sampling efforts should focus on finding key PAH source markers that will improve the ability to separate wood combustion originated PAHs from those generated by anthropogenic sources. The lack of insight of finger prints from various emission sources leads to inadequate description of the source identification of $PM_{2.5}$. Therefore, it becomes essential to have a more comprehensive knowledge of the source fingerprints of chemicals in $PM_{2.5}$. There are uncertainties in the estimation of source contribution by using PCA and diagnostic binary ratios. Further source apportionment techniques such as a positive matrix factorisation (PMF) and a chemical mass balance (CMB) model should be conducted to increase the reliability of source contributions.

National Policy for Controlling PAH Concentrations in Ambient Air of Thailand

Polycyclic Aromatic Hydrocarbons (PAHs) constitutes a large group of chemically related substances many of which are recognized as carcinogenic substances. To minimise human exposure there are already numerous regulations which limit their existence in ambient air. There are currently no EU Directives or other guidance to member states, which bear directly on either emissions or air quality objectives of PAH. PAH are, however, covered by the Persistent Organic Pollutant (POP's) -Protocol under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution [UN ECE CLRTAP]; under the Protocol, emissions of four PAH compounds have to be reported annually; in addition, emissions of PAH in 2010 may not exceed the levels of 1990 (or any other base year between 1985 and 1995). The Protocol will enter into force after 16 ratifications, which is expected between 2001 and 2002. The European Community is a party to the Convention and will therefore have to fulfil the obligations of the Protocol after ratification. Of the EU member states currently only Italy has legally enforceable ambient air standards for PAH but five others have sufficient concern that they have issued guidance for planning and policy purposes. All have used B[a]P as a marker for PAH and one (Sweden) has gone further and set a value for Fluo as well. As illustrated in Table 8.1, the average concentrations of B[a]P in $PM_{2.5}$ collected from Chiang-Mai, Bangkok and Phuket were clearly illustrated. The statistical descriptions of particulate B[a]P collected at Chinag-Mai, Bangkok and Phuket were 115±159 pg m^{-3}, 221±100 pg m^{-3} and 17.4±19.0 pg m^{-3}, respectively (see Fig. 8.1).

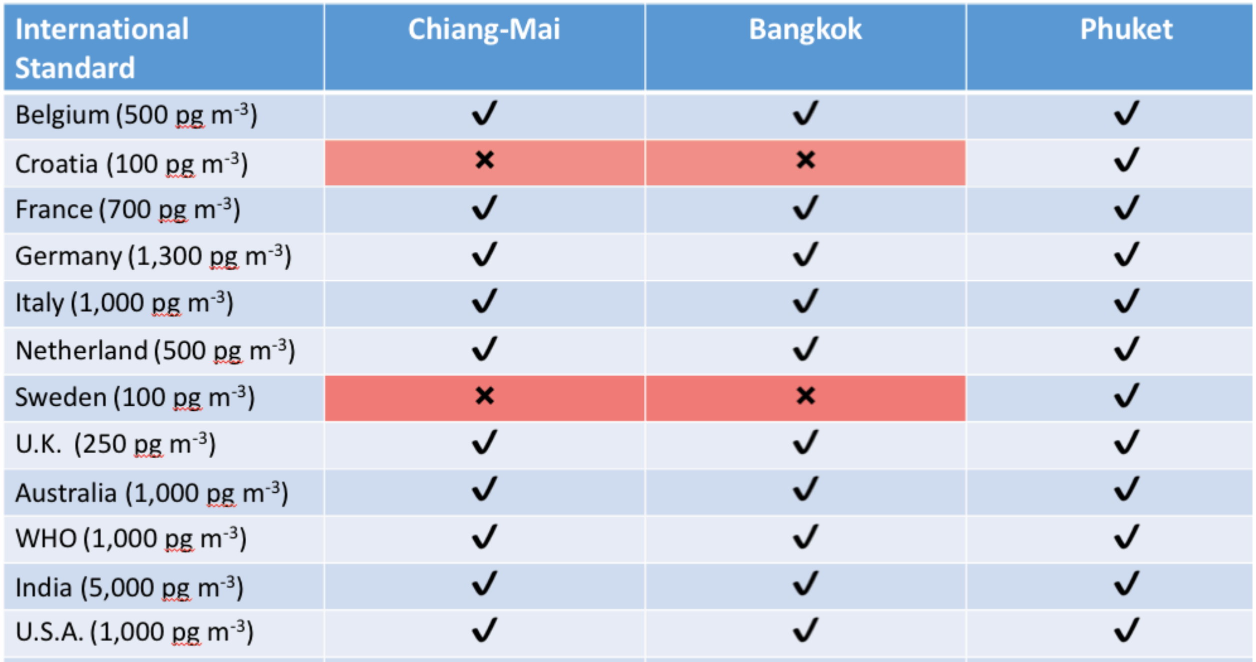
Table 8.1. Statistical descriptions of PAH contents in $PM_{2.5}$ collected at Chiang-Mai, Bangkok and Phuket



	Nisbet and LaCoy (1992)	Chiangmai		Bangkok		Phuket	
Conc. [pg/m3]	TEF	Aver	Stdev	Aver	Stdev	Aver	Stdev
acenapthene	0.001	34.7	37.9	27.9	13.8	14.0	9.63
fluorene	0.001	29.3	34.1	33.3	18.9	11.2	7.95
phenanthrene	0.001	112	177	123	36.9	40.9	41.1
anthracene	0.010	17.9	20.2	21.1	6.8	6.68	4.54
fluoranthene	0.001	50.8	43.7	79.1	38.7	12.0	12.0
pyrene	0.001	52.8	46.7	98.1	43.9	11.0	12.7
benzo[a]anthracene	0.100	109	86.6	116	41.1	34.0	16.3
chrysene	0.010	49.4	47.2	96.3	47.4	6.70	7.02
benzo[b]fluoranthene	0.100	166	161	261	115	23.9	22.0
benzo[k]fluoranthene	0.100	183	190	289	148	23.8	22.9
benzo[a]fluoranthene		24.6	24.8	32.8	15.4	3.17	3.00
benzo[e]pyrene		91.1	84.0	159	70.4	14.4	13.4
benzo[a]pyrene	1.000	155	159	221	100	17.4	19.0
perylene		17.5	16.6	24.0	11.2	4.83	5.79
indeno[1,2,3-cd]pyrene	0.100	410	369	439	224	50.7	50.0
benzo[ghi]perylene	0.010	384	370	669	394	57.5	59.0
dibenzo[a,h]anthracene	1.000	90.1	83.0	98.6	59.4	13.3	11.8
coronene		132	119	178	129	23.9	20.8
dibenzo(a,e)pyrene		48.6	52.7	75.8	63.9	8.54	9.08

It is worth mentioning that the annual concentration of B[a]P collected at Chiang-Mai, Bangkok and Phuket were 6.5 times, 4.5 times and 57 times lower than WHO guideline, which is 1,000 pg m^{-3}. It is also interesting to note that the annual concentration of B[a]P collected at Chiang-Mai, Bangkok and Phuket were 33 times, 23 times and 285 times lower than India guideline, which is 5,000 pg m^{-3}. Although the annual concentration of B[a]P collected from the tree cities are generally lower than the majority of international guideline, there are some international standards that have very strict regulations. Croatia and Sweden limit B[a]P content in ambient air not to exceed 100 pg m^{-3}. In the case of adopting Croatia and Sweden's regulation, the annual concentration of B[a]P collected at Chiang-Mai and Bangkok will exceed the guideline (Table 8.2).

Table 8.2. International guideline of B[a]P in comparison with those annual concentration collected at Chiang-Mai, Bangkok, and Phuket



International Standard	Chiang-Mai	Bangkok	Phuket
Belgium (500 pg m^{-3})	✓	✓	✓
Croatia (100 pg m^{-3})	✗	✗	✓
France (700 pg m^{-3})	✓	✓	✓
Germany (1,300 pg m^{-3})	✓	✓	✓
Italy (1,000 pg m^{-3})	✓	✓	✓
Netherland (500 pg m^{-3})	✓	✓	✓
Sweden (100 pg m^{-3})	✗	✗	✓
U.K. (250 pg m^{-3})	✓	✓	✓
Australia (1,000 pg m^{-3})	✓	✓	✓
WHO (1,000 pg m^{-3})	✓	✓	✓
India (5,000 pg m^{-3})	✓	✓	✓
U.S.A. (1,000 pg m^{-3})	✓	✓	✓

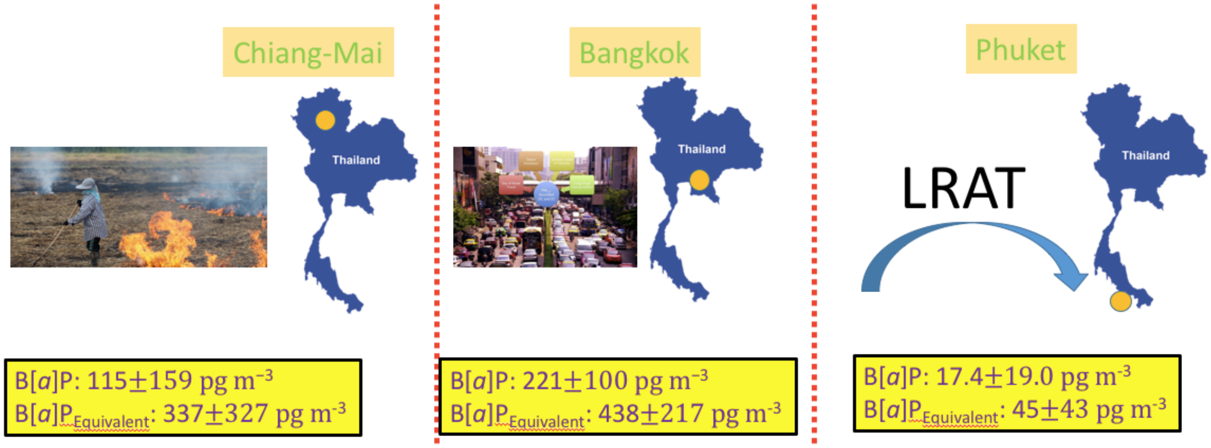


Figure 8.1. Annual concentration of $PM_{2.5}$ bounded B[a]P collected at Chiang-Mai, Bangkok and Phuket

As a consequence, it appears rationale to adopt the WHO, Italy, Australia and US EPA guideline, which regulate B[a]P content not to exceed 1 ng m^{-3} or 1,000 ng m^{-3} in 24 h of monitoring period. By applying these four guideline, the annual concentration of B[a]P will fall in acceptable level and this will allow the government to implement other policies for enhancing air quality level to meet U.K., Croatia and Sweden's guideline.

Acknowledgement

We would like to thank the Thailand Research Fund (TRF) for financial support and special thanks are extended to the Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Science (IEECAS) for providing the necessary research equipment and sample analysis. We would like to also express our sincere gratitude to the research staffs of National Astronomical Research Institute of Thailand (NARIT), Prince of Songkla University and Rajchbat ValaiAlongkorn University for their kind assistances on field samplings.

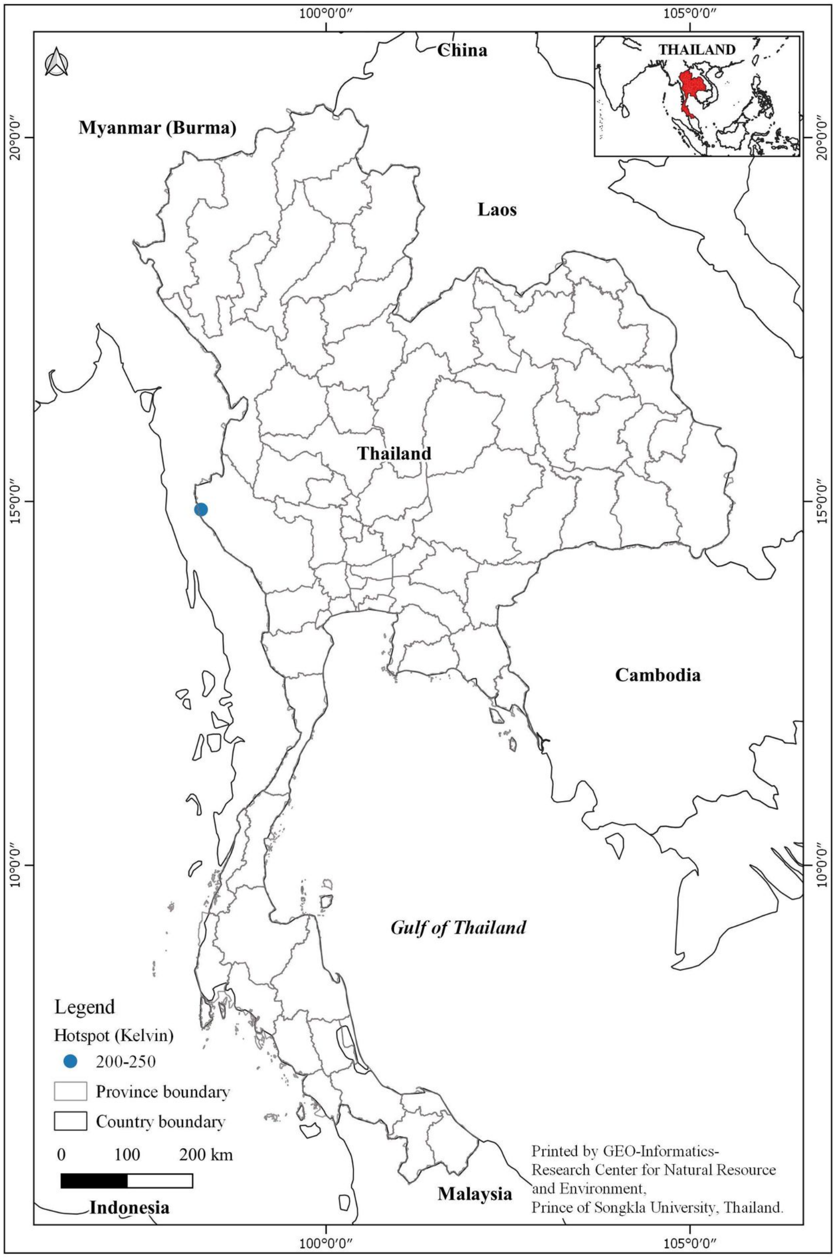
I would also like to express my sincere gratitude to Prof. Dr .Junji Cao and Prof. Dr. Yongming Han for supervising Dr. Danai Tipmanee and Ms. Chormsri Choochuay for learning DRI standard operating procedure (i.e. DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples-Method IMPROVE_A) which was developed by Desert Research Institute, Division of Atmospheric Sciences 2214 Raggio Parkway Reno, NV 89506. We were fortunate enough to learn the technique of combustion chamber experiment (i.e. 8 cubic meter cavity container) coupled with a dilution sampler (Model 18, Baldwin Environmental Inc. Reno, NV, USA) as well as the concept of modified combustion efficiency (MCE), calculation of AAE and quantification of Brown Carbon absorption, and computation of absorption emission factor from Dr. Qiyuan Wang. It was so generous of Dr. Qiyuan to transfer the knowledge of quantification of Black Carbon mass, size and mixing state and light absorption measurements for the combustion chamber experiment.

Dr. Li Xing and Dr. Guohui Li, two experts of the Weather Research and Forecasting Model compled with Chemistry (WRF-Chem) have also transferred some insights associated with using this physico-chemical model to simulate elemental carbon concentrations in Thailand in 2017. The goals were to quantify the respective contributions of local emissions and regional transport outside Thailand to EC pollution in Thailand, and to identify the most effective emission control strategy for decreasing EC pollution. The simulated EC concentrations in Chiang Mai, Bangkok, and Phuket were comparable with the observation data.

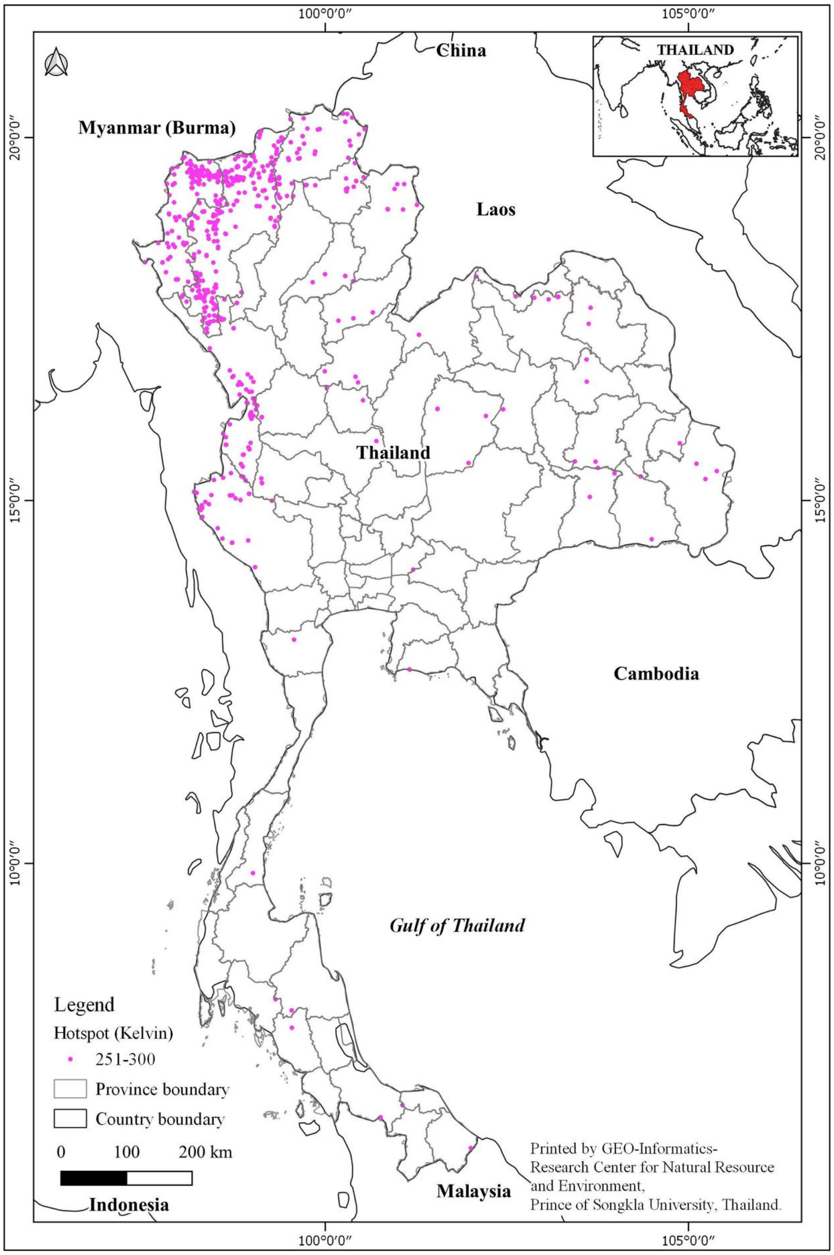
Last but not least after more than three years of research collaboration with IEECAS, we have learned a lot of "the frontier spirit" for pioneering works in atmospheric and sedimentology research from our Chinese friends. As Mr. Xi Jinping had clearly stated in the 19th National Congress of the Communist Party of China, which was successfully held in Beijing , that "we would complete the building of a moderately prosperous society in all respects by 2020, basically realise socialist modernisation by 2035, and develop China into a great modern socialist country that is prosperous, strong, democratic, culturally advanced, harmonious, and beautiful by the middle of the century". China and Thailand are major Asia-Pacific countries, which are, at the same time, close neighbours and friends. The 19th National Congress will also provide China-Thailand relations with new opportunities.Without any doubt, this bilateral "Shino-Thai Research Collaboration" does not only influence the research movement activities under the context of climate change but also highly impact the long-term cultural and socio-economic prosperity for both countries.

Appendix

Appendix 1. Hot spot distribution (200~250 °K) in Thailand in March 2020



5128 Appendix 2. Hot spot distribution (251~300 °K) in Thailand in March 2020



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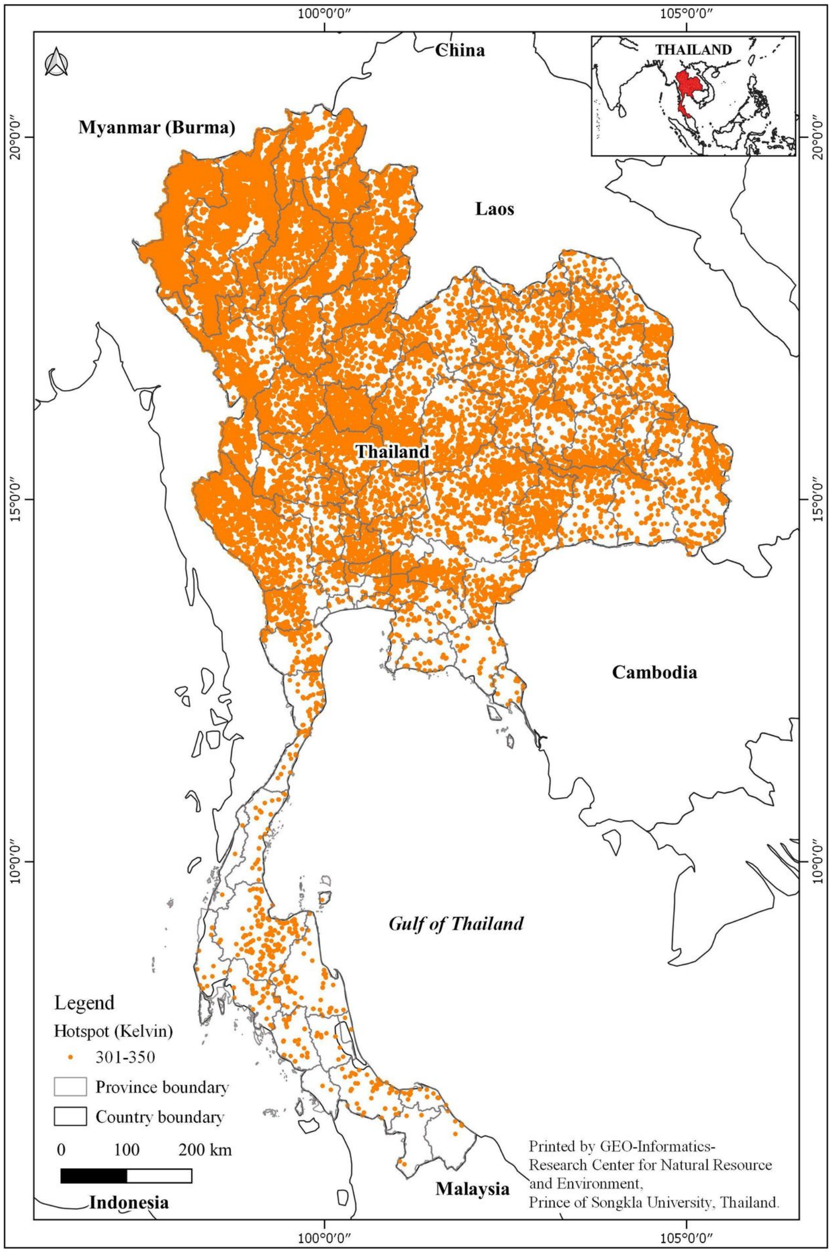
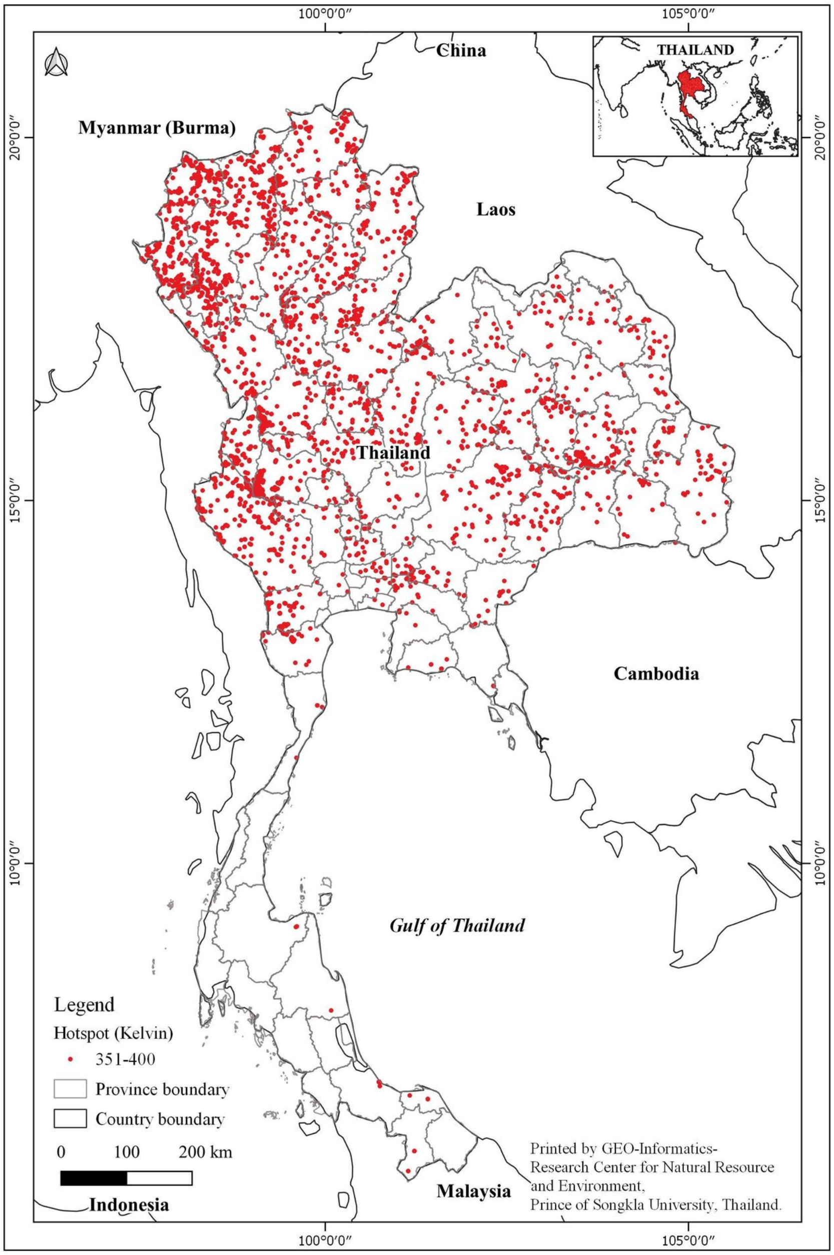
Appendix 3. Hot spot distribution (301~350 °K) in Thailand in March 2020



5136 Appendix 4. Hot spot distribution (351~400 °K) in Thailand in March 2020



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Appendix 5. Analytical results of NIST SRM1941b

ข้อมูล SRM

SRM	CODE	ค่าที่กำกับมา (นนก./ก.นน.แห้ง)	ค่าที่วิเคราะห์ได้ (นนก./ก.นน.แห้ง)	%Accuracy
Phenanthrene	Phe	406±44	464±16	86±4
Fluoranthene	Fluo	651±50	721±45	88±7
Pyrene	Pyr	581±39	538±34	106±7
Chrysene	Chry	291±31	336±25	83±8
Benzo[a]anthracene	B[a]A	335±25	289±26	114±8
Benzo[b]fluoranthene	B[b]F	453±21	480±25	94±6
Benzo[k]fluoranthene	B[k]F	225±18	229±19	100±8
Benzo[e]pyrene	B[e]P	325±25	321±10	101±3
Indeno[1,2,3-cd] pyrene	Ind	341±57	291±14	115±4
Benzo[g,h,i]perylene	B[g,h,i]P	307±45	267±17	113±6

Appendix 6. Analytical results of PAHs (ng Kg^{-1} dry weight) in Songkla Lake sediments

CORE 1

สถานี	**Phe**	**An**	**Fluo**	**Pyr**	**11H-B[a]F**	**11H-B[b]F**	**B[a]A**	**Chry**	**B[b]F**	**B[k]F**	**B[e]P**	**B[a]P**	**Ind**	**D[a,h]A**	**B[g,h,i]P**	**∑PAHs**
SL101	11.89	1.97	13.73	16.96	1.91	3.27	2.71	3.91	17.86	2.44	6.58	31.4	34.2	1.11	19.41	169.37
SL102	15.14	2.61	21.17	36.96	2.56	4.64	3.17	4.68	24.6	2.56	10.19	49.38	51.44	0.91	49.19	279.2
SL103	18.2	2.9	25.1	29.53	4.16	7.52	5.08	7.47	20.69	2.72	7.43	35.66	39.2	1.17	20.85	227.67
SL104	16.54	2.75	21.66	25.17	3.68	6.3	3.55	5.73	25.02	2.85	8.24	41.22	39.22	1.07	24.37	227.36
SL105	27.09	4.68	65.93	197.31	4.73	6.69	3.51	7.47	69.04	16.07	7.12	143.76	239.17	1.09	424.01	1217.67
SL106	18.06	2.93	33.88	32.71	10.09	14.41	6.16	15.41	27.79	3.44	9.37	58.69	39.42	1.46	19.98	293.81
SL107	13.7	2.25	32.54	26.98	11.89	16.16	5.28	18.59	11.82	2.59	7.25	38.46	27.99	1.15	11.08	227.72
SL108	18.14	3.22	37.67	35.04	12.32	17.03	5.2	33.43	20.65	2.21	6.63	45.54	25.82	0.96	13.18	277.04
SL109	24.22	3.97	43.44	42.69	14.42	21.03	4.83	52.93	19.27	2.2	5.37	55.32	23.74	1.32	11.75	326.49
SL110	31.3	5.5	38.89	49.18	23.12	36.49	10.74	45.87	24.83	3.04	4.23	90.54	26.82	0.82	8.51	399.88
SL111	43.51	7.19	33.39	41.74	13.66	19.38	3.55	94.75	7.5	2.14	1.35	65.07	13.41	0.38	4.87	351.89
SL112	21.27	5.99	37.06	47.42	21.91	30.78	7.7	121.31	9.01	3.19	2.2	68.95	11.69	0.84	5.55	394.9
SL113	25.65	7.39	33.66	41.48	16.43	25.2	5.56	125.29	13.17	2.56	1.92	124.27	16.31	1.95	7.37	448.2
SL114	30.11	6.32	24.17	29.03	18.01	22.74	5.82	81.45	6.01	2.07	1.05	78.46	10.94	0.75	4.02	320.93
SL115	63.7	7.97	31.92	40.81	14.75	20.91	5.16	96.36	2.55	1	1.2	44.81	10.84	1.12	4.36	347.48
SL116	49.9	8.61	38.06	46.94	25.1	33.63	8.94	89.5	3.74	1.36	1.48	60.25	13.71	0.95	2.64	384.81
SL117	32.12	5.38	23.2	27.33	14.24	20.22	4.56	68.18	2.16	1.63	1.15	61.04	9.5	1.4	2.58	274.69
SL118	17.75	4.96	24.53	27.84	18.44	24.73	6.52	74.69	2.07	1.2	0.83	63.79	11.15	0.94	2.83	282.27
SL119	19.99	4.4	26.18	29.83	23.08	25.92	8.71	71.74	3.71	1.28	0.94	43.51	11.34	0.21	2.57	273.4
SL120	20.24	4.66	31.66	35.24	29.23	31.37	9.51	75.38	4.39	1.71	1.38	66.01	12.92	0.99	2.97	327.66
SL121	19.3	5.45	32.46	40.21	31.64	31.35	10.85	54.64	8.05	2.75	2.96	131.42	22.08	1.38	5.6	400.14
SL122	18.12	4.3	36.02	43.51	31.32	33.3	11.87	37.73	8.21	2.55	2.66	50.68	15.3	0.54	2.34	298.43
SL123	16.03	5.34	35.92	46.95	37.08	43.51	15.76	37.52	11.41	4.11	3.37	93.95	20.03	0.84	4.02	375.84
SL124	24.19	5.73	36.93	66.67	30.04	42.82	7.05	20.2	17.24	4.19	4.84	125.72	21.97	0.58	3.17	411.32
SL125	22.25	4.54	34.32	49.98	21.54	36.63	8.53	16.11	20.66	5.71	7.86	158.22	15.06	0.86	5.62	407.9
SL126	16.81	2.93	15.89	24.35	14.56	23.62	3.55	10.97	11.21	3.65	3.04	77.2	32.86	0.42	3.01	244.07

SL127	11.91	2.97	18.37	23.77	23.35	30.39	15.44	11.57	10.92	4.17	2.63	60.26	28.84	0.83	4.79	250.21
SL128	14.03	3.3	20.11	26.21	33.81	64.24	8.09	22.26	7.54	3.71	4.9	156.45	15.16	1.38	4.83	386.01
SL129	12.85	2.01	12.01	14.78	13.04	22.02	6.48	14.68	4.44	1.67	1.68	53.59	12.65	0.39	2.07	174.35
Average	23.24	4.56	30.34	41.26	17.93	24.7	7.03	45.51	14.33	3.13	4.13	74.95	29.41	0.96	23.36	344.85
S.D.	11.79	1.82	10.75	32.06	9.83	13.34	3.42	37.1	13.14	2.71	2.88	37.38	41.81	0.38	77.7	296.1

CORE 2

สถานี	**Phe**	**An**	**Fluo**	**Pyr**	**11H-B[a]F**	**11H-B[b]F**	**B[a]A**	**Chry**	**B[b]F**	**B[k]F**	**B[e]P**	**B[a]P**	**Ind**	**D[a,h]A**	**B[g,h,i]P**	**∑PAHs**
SL201	6.34	1.27	11.22	16.06	7.1	6.77	3.8	6.35	11.15	2.15	5.95	21.17	23.21	0.99	6.71	130.24
SL202	5.56	1.13	14.25	23.78	9.97	9.74	5.89	8.9	16.43	3.24	6.97	22.41	24.2	1.47	6.68	160.62
SL203	5.13	0.84	12.81	18.11	6.92	8.85	3.19	7.33	10.09	2.59	5.04	18.44	20.42	0.55	6.81	127.12
SL204	7.19	0.93	15.58	16.66	18.78	9.65	2.82	7.91	7.02	1.54	3.49	17.8	15.18	0.41	5.07	130.03
SL205	6.33	1.35	17.05	13.77	22.74	10.95	3.23	8.6	7.09	2.44	4.42	33.08	19.44	0.47	6.9	157.86
SL206	5.72	0.73	10	6.23	12.74	5.16	1.85	5.47	8.16	2.26	4.49	26.25	19.65	0.63	6.32	115.66
SL207	5.33	0.82	8.89	4.52	11.48	5.11	1.88	5.08	7.37	1.97	3.63	18.62	16.12	0.85	4.91	96.58
SL208	4.19	0.64	9.04	4.7	11.93	5.77	2.06	5.08	7.26	2.07	3.39	16.33	14.75	0.44	4.22	91.87
SL209	4.93	1.35	14.43	7.16	20.8	10.65	4.3	7.51	14.89	4.16	6.22	33.86	29.2	1.03	8.81	169.3
SL210	2.77	0.39	3.56	2.3	3.86	1.96	0.95	2.16	3.84	1.13	1.57	8.49	8.39	0.22	2.98	44.57
SL211	3.11	0.26	2.13	2.75	1.19	0.54	0.34	0.85	1.69	0.48	0.74	3.49	5.49	0.18	2.86	26.1
SL212	2.08	0.21	1.49	1.23	1.39	0.54	0.39	1.16	1.63	0.38	0.5	2.95	4.16	0.12	1.78	20.01
SL213	3.66	0.23	1.82	1.53	1.18	0.51	0.45	1.15	1.64	0.44	0.55	2.8	4.06	0.11	1.62	21.75
SL214	1.97	0.19	1.81	2.74	1.13	0.55	0.32	0.77	1.47	0.46	0.71	3.25	5.17	0.16	2.89	23.59
SL215	3.78	0.21	2.66	4.79	1.19	0.54	0.37	1.12	1.49	0.42	0.92	3.28	4.58	0.08	3.81	29.24
SL216	1.84	0.19	1.83	3.28	1.2	0.54	0.41	1.01	1.56	0.44	0.74	3.37	5.3	0.17	3.38	25.26
Average	4.37	0.67	8.04	8.1	8.35	4.86	2.02	4.4	6.42	1.64	3.08	14.72	13.71	0.49	4.73	85.61
S.D.	1.7	0.44	5.77	7.11	7.5	4.15	1.72	3.15	4.9	1.16	2.28	11	8.44	0.41	2.12	61.86

CORE 3 (ng kg^{-1} dry weight)

สถานี	**Phe**	**An**	**Fluo**	**Pyr**	**11H-B[a]F**	**11H-B[b]F**	**B[a]A**	**Chry**	**B[b]F**	**B[k]F**	**B[e]P**	**B[a]P**	**Ind**	**D[a,h]A**	**B[g,h,i]P**	**∑PAHs**

SL301	7.53	1.31	19.53	16.05	9.92	11.91	4.01	9.22	11.62	2.52	5.76	30.61	24.48	2.01	8.43	164.91
SL302	5.85	1.28	18.18	18.91	11.76	12.16	4.73	9.7	13.44	2.87	6.51	28.65	23.06	1.75	8.33	167.18
SL303	5.59	1.34	17.76	18.66	13.06	13.14	5.78	10.94	14.95	2.76	6.54	23.89	24.82	1.5	6.89	167.62
SL304	5.97	1.45	15.51	16.24	12.35	11.43	5	9.41	15.04	2.99	6.47	21.27	23.15	1.53	6.88	154.69
SL305	5.12	1.19	13.08	13.4	8.79	8.49	4.71	7.86	12.05	2.5	5.2	16.9	19.72	1.36	5.53	125.9
SL306	12.24	0.97	11.68	12.17	6.17	6.08	3.38	6.21	8.27	1.69	3.41	11.46	13.92	0.56	5.4	103.61
SL307	10.8	0.67	9.6	8.93	4.75	4.89	2.53	5.05	8.92	1.65	3.5	11.88	13.28	0.7	4.27	91.42
SL308	4.99	0.72	8.99	8.31	4.5	5.35	2.57	5.69	7.28	1.46	2.9	10.27	11.97	0.68	3.65	79.33
SL309	6.02	0.76	8.3	7.75	4.6	4.69	2.41	5.33	7.44	1.42	2.71	10	11.76	0.68	3.58	77.45
SL310	4.8	0.53	6.05	5.57	2.68	3.01	1.63	3.86	5.69	1.17	2	7.46	9.51	0.7	3.03	57.69
SL311	9.32	0.57	5.63	5.51	2.06	2.25	1.09	3.2	3.94	0.98	1.56	6.13	8.06	0.3	2.87	53.47
SL312	6.54	0.4	4.28	4.08	1.51	1.74	0.81	2.6	4.03	0.85	1.24	5.09	6.48	0.35	2.5	42.5
SL313	7.18	0.27	2.48	2.68	1.56	0.68	0.38	1.69	2.2	0.49	0.69	3.04	4.69	0.2	1.76	29.99
SL314	6.76	0.31	2.49	2.38	1.78	0.88	0.36	1.76	3.08	0.73	0.84	4.54	5.75	0.18	2.17	34.01
SL315	5.44	0.17	1.95	2.21	1.45	0.66	0.3	1.78	2.32	0.56	0.59	3.74	4.55	0.17	2.02	27.91
SL316	6.19	0.32	2.26	2.2	1.24	0.51	0.31	1.09	1.95	0.47	0.51	4.34	4.02	0.12	1.32	26.85
SL317	5.35	0.34	2.15	2.18	1.43	0.64	0.35	1.26	1.88	0.48	0.5	2.66	4.2	0.18	1.53	25.13
SL318	6.89	0.28	2.36	2.18	1.53	0.55	0.33	1.4	1.91	0.43	0.47	2.08	4	0.22	1.15	25.78
SL319	5.08	0.23	1.99	2.14	1.29	0.47	0.33	1.63	2.2	0.58	0.61	2.71	4.92	0.12	1.7	26
SL320	3.86	0.26	2.06	2	1.6	0.58	0.34	1.54	2.04	0.44	0.55	2.31	3.86	0.09	1.59	23.12
SL321	4.08	0.24	1.61	1.62	1.23	0.39	0.24	0.99	1.81	0.41	0.47	2.13	3.69	0.2	1.46	20.57
SL322	5.62	0.26	1.84	1.7	1.19	0.42	0.3	0.97	1.68	0.47	0.45	2.23	3.9	0.16	1.56	22.75
SL323	6.23	0.3	1.98	1.87	1.08	0.36	0.31	0.99	1.91	0.44	0.43	2.07	4.4	0.07	1.5	23.94
SL324	5.21	0.24	1.92	2.01	1.07	0.4	0.3	1.01	1.92	0.42	0.51	2.39	5.08	0.13	1.58	24.19
SL325	2.37	0.21	1.5	1.6	1.14	0.35	0.32	1.17	1.88	0.43	0.47	2.07	4.3	0.16	1.41	19.38
SL326	6.05	0.23	2.45	2.53	1.09	0.47	0.42	1.25	1.64	0.37	0.44	1.98	4.12	0.15	1.62	24.81
SL327	6.58	0.24	2.08	1.98	1	0.34	0.25	0.9	1.43	0.3	0.47	1.78	3.86	0.16	1.34	22.71
SL328	5.14	0.33	2.04	1.96	1.09	0.36	0.34	1.02	1.68	0.35	0.43	1.82	4.3	0.12	1.43	22.41
Average	6.17	0.55	6.13	6.03	3.68	3.33	1.57	3.55	5.15	1.08	2.01	8.05	9.28	0.52	3.09	60.19
S.D.	1.98	0.41	5.84	5.76	3.86	4.25	1.79	3.22	4.52	0.88	2.16	8.54	7.24	0.57	2.25	51.33

Appendix 7. Analytical results of PAHs (ng Kg^{-1} dry weight) in Nonghan Lake sediments

Core 1

สถานี	Phe	An	Fluo	Pyr	11H-B[a]F	11H-B[b]F	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑PAHs
HK101	52.31	8.24	42.78	37.01	7.91	11.52	7	13.11	32.5	5.2	12.84	36.51	47.36	1.97	17.5	333.76
HK102	42.05	6.4	38.55	34.33	9.26	12.53	6.09	13.07	33.13	5.6	13.55	44.21	43.6	1.56	15.68	319.61
HK103	44.73	7.71	41.69	34.55	9.63	13.93	7.97	14.8	40.63	7.03	15.83	38.81	54.23	1.81	19.85	353.2
HK104	52.55	7.92	50.14	41.95	10.94	16.15	8.63	17.79	37.63	6.69	15.72	49.71	51.03	1.7	18.6	387.15
HK105	41.11	7.67	40.86	32.92	10.07	14.34	7.25	15.2	39.18	6.59	14.97	42.6	48.7	1.9	17.38	340.74
HK106	46.56	8.29	46.83	41.63	10.79	16.54	8.66	17.81	38.5	6.83	14.85	48.98	49.69	2.27	17.45	375.68
HK107	42.16	7.02	44.49	40.27	14.49	21.49	10.75	21.52	46.77	7.07	17.05	52.02	51.37	2.9	17.78	397.15
HK108	26.3	4.77	39.25	35.76	13.92	22.38	9.16	22.24	45.32	6.5	15.78	46.91	42.53	1.71	14.43	346.96
HK109	30.69	4.27	35.48	34.05	13.34	17.33	6.03	15.84	40.09	6	15.78	83.27	35.84	1.12	13.14	352.27
HK110	20.57	4.4	33.75	29.48	14.04	19.81	8	18.31	39.33	5.48	13.51	44.21	33.03	2.28	11.69	297.89
HK111	19.06	3.69	28.3	25.04	121.03	16.2	5.5	12.83	34.39	4.1	10.29	30.57	23.98	2.37	7.43	344.78
HK112	16.82	4.18	30.86	30.84	15.94	20.12	8.86	16.74	38.96	5.77	11.99	33.84	34.31	2.44	10.22	281.89
HK113	16.42	3.47	25.53	26.51	15.19	16.66	9.13	15.48	40.03	6.28	12.65	37.01	39.96	2.42	11.71	278.45
HK114	13.26	3.47	25	25.21	13.42	16.89	7.31	14.19	36.18	5.28	11.77	27.68	31.59	1.98	8.82	242.05
HK115	12.5	3.21	21.46	24.99	13.55	16.64	8.74	16.88	54.62	7.91	15.83	21.05	38.24	1.49	9.54	266.65
HK116	11.43	3.24	19.9	24.59	12.51	16.76	8.8	18	61.26	6.88	17.73	22.26	41.46	1.45	9.34	275.61
HK117	10.24	2.94	17.28	22.04	11.52	16.27	9.08	20.33	65.82	8.87	20.51	17.25	42.29	1.47	8.77	274.68
HK118	12.74	3.17	18.24	22.84	12.02	17.04	8.93	21.66	86.03	9.64	24.78	20.5	55.02	1.96	12.09	326.66
HK119	14.89	3.7	20.74	26.02	14.77	21.19	11.79	30.53	109.44	14.18	31.63	24.37	62.31	2.05	11.62	399.23
HK120	10.33	3.58	20.16	25.88	15.18	22.52	12.03	30.98	120.05	15.39	32.62	23.41	63.4	2.23	11.78	409.54
HK121	13.84	4.84	29.45	40.86	25.68	36.47	22.39	63.46	203.18	25.89	54.07	30.88	100.99	3.7	16.84	672.54
HK122	18.26	4.2	26.04	36.83	22.92	31.32	17.51	52.6	194.65	20.73	51.83	29.71	76.31	3.07	13.18	599.16
HK123	17.9	4.59	27.14	40.51	26.94	34.43	18.65	54.75	192.1	23.35	51.71	29.83	97.45	2.93	17.81	640.09
HK124	15.49	4.92	30.78	47.83	29.02	41.14	24.97	73.2	274.03	37.04	73.47	38.48	135.59	4.35	23.47	853.78
HK125	21.23	5.78	35.17	62.07	42.12	58.3	34.97	99.7	382.79	42.83	93.67	42.41	159.7	5.74	25.16	1111.64
HK126	24.14	6.02	38.85	64.66	39.08	55.5	32.19	98.17	355.13	43.53	84.5	43.37	128.79	4.25	20.17	1038.35

Average	24.91	5.07	31.87	34.95	20.97	23.21	12.32	31.12	101.61	13.1	28.81	36.92	61.11	2.43	14.67	443.06
S.D.	14.03	1.77	9.52	10.92	22.23	12.39	7.97	25.91	102.27	11.87	24.08	13.77	34.93	1.06	4.69	297.42

Core 2

สถานี	**Phe**	**An**	**Fluo**	**Pyr**	**11H-B[a]F**	**11H-B[b]F**	**B[a]A**	**Chry**	**B[b]F**	**B[k]F**	**B[e]P**	**B[a]P**	**Ind**	**D[a,h]A**	**B[g,h,i]P**	**∑PAHs**
HK201	37.12	6.49	36.79	36.79	12.57	16.21	6.77	13.45	32.72	5.28	12.7	29.75	50.18	1.04	17.11	314.97
HK202	38.12	6.89	41.1	42.7	16.39	20.84	8.14	16.71	31.26	5.02	12.84	27.12	48.09	1.33	16.16	332.71
HK203	37.86	6.43	36.04	37.28	10.53	14.43	7.16	13.47	24.87	4.22	10.54	23.34	43.23	2.03	15.31	286.74
HK204	36.31	6.56	37.6	43.29	19.59	25.01	8.81	18.98	35.78	5.62	12.53	29.79	45.91	1.47	15.07	342.32
HK205	19.12	5.2	36.68	43.45	26.56	31.99	8.14	20.19	36.87	4.51	10.8	38.24	37.12	2.42	10.42	331.71
HK206	22.74	5.41	43.94	42.5	24.5	29.4	8.22	16.18	35.95	5.17	10.44	48.7	40.23	1.64	13.17	348.19
HK207	22.92	5.77	44.02	42.02	22.08	29.39	9.2	17.01	45.18	3.95	12.37	47.35	43.97	0.88	12.39	358.5
HK208	26.72	6.33	43.45	43.28	18.66	25.76	9.41	17.75	47.61	6.21	16.68	56.55	52.34	2.5	14.07	387.32
HK209	34.35	5.72	45.81	45.25	18.51	26.13	9.63	20.19	55.02	5.95	16.88	28.13	46.11	2.35	11.82	371.85
HK210	26.05	6.73	41.21	38.38	15.96	26.2	10.1	20.58	66.26	7.71	22.34	38.72	57.72	2.6	13.77	394.33
HK211	17.95	3.93	26.01	22.57	9.26	15.21	4.45	13.01	36.86	4.95	13.46	16.06	32.11	0.75	7.71	224.29
HK212	17.81	4.1	28.03	22.54	9.89	18.46	6.84	15.54	50.86	6.66	16.74	24.72	40.5	0.84	10.43	273.96
HK213	16.97	3.2	21.53	18.92	9.82	14.52	5.01	14.61	42.75	5.57	15.63	18.81	37.46	2.25	8.36	235.41
HK214	11.98	2.87	18.67	17.1	9.25	13.32	4.95	14.72	38.79	6.31	15.46	17.02	36.45	1.03	7.57	215.49
HK215	15.03	1.75	12.35	12.55	7.08	8.54	3.78	11.91	38.35	5.05	13.39	12.43	29.55	0.87	5.46	178.09
HK216	17.22	1.54	12.51	12.94	5.42	8.82	4.48	12.31	36.46	4.15	12.79	12.51	23.98	0.56	4.75	170.44
Average	24.89	4.93	32.86	32.6	14.75	20.26	7.19	16.04	40.97	5.4	14.1	29.33	41.56	1.54	11.47	297.9
S.D.	9.1	1.8	11.44	12.34	6.44	7.55	2.09	2.89	10.13	1.01	3.08	13.36	8.76	0.72	3.83	94.54

Core 3

สถานี	**Phe**	**An**	**Fluo**	**Pyr**	**11H-B[a]F**	**11H-B[b]F**	**B[a]A**	**Chry**	**B[b]F**	**B[k]F**	**B[e]P**	**B[a]P**	**Ind**	**D[a,h]A**	**B[g,h,i]P**	**∑PAHs**
HK301	26.98	3.86	27.09	24.83	7.05	12.13	5.86	13.32	19.14	3.79	8.13	14.16	24.43	1.6	10.36	202.73
HK302	26.13	3.72	23.35	20.7	3.61	9.22	3.5	4.38	12.27	3.18	7.53	13.52	24.94	1.61	11.38	169.04
HK303	35	5	29.63	26.3	2.6	4.76	3.57	4.03	13.17	3.58	7.8	15.92	37	1.5	14.84	204.7

HK304	27.07	3.15	24.32	20.25	2.25	3.88	3.14	2.32	9.46	2.7	5.64	13.98	27.89	1.42	12.58	160.05
HK305	21.84	2.84	19.54	15.5	1.91	3.01	2.38	5.82	9.9	2.51	5.26	12.62	24.03	2.06	10.5	139.72
HK306	17.54	2.29	15.06	12.61	1.68	2.6	1.93	4.26	8.15	1.83	4.65	9.48	19	1.18	8.72	110.98
HK307	18.95	2.75	16.42	15.04	2.64	4.43	2.88	5.52	7.77	1.75	4.68	10.75	19.3	1.29	7.92	122.09
HK308	20.58	3.24	16.7	14.51	4.17	6.47	3.09	2.37	11.22	1.94	4.71	12.02	17.41	1.78	6.83	127.04
HK309	22.04	1.36	18.04	14.15	3.99	6.19	2.39	7.19	13.96	2.01	6.32	9.56	17.25	4.47	6.93	135.85
HK310	17.65	2.47	16.5	10.67	3.42	5.13	2.69	7.31	13.48	2.15	4.86	21.3	18.27	1.3	5.66	132.86
HK311	15.28	2.35	20.17	10.84	4.35	6.3	2.53	3.38	14.38	2.5	4.61	23.86	16.46	2.05	5.32	134.38
HK312	14.89	2.61	25.28	13.7	4.86	6.9	2.84	8.61	12.22	2.07	4.09	23.96	16.74	1.47	5.77	146.01
HK313	13.06	3.1	29.55	16.87	6.41	9.63	3.32	8.7	14.33	2.14	4.76	24.11	18.57	1.81	6.88	163.24
HK314	21.09	5.75	51.73	34.12	16.51	20.13	6	14.79	26.39	3.37	7.86	38.18	26.96	1.12	8.75	282.75
HK315	18.13	5.23	29.14	21.58	10.61	13.48	3.85	7.96	51	5.96	13.34	23.33	36.1	1.72	9.77	251.2
HK316	17.56	6.75	39.37	34.74	21.85	28.29	10.49	19.54	55.25	6.37	16.83	25.09	39.4	1.75	9.82	333.1
HK317	23.06	9.75	56.85	51.44	39.31	49.53	18.22	33.58	82.78	10.17	26.63	26.61	63.12	1.66	13.57	506.28
HK318	26.46	13.32	68.71	55.31	45.22	56.93	24.73	41.86	113.42	14.16	34.05	33.28	80.1	2.5	16.31	626.36
HK319	19.21	7.52	52.57	37.13	32.3	44.39	17.75	41.4	127.85	15.68	35.7	26.75	77.85	2.86	14.03	552.99
HK320	19.9	9.23	55.6	40.89	38.77	48.77	21.45	44.84	147.86	17.73	39.61	40.2	105.14	2.59	17.5	650.08
Average	21.12	4.81	31.78	24.56	12.68	17.11	7.13	14.06	38.2	5.28	12.35	20.93	35.5	1.89	10.17	257.57
S.D.	5.21	3.09	16.39	13.41	14.51	18.02	7.25	14.3	44.22	5.02	11.73	9.25	25.55	0.77	3.64	192.37

Appendix 8. Analytical results of PAHs (ng Kg^{-1} dry weight) in Phayao Lake sediments

CORE 1

สถานี	Phe	An	Fluo	Pyr	11H-B[a]F	11H-B[b]F	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑PAHs
PY101	2.18	0.16	0.99	0.63	0.16	0.10	0.09	0.39	0.00	0.88	0.00	0.00	0.00	0.00	0.05	5.63
PY102	1.78	0.13	0.83	0.76	0.14	0.05	0.08	0.23	0.02	0.11	0.02	0.02	0.02	0.01	0.03	4.20
PY103	1.83	0.14	0.85	0.78	0.14	0.05	0.08	0.24	0.02	0.11	0.02	0.02	0.02	0.01	0.03	4.32
PY104	1.54	0.10	0.69	0.70	0.11	0.05	0.05	0.14	0.02	0.05	0.00	0.00	0.02	0.00	0.02	3.47
PY105	1.45	0.10	0.55	0.60	0.10	0.03	0.05	0.14	0.01	0.05	0.00	0.00	0.02	0.00	0.02	3.11
PY106	2.38	0.18	1.23	1.32	0.27	0.08	0.19	0.47	0.02	0.13	0.01	0.01	0.01	0.00	0.02	6.30
PY107	1.72	0.09	0.78	0.84	0.15	0.03	0.12	0.35	0.02	0.08	0.01	0.01	0.01	0.00	0.01	4.23
PY108	2.58	0.20	1.34	1.23	0.23	0.10	0.09	0.27	0.04	0.17	0.02	0.02	0.02	0.02	0.04	6.37
PY109	2.95	0.18	1.66	1.61	0.31	0.13	0.17	0.53	0.03	0.21	0.02	0.01	0.02	0.01	0.03	7.86
PY110	2.03	0.14	1.13	1.10	0.21	0.10	0.13	0.40	0.04	0.29	0.02	0.01	0.02	0.01	0.04	5.69
PY111	3.47	0.16	2.73	2.47	0.57	0.24	0.39	1.29	0.04	0.21	0.02	0.00	0.02	0.00	0.03	11.65
PY112	2.71	0.27	1.79	1.46	0.44	0.44	0.41	0.69	0.07	0.23	0.06	0.06	0.56	0.91	0.49	10.58
PY113	4.90	0.41	3.33	3.26	0.91	0.44	0.74	1.95	0.04	0.37	0.02	0.01	0.02	0.03	0.03	16.47
PY114	4.77	0.41	2.30	1.99	0.46	0.27	0.30	0.75	0.04	0.17	0.02	0.01	0.01	0.00	0.03	11.53
PY115	4.38	0.36	2.17	1.95	0.41	0.22	0.33	0.82	0.03	0.27	0.02	0.01	0.00	0.00	0.02	10.99
PY116	1.09	0.12	0.65	0.71	0.19	0.11	0.20	0.39	0.05	0.14	0.03	0.02	0.02	0.01	0.03	3.76
PY117	5.04	0.36	2.73	2.53	0.55	0.29	0.58	1.03	0.04	0.97	0.02	0.01	0.02	0.00	0.03	14.18
PY118	4.75	0.40	3.41	3.21	0.75	0.40	0.60	1.61	0.04	0.24	0.02	0.01	0.02	0.00	0.03	15.50
PY119	4.21	0.36	3.21	3.24	0.80	0.39	0.66	1.73	0.04	0.22	0.02	0.01	0.02	0.00	0.03	14.95
PY120	4.15	0.39	3.14	3.07	0.71	0.40	0.62	1.55	0.04	0.23	0.02	0.01	0.02	0.00	0.03	14.37
PY121	4.18	0.38	3.21	2.96	0.71	0.34	0.50	1.30	0.03	0.16	0.02	0.01	0.02	0.00	0.03	13.85
PY122	4.19	0.40	2.98	3.41	1.01	0.39	0.58	1.45	0.02	0.09	0.01	0.01	0.00	0.00	0.02	14.55
Average	3.10	0.25	1.89	1.81	0.42	0.21	0.32	0.80	0.03	0.24	0.02	0.01	0.04	0.05	0.05	9.25
S.D.	1.32	0.12	1.04	1.03	0.29	0.15	0.23	0.58	0.02	0.23	0.01	0.01	0.12	0.19	0.10	4.68

CORE 2

สถานี	Phe	An	Fluo	Pyr	11H-B[a]F	11H-B[b]F	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑PAHs
PY201	1.38	0.13	0.49	0.35	0.42	0.14	0.29	0.45	0.00	0.56	0.05	0.14	0.05	0.00	0.06	4.51
PY202	1.15	0.10	0.41	0.26	0.08	0.06	0.18	0.20	0.07	0.23	0.10	0.06	0.09	0.00	0.12	3.11
PY203	1.15	0.10	0.41	0.26	0.08	0.06	0.18	0.20	0.07	0.23	0.10	0.06	0.09	0.00	0.12	3.11
PY204	1.73	0.20	0.83	0.60	0.18	0.08	0.19	0.31	1.82	0.00	0.30	0.19	0.47	0.00	0.79	7.68
PY205	3.00	0.23	1.55	1.07	0.29	0.23	0.28	0.56	0.03	0.08	0.02	0.01	0.03	0.00	0.05	7.43
PY206	3.40	0.23	1.86	1.24	0.34	0.24	0.30	0.69	0.02	0.10	0.02	0.01	0.04	0.00	0.06	8.56
PY207	2.14	0.15	1.00	0.68	0.19	0.16	0.23	0.38	0.16	0.42	0.14	0.04	0.18	0.00	0.24	6.10
PY208	2.75	0.21	1.68	1.31	0.39	0.27	0.37	0.72	0.18	0.15	0.02	0.01	0.04	0.00	0.05	8.15
PY209	2.95	0.24	1.54	1.12	0.31	0.22	0.34	0.63	0.03	0.06	0.02	0.01	0.04	0.00	0.05	7.56
PY210	3.24	0.28	1.59	1.13	0.05	0.26	0.32	0.80	0.02	0.00	0.00	0.04	0.04	0.00	0.06	7.82
PY211	2.12	0.16	0.82	0.68	0.04	0.09	0.12	0.30	0.03	0.08	0.00	0.00	0.00	0.00	0.06	4.50
PY212	1.82	0.33	1.16	1.13	0.00	0.24	0.27	0.00	0.03	0.00	0.02	0.01	0.04	0.00	0.05	5.09
PY213	2.32	0.20	1.27	1.25	0.38	0.25	0.32	0.67	0.03	0.10	0.02	0.02	0.04	0.00	0.05	6.91
PY214	2.77	0.28	1.29	1.33	0.40	0.29	0.46	0.78	0.03	0.07	0.02	0.01	0.03	0.00	0.04	7.79
PY215	4.05	0.41	2.63	2.86	0.99	0.60	0.86	1.65	0.03	0.08	0.02	0.01	0.03	0.00	0.05	14.27
PY216	1.77	0.17	0.71	0.73	0.26	0.16	0.17	0.39	0.02	0.00	0.02	0.01	0.04	0.00	0.04	4.51
PY217	2.47	0.22	0.99	1.11	0.34	0.25	0.31	0.00	0.03	0.00	0.02	0.04	0.04	0.00	0.05	5.85
PY218	1.85	0.20	0.95	1.05	0.39	0.28	0.00	0.55	0.02	0.07	0.02	0.01	0.02	0.00	0.04	5.45
PY219	2.14	0.33	1.02	1.04	0.40	0.29	0.26	0.65	0.03	0.07	0.02	0.01	0.03	0.00	0.03	6.32
PY220	1.86	0.29	0.74	0.75	0.21	0.19	0.15	0.24	0.03	0.08	0.00	0.00	0.00	0.00	0.00	4.53
PY221	3.55	0.33	1.56	1.51	0.46	0.36	0.35	0.76	0.02	0.07	0.02	0.01	0.03	0.00	0.04	9.08
PY222	3.52	0.34	1.29	1.21	0.38	0.25	0.24	0.52	0.02	0.10	0.00	0.00	0.03	0.00	0.00	7.89
PY223	3.07	0.29	1.94	2.59	0.97	0.31	0.89	1.61	0.06	0.14	0.04	0.04	0.07	0.00	0.09	12.12
PY224	3.07	0.29	1.94	2.59	0.97	0.31	0.89	1.61	0.06	0.14	0.04	0.04	0.07	0.00	0.09	12.12
PY225	3.22	0.24	1.02	1.07	0.26	0.26	0.15	0.43	0.03	0.00	0.00	0.00	0.00	0.00	0.08	6.75
PY226	2.53	0.16	0.52	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.70
PY227	1.23	0.10	0.68	0.73	0.27	0.22	0.27	0.50	0.02	0.14	0.00	0.08	0.03	0.00	0.03	4.29
PY228	3.81	0.26	2.25	2.31	0.81	0.61	0.44	1.01	0.03	0.11	0.00	0.00	0.04	0.00	0.05	11.75
PY229	1.85	0.25	0.90	0.91	0.28	0.24	0.23	0.34	0.13	0.33	0.00	0.00	0.00	0.00	0.00	5.47
PY230	3.04	0.32	1.68	1.82	0.56	0.45	0.25	0.51	0.03	0.05	0.00	0.00	0.00	0.00	0.00	8.69
PY231	0.77	0.07	0.78	0.79	0.34	0.26	0.12	0.36	0.02	0.05	0.00	0.00	0.00	0.00	0.00	3.56
PY232	0.77	0.06	0.76	0.80	0.38	0.23	0.12	0.30	0.00	0.06	0.00	0.00	0.00	0.00	0.00	3.48
PY233	0.59	0.09	0.56	0.72	0.28	0.24	0.33	0.54	0.00	0.15	0.02	0.01	0.02	0.01	0.00	3.55
PY234	0.77	0.08	0.53	0.70	0.23	0.19	0.21	0.39	0.02	0.03	0.01	0.01	0.02	0.00	0.02	3.22
PY235	1.44	0.14	1.06	1.41	0.47	0.38	0.38	0.76	0.02	0.04	0.01	0.01	0.00	0.00	0.00	6.12
PY236	2.28	0.25	1.63	2.37	0.77	0.59	0.51	1.05	0.02	0.07	0.01	0.01	0.02	0.01	0.04	9.63
PY237	1.49	0.15	1.01	1.41	0.47	0.34	0.28	0.66	0.03	0.07	0.02	0.01	0.02	0.00	0.03	6.00

PY238	2.53	0.26	0.69	0.87	0.22	0.15	0.09	0.20	0.05	0.08	0.02	0.02	0.03	0.00	0.05	5.25
PY239	1.26	0.12	0.60	0.82	0.28	0.22	0.19	0.43	0.03	0.07	0.02	0.01	0.02	0.00	0.04	4.12
PY240	2.22	0.21	1.03	1.47	0.47	0.34	0.29	0.64	0.03	0.09	0.02	0.01	0.03	0.01	0.04	6.91
PY241	1.47	0.13	0.42	0.52	0.15	0.09	0.06	0.11	0.03	0.10	0.03	0.02	0.05	0.00	0.04	3.22
PY242	0.43	0.02	0.22	0.34	0.12	0.09	0.08	0.18	0.03	0.08	0.03	0.02	0.03	0.00	0.05	1.73
PY243	3.30	0.31	0.99	1.57	0.37	0.26	0.24	0.52	0.03	0.06	0.02	0.02	0.04	0.00	0.05	7.77
PY244	0.01	0.07	0.16	0.04	0.03	0.02	0.05	0.05	0.08	0.00	0.00	0.02	0.00	0.06	0.34	0.93
PY245	0.02	0.02	0.18	0.03	0.04	0.04	0.08	0.13	0.09	0.02	0.01	0.02	0.00	0.03	0.33	1.03
Average	2.10	0.20	1.05	1.09	0.34	0.24	0.27	0.53	0.08	0.10	0.03	0.02	0.04	0.00	0.08	6.17
S.D.	1.03	0.10	0.57	0.66	0.25	0.14	0.20	0.39	0.27	0.11	0.05	0.04	0.07	0.01	0.13	2.94

Appendix 9. Raw data of chemical species in $PM_{2.5}$ Collected at Chiang-Mai

No	Sample ID			TC	OC	EC	OC/EC	OC1	OC2	OC3	OC4	EC1	EC2	EC3	OP2	OP5	EC1-OP2	F-	Cl-	NO2-	NO3-	SO42-	Na+	NH4+	K+	Mg2+	Ca2+
		m3	hours	ug/m3	ug/m3	ug/m3		ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3		ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3
1	CM 1	21.60	72.00	21.46	16.51	4.95	3.33	0.21	2.52	6.62	7.16	4.70	0.22	0.03	0.00	2.62	4.70	0.14	0.38	0.00	0.98	10.31	1.70	0.19	1.05	0.09	1.45
2	CM 2	21.60	72.00	20.23	17.06	3.17	5.38	0.19	2.30	6.81	5.50	4.98	0.28	0.17	2.26	2.76	2.72	0.12	0.34	0.00	0.00	5.97	1.75	0.19	0.84	0.07	1.43
3	CM 3	21.60	72.00	32.81	26.82	5.99	4.48	0.30	4.69	11.37	10.46	5.42	0.33	0.24	0.00	2.83	5.42	0.14	0.34	0.27	1.51	5.21	1.79	1.59	1.90	0.13	1.44
4	CM 4	21.60	72.00	5.97	5.38	0.59	9.17	0.09	0.83	2.16	1.25	1.54	0.10	0.00	1.05	1.09	0.48	0.09	0.35	0.26	0.77	3.07	1.44	0.70	0.45	0.10	0.87
5	CM 5	21.60	72.00	17.36	15.44	1.92	8.02	0.18	2.23	5.77	5.26	3.61	0.22	0.09	1.99	1.59	1.62	0.11	0.30	0.34	1.08	10.75	1.59	2.83	1.38	0.13	1.23
6	CM 6	21.60	72.00	19.43	16.16	3.27	4.94	0.24	2.38	5.96	5.76	4.99	0.10	0.00	1.83	2.37	3.17	0.11	0.30	0.30	1.25	13.36	1.69	3.61	1.38	0.14	1.39
7	CM 7	21.60	72.00	13.94	12.04	1.90	6.33	0.09	1.45	5.25	3.73	3.29	0.13	0.00	1.52	1.40	1.77	0.11	0.38	0.34	1.01	4.53	1.66	0.98	0.99	0.11	1.21
8	CM 8	21.60	72.00	32.56	25.30	7.26	3.48	0.29	4.59	11.28	8.75	7.10	0.34	0.22	0.40	3.52	6.70	0.11	0.30	0.29	0.90	6.53	1.66	1.60	1.87	0.13	1.57
9	CM 9	21.60	72.00	15.98	12.98	3.00	4.33	0.20	1.86	5.01	3.97	4.77	0.17	0.01	1.95	2.65	2.83	0.08	0.30	0.26	0.60	8.34	1.81	1.86	1.14	0.13	1.44
10	CM 10	21.60	72.00	15.18	12.18	3.00	4.06	0.12	1.66	4.87	4.47	3.88	0.17	0.01	1.06	2.54	2.82	0.11	0.32	0.26	0.55	8.47	1.65	2.26	1.07	0.11	1.16
11	CM 11	21.60	72.00	13.66	11.65	2.01	5.79	0.14	1.69	4.55	3.58	3.55	0.15	0.01	1.70	2.33	1.85	0.11	0.40	0.24	0.73	6.50	1.52	1.58	0.91	0.11	1.09
12	CM 12	21.60	72.00	15.16	12.68	2.48	5.12	0.15	1.83	5.22	4.03	3.77	0.17	0.00	1.47	1.90	2.31	0.12	0.30	0.30	0.74	5.56	1.48	1.53	0.97	0.10	1.26
13	CM 13	21.60	72.00	19.43	16.03	3.40	4.71	0.19	2.23	6.59	4.65	5.56	0.20	0.01	2.36	2.74	3.20	0.11	0.31	0.00	0.95	4.77	1.71	0.98	1.14	0.13	1.35
14	CM 14	14.40	48.00	15.43	13.12	2.31	5.68	0.09	1.88	4.72	3.86	4.67	0.21	0.00	2.56	2.35	2.10	0.15	0.58	0.44	1.23	8.58	2.26	2.05	1.07	0.15	1.47
15	CM 15	21.60	72.00	26.26	20.52	5.74	3.58	0.23	3.16	8.83	8.31	5.48	0.23	0.03	0.00	2.76	5.48	0.14	0.33	0.26	1.43	8.16	1.61	2.44	1.34	0.12	1.44
16	CM 16	21.60	72.00	10.88	9.72	1.16	8.35	0.15	1.42	4.81	2.17	2.20	0.13	0.00	1.17	1.03	1.03	0.08	0.56	0.29	0.56	1.29	1.48	0.29	0.36	0.12	0.89
17	CM 17	21.60	72.00	18.32	15.40	2.92	5.26	0.15	2.19	6.52	4.23	4.99	0.24	0.01	2.31	2.39	2.68	0.10	0.32	0.31	0.79	5.07	1.58	0.96	1.14	0.11	1.25
18	CM 18	21.60	72.00	13.70	11.14	2.56	4.34	0.06	1.49	4.34	3.40	4.22	0.19	0.00	1.84	1.84	2.38	0.10	0.44	0.42	0.54	10.77	1.88	2.27	1.02	0.13	1.29
19	CM 19	21.60	72.00	6.97	5.97	1.00	5.97	0.12	1.05	2.54	1.42	1.66	0.19	0.00	0.85	1.11	0.81	0.09	0.35	0.55	0.71	3.00	1.50	0.69	0.49	0.10	1.01
20	CM 20	21.60	72.00	5.83	5.00	0.83	6.06	0.01	0.78	1.99	1.36	1.52	0.16	0.00	0.85	0.81	0.66	0.08	0.37	0.53	0.66	7.22	1.22	1.77	0.56	0.11	0.93
21	CM 21	21.60	72.00	6.89	6.04	0.85	7.12	0.08	0.79	3.06	1.33	1.44	0.18	0.00	0.77	0.77	0.67	0.11	0.46	0.33	0.54	1.46	1.08	0.26	0.20	0.07	0.92
22	CM 22	21.60	72.00	3.65	3.31	0.34	9.81	0.10	0.53	1.97	0.62	0.37	0.05	0.00	0.08	0.17	0.29	0.07	0.85	0.34	0.50	0.65	1.31	0.24	0.29	0.13	1.01
23	CM 23	21.60	72.00	3.43	2.91	0.52	5.63	0.05	0.51	1.36	0.70	0.66	0.15	0.00	0.29	0.33	0.37	0.08	0.38	0.00	0.40	1.42	1.20	0.20	0.15	0.10	0.71
24	CM 24	21.60	72.00	4.89	4.13	0.76	5.47	0.10	0.59	1.93	0.98	1.13	0.15	0.01	0.53	0.62	0.60	0.08	0.43	0.35	0.42	0.92	0.98	0.21	0.16	0.09	0.89
25	CM 25	21.60	72.00	2.79	2.53	0.26	9.67	0.06	0.35	1.44	0.49	0.37	0.08	0.00	0.19	0.22	0.18	0.10	0.40	0.46	0.50	1.38	1.68	0.27	0.17	0.13	0.75
26	CM 26	21.60	72.00	13.60	11.55	2.04	5.66	0.06	1.52	4.53	3.50	3.89	0.09	0.00	1.94	1.94	1.95	0.06	0.31	0.30	0.41	8.87	1.36	1.85	1.17	0.10	1.19
27	CM 27	21.60	72.00	3.58	3.31	0.27	12.37	0.01	0.51	1.98	0.67	0.34	0.06	0.00	0.13	0.22	0.21	0.08	0.58	0.46	0.43	0.69	1.07	0.21	0.22	0.15	1.50
28	CM 28	21.60	72.00	3.11	2.70	0.41	6.54	0.00	0.46	1.40	0.62	0.52	0.12	0.00	0.22	0.28	0.30	0.08	0.43	0.31	0.45	0.57	0.73	0.25	0.17	0.10	0.95
29	CM 29	21.60	72.00	2.95	2.59	0.36	7.19	0.00	0.40	1.37	0.57	0.48	0.13	0.00	0.26	0.27	0.23	0.10	0.37	0.43	0.48	1.06	1.05	0.26	0.17	0.10	0.92
30	CM 30	21.60	72.00	3.86	3.49	0.37	9.52	0.05	0.38	2.25	0.58	0.49	0.10	0.00	0.23	0.24	0.26	0.09	0.37	0.40	0.45	0.76	1.02	0.25	0.16	0.13	0.88
31	CM 31	21.60	72.00	4.05	3.54	0.51	6.91	0.08	0.50	1.73	0.77	0.83	0.14	0.00	0.45	0.44	0.37	0.10	0.37	0.37	0.44	0.96	1.01	0.20	0.16	0.09	0.85
32	CM 32	21.60	72.00	5.59	4.80	0.80	6.02	0.08	0.56	2.26	1.23	1.31	0.15	0.00	0.67	0.74	0.65	0.08	0.31	0.48	0.49	2.63	1.20	0.44	0.23	0.10	0.91
33	CM 33	43.20	144.00	0.74	0.67	0.07	10.00	0.03	0.16	0.40	0.08	0.01	0.05	0.00	0.00	0.01	0.01	0.05	0.18	0.00	0.19	0.18	0.45	0.00	0.00	0.03	0.27
34	CM 34	21.60	72.00	2.42	2.05	0.38	5.42	0.01	0.34	1.14	0.41	0.38	0.15	0.00	0.15	0.22	0.23	0.10	0.52	0.38	0.45	0.96	1.42	0.21	0.19	0.11	0.72
35	CM 35	21.60	72.00	3.37	2.96	0.41	7.17	0.10	0.44	2.05	0.35	0.34	0.09	0.00	0.01	0.21	0.33	0.10	0.43	0.47	0.49	0.85	1.12	0.28	0.20	0.08	0.73
36	CM 36	21.60	72.00	2.02	1.69	0.33	5.09	0.00	0.30	1.09	0.30	0.26	0.08	0.00	0.00	0.23	0.26	0.09	0.38	0.35	0.45	1.54	1.10	0.21	0.16	0.11	0.76
37	CM 37	21.60	72.00	2.52	2.20	0.32	6.87	0.06	0.43	1.12	0.45	0.36	0.09	0.00	0.13	0.17	0.23	0.09	0.39	0.64	0.56	1.47	1.17	0.25	0.17	0.10	0.87
38	CM 38	21.60	72.00	2.01	1.62	0.38	4.23	0.01	0.31	0.97	0.34	0.26	0.12	0.00	0.00	0.16	0.26	0.08	0.42	0.30	0.37	0.56	0.55	0.26	0.20	0.08	0.71
39	CM 39	28.80	96.00	1.18	1.00	0.18	5.61	0.01	0.25	0.59	0.15	0.11	0.07	0.00	0.00	0.11	0.11	0.06	0.29	0.23	0.26	1.03	0.86	0.15	0.12	0.08	0.53
40	CM 40	21.60	72.00	4.86	4.59	0.27	17.15	0.30	1.10	2.48	0.52	0.33	0.13	0.00	0.20	0.25	0.13	0.12	0.38	0.00	0.48	0.97	1.03	0.27	0.17	0.08	0.74
41	CM 41	21.60	72.00	16.38	14.03	2.36	5.96	0.14	2.01	5.14	5.10	3.77	0.17	0.05	1.63	1.39	2.13	0.08	0.44	0.00	0.96	15.70	1.52	3.98	1.30	0.13	1.14
42	CM 42	21.60	72.00	12.38	10.82	1.56	6.91	0.03	1.61	4.20	3.40	2.97	0.16	0.02	1.58	1.85	1.39	0.09	0.35	0.30	0.80	10.18	1.16	2.01	0.91	0.10	1.02
43	CM 43	21.60	72.00	8.79	7.57	1.22	6.20	0.11	1.02	3.45	2.02	1.87	0.31	0.00	0.96	0.90	0.91	0.07	0.40	0.30	0.73	3.79	1.25	0.65	0.42	0.12	2.08
44	CM 44	21.60	72.00	12.66	10.95	1.72	6.38	0.10	1.39	4.52	3.38	3.11	0.17	0.00	1.56	1.45	1.55	0.09	0.39	0.32	0.47	6.71	1.33	1.34	0.75	0.11	1.13
45	CM 45	21.60	72.00	7.07	6.12	0.94	6.50	0.08	0.85	2.52	1.64	1.79	0.17	0.00	1.02	0.93	0.77	0.08	0.35	0.29	0.43	6.40	1.29	1.11	0.57	0.09	0.99
46	CM 46	21.60	72.00	5.96	5.17	0.79	6.54	0.06	0.75	2.41	1.34	1.24	0.16	0.00	0.61	0.61	0.63	0.09	0.35	0.31	0.40	2.04	1.26	0.21	0.25	0.08	0.84
47	CM 47	21.60	72.00	4.80	4.16	0.65	6.44	0.00	0.69	1.54	1.02	1.42	0.13	0.00	0.91	0.86	0.52	0.08	0.36	0.41	0.68	9.86	1.49	2.12	0.60	0.13	0.99
48	CM 48	21.60	72.00	3.87	3.68	0.19	19.18	0.00	0.56	2.10	0.80	0.34	0.06	0.00	0.22	0.30	0.13	0.09	0.67	0.28	0.89	0.92	1.57	0.27	0.26	0.17	1.00
49	CM 49	21.60	72.00	3.27	2.83	0.45	6.31	0.08	0.54	1.27	0.60	0.60	0.17	0.00	0.33	0.30	0.27	0.08	0.39	0.33	0.60	4.67	1.34	0.68	0.31	0.11	0.89
50	CM 50	21.60	72.00	5.70	4.99	0.72	6.98	0.10	0.67	2.67	1.14	0.98	0.15	0.00	0.41	0.53	0.57	0.08	0.41	0.32	0.55	2.17	1.34	0.30	0.22	0.09	0.88

Appendix 10. Raw data of chemical species in $PM_{2.5}$ Collected at Bangkok

No	Sample ID			TC	OC	EC	OC/EC	OC1	OC2	OC3	OC4	EC1	EC2	EC3	OP2
		m3	hours	ug/m3	ug/m3	ug/m3		ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3
1	Bkk 1	15.3	51	11.37	8.48	2.89	2.93	0.00	1.35	3.43	2.58	3.55	0.47	0.00	1.12
2	Bkk 2	21.6	72	13.80	9.54	4.26	2.24	0.06	1.83	4.17	3.48	4.05	0.21	0.00	0.00
3	Bkk 3	21.6	72	10.41	7.18	3.23	2.22	0.01	1.16	3.09	2.07	3.86	0.22	0.00	0.84
4	Bkk 4	21.6	72	15.15	10.73	4.42	2.43	0.07	1.65	4.74	3.85	4.61	0.23	0.00	0.41
5	Bkk 5	21.6	72	8.27	5.95	2.31	2.57	0.01	0.98	2.53	1.55	2.97	0.24	0.00	0.89
6	Bkk 6	21.6	72	8.95	7.18	1.77	4.05	0.01	1.20	3.16	1.81	2.55	0.23	0.00	1.00
7	Bkk 7	21.3	71	13.39	10.78	2.61	4.14	0.04	1.55	4.13	3.46	4.02	0.19	0.00	1.60
8	Bkk 8	21.6	72	13.42	9.53	3.89	2.45	0.80	1.79	3.66	3.27	3.64	0.23	0.02	0.00
9	Bkk 9	21.6	72	10.23	6.82	3.41	2.00	0.01	1.24	2.60	2.06	4.09	0.23	0.00	0.90
10	Bkk 10	21.6	72	9.89	7.39	2.49	2.96	0.02	1.15	3.46	2.04	2.97	0.25	0.00	0.73
11	Bkk 11	21.6	72	8.09	5.79	2.31	2.51	0.00	0.92	2.44	1.64	2.84	0.26	0.00	0.79
12	Bkk 12	21.6	72	6.52	4.10	2.42	1.69	0.00	0.76	1.88	1.07	2.56	0.24	0.00	0.38
13	Bkk 13	21.6	72	6.98	4.88	2.09	2.33	0.00	0.85	1.92	1.30	2.62	0.28	0.00	0.81
14	Bkk 14	21.6	72	7.93	5.81	2.12	2.74	0.00	0.97	2.62	1.48	2.56	0.28	0.00	0.73
15	Bkk 15	21.6	72	6.50	4.05	2.45	1.65	0.00	0.81	2.00	1.08	2.33	0.28	0.00	0.15
16	Bkk 16	21.6	72	5.20	3.70	1.51	2.46	0.04	0.63	1.82	0.81	1.68	0.22	0.00	0.40
17	Bkk 17	20.82	69.4	6.68	4.77	1.91	2.49	0.00	0.78	2.39	1.13	2.17	0.21	0.00	0.47
18	Bkk 18	21.6	72	6.04	4.67	1.37	3.42	0.00	0.81	2.14	1.21	1.72	0.16	0.00	0.51
19	Bkk 19	21.6	72	8.13	6.32	1.81	3.48	0.01	0.90	2.99	1.59	2.42	0.24	0.00	0.84

20	Bkk 20	21.3	71	6.78	5.07	1.72	2.95	0.00	0.86	2.51	1.28	1.98	0.15	0.00	0.41
21	Bkk 21	21.6	72	5.03	3.81	1.22	3.12	0.00	0.63	1.81	0.94	1.38	0.27	0.00	0.44
22	Bkk 22	19.8	66	6.15	4.07	2.08	1.96	0.00	0.70	2.22	1.12	1.92	0.19	0.00	0.03
23	Bkk 23	15.21	50.7	8.48	6.77	1.71	3.96	1.17	1.40	2.67	1.19	1.70	0.35	0.00	0.34
24	Bkk 24	20.7	69	5.73	4.62	1.11	4.16	0.00	0.92	2.18	1.13	1.30	0.20	0.00	0.39
25	Bkk 25	21.6	72	5.81	4.74	1.06	4.46	0.09	0.87	2.15	1.05	1.51	0.13	0.00	0.58
26	Bkk 26	18	60	6.08	5.23	0.85	6.15	0.00	0.90	2.56	1.27	1.16	0.20	0.00	0.50
27	Bkk 27	21.6	72	6.93	5.26	1.67	3.14	0.00	0.99	2.38	1.31	2.02	0.22	0.00	0.56
28	Bkk 28	21.6	72	8.08	5.26	2.82	1.86	0.03	0.92	2.62	1.39	2.98	0.14	0.00	0.30
29	Bkk 29	11.55	38.5	8.35	6.79	1.57	4.33	0.00	1.09	3.44	1.56	1.95	0.33	0.00	0.71
30	Bkk 30	16.8	56	7.85	5.84	2.01	2.90	0.00	0.93	2.90	1.37	2.34	0.31	0.00	0.64
31	Bkk 31	17.55	58.5	7.12	5.80	1.32	4.38	0.00	0.82	2.98	1.35	1.69	0.29	0.00	0.65
32	Bkk 32	12.9	43	7.82	6.45	1.37	4.70	0.00	1.24	3.24	1.39	1.64	0.31	0.00	0.57
33	Bkk 33	20.4	68	7.07	5.05	2.03	2.49	0.00	0.83	2.46	1.20	2.38	0.21	0.00	0.56
34	Bkk 34	11.28	37.6	9.16	7.26	1.90	3.81	0.00	1.14	3.69	1.65	2.36	0.33	0.00	0.79
35	Bkk 35	10.62	35.4	11.68	8.91	2.78	3.20	0.00	1.58	4.39	2.11	3.19	0.41	0.00	0.83
36	Bkk 36	15.24	50.8	12.43	9.75	2.68	3.64	0.00	1.49	4.30	2.70	3.60	0.33	0.00	1.25
37	Bkk 37	17.73	59.1	12.52	8.95	3.57	2.51	0.00	1.36	4.14	2.44	4.27	0.30	0.00	1.00
38	Bkk 38	21.69	72.3	3.58	2.79	0.79	3.52	0.00	0.47	1.53	0.59	0.80	0.19	0.00	0.20
39	Bkk 39	16.2	54	3.05	2.64	0.40	6.56	0.00	0.38	1.70	0.57	0.24	0.16	0.00	0.00
40	Bkk 40	21.72	72.4	3.48	2.84	0.64	4.42	0.00	0.49	1.56	0.58	0.65	0.21	0.00	0.21
41	Bkk 41	23.16	77.2	8.40	5.47	2.92	1.87	0.00	0.97	2.48	1.41	3.37	0.17	0.00	0.62
42	Bkk 42	21.66	72.2	7.00	4.82	2.17	2.22	0.00	0.85	2.20	1.21	2.57	0.17	0.00	0.57
43	Bkk 43	21.6	72	9.56	6.93	2.63	2.63	0.00	1.08	3.03	1.85	3.41	0.19	0.00	0.97
44	Bkk 44	21.6	72	5.30	4.25	1.05	4.04	0.00	0.69	2.05	0.98	1.44	0.15	0.00	0.54
45	Bkk 45	21.54	71.8	10.19	7.59	2.60	2.92	0.00	1.15	3.04	2.36	3.35	0.29	0.00	1.03
46	Bkk 46	18.15	60.5	8.66	6.94	1.72	4.04	0.02	1.07	2.86	1.96	2.48	0.27	0.00	1.04
47	Bkk 47	20.19	67.3	9.13	7.40	1.74	4.26	0.01	1.08	2.91	2.20	2.73	0.21	0.00	1.21
48	Bkk 48	21.66	72.2	7.39	5.49	1.91	2.88	0.00	0.94	2.41	1.43	2.46	0.16	0.00	0.71
49	Bkk 49	21.81	72.7	10.32	7.72	2.60	2.96	0.00	1.29	3.14	2.42	3.30	0.17	0.00	0.86
50	Bkk 50	21.72	72.4	7.59	5.74	1.85	3.10	0.00	0.98	2.63	1.48	2.37	0.14	0.00	0.66
51	Bkk 51	22.2	74	8.93	6.81	2.12	3.22	0.00	1.01	3.09	1.73	2.93	0.16	0.00	0.98
52	Bkk 52	16.86	56.2	8.59	6.70	1.88	3.56	0.13	1.22	3.23	1.31	2.43	0.28	0.00	0.82
53	Bkk 53	21.6	72	6.75	5.56	1.18	4.71	0.05	0.91	2.50	1.35	1.71	0.22	0.00	0.75
54	Bkk 54	20.58	68.6	7.48	5.93	1.55	3.83	0.06	0.92	2.56	1.53	2.22	0.18	0.00	0.85
55	Bkk 55	18.09	60.3	10.91	8.55	2.37	3.61	0.08	1.39	3.72	2.21	3.24	0.28	0.00	1.15
56	Bkk 56	21.66	72.2	8.25	6.40	1.85	3.46	0.04	0.94	2.92	1.65	2.55	0.14	0.00	0.85
57	Bkk 57	21.69	72.3	7.89	6.65	1.24	5.37	0.04	0.95	2.67	2.06	2.02	0.16	0.00	0.93
58	Bkk 58	21.9	73	9.10	7.61	1.49	5.12	0.06	1.12	3.22	2.20	2.34	0.17	0.00	1.02
59	Bkk 59	21.6	72	2.99	2.72	0.27	9.96	0.00	0.51	1.58	0.46	0.30	0.15	0.00	0.17
60	Bkk 60	21.6	72	15.32	10.59	4.73	2.24	0.13	1.66	5.20	3.59	4.51	0.22	0.00	0.00
61	Bkk 61	21.87	72.9	29.06	22.75	6.31	3.60	0.29	3.57	10.73	8.16	5.88	0.29	0.14	0.00

62	Bkk 62	21.18	70.6	25.95	19.52	6.43	3.04	0.30	3.18	8.88	7.16	6.25	0.18	0.00	0.00
63	Bkk 63	21.63	72.1	17.70	13.21	4.49	2.94	0.22	2.07	5.71	5.21	4.22	0.19	0.08	0.00
64	Bkk 64	21.66	72.2	12.99	8.61	4.39	1.96	0.17	1.60	3.68	3.16	4.20	0.19	0.00	0.00
65	Bkk 65	21.51	71.7	15.37	10.74	4.62	2.32	0.24	1.84	4.86	3.81	4.42	0.20	0.00	0.00
66	Bkk 66	21.84	72.8	14.96	10.73	4.24	2.53	0.15	1.81	4.88	3.89	4.03	0.21	0.00	0.00
67	Bkk 67	21.69	72.3	10.20	7.17	3.03	2.36	0.10	1.28	3.02	2.04	3.55	0.21	0.00	0.72
68	Bkk 68	21.63	72.1	11.52	7.72	3.80	2.03	0.10	1.47	3.36	2.75	3.62	0.21	0.00	0.03
69	Bkk 69	21.84	72.8	14.87	10.57	4.30	2.46	0.13	1.75	5.01	3.67	4.11	0.18	0.01	0.00
70	Bkk 70	21.78	72.6	17.43	13.48	3.96	3.41	0.12	2.06	6.93	4.37	3.74	0.21	0.00	0.00
71	Bkk 71	21.63	72.1	12.07	8.75	3.32	2.63	0.16	1.43	3.45	2.53	4.31	0.19	0.00	1.18
72	Bkk 72	21.63	72.1	8.72	6.90	1.82	3.78	0.23	1.32	2.79	1.66	2.48	0.25	0.00	0.91
73	Bkk 73	21.6	72	19.30	14.70	4.60	3.20	0.19	2.41	7.04	5.05	4.35	0.23	0.02	0.00

Appendix 11. Raw data of chemical species in $PM_{2.5}$ Collected at Phuket

No	Sample ID			**TC**	**OC**	**EC**	**OC/EC**	OC 1	OC 2	OC 3	OC 4	EC 1	EC 2	EC 3	OP 2	OP 5	**EC1-OP2**	**F-**	**Cl-**	**NO 2-**	**NO 3-**	**SO 42-**	**Na +**	**NH 4+**	**K+**	**Mg 2+**	**Ca2 +**
		m3	hours	**ug/m3**	**ug/m3**	**ug/m3**		**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**		**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**	**ug/m3**
1	Phuket 1	21.6	72	3.78	3.24	0.53	6.07	0.03	0.57	1.74	0.67	0.62	0.15	0.00	0.23	0.46	0.38	0.09	0.35	0.00	0.32	2.18	1.12	0.21	0.19	0.11	0.88
2	Phuket 2	21.6	72	3.80	3.20	0.60	5.29	0.01	0.61	1.57	0.71	0.76	0.15	0.00	0.30	0.50	0.46	0.09	0.41	0.30	0.58	2.35	1.40	0.22	0.29	0.11	0.92
3	Phuket 3	21.6	72	4.06	3.48	0.58	5.98	0.00	0.66	1.78	0.70	0.76	0.16	0.00	0.34	0.51	0.42	0.09	0.46	0.33	0.76	1.38	1.22	0.30	0.25	0.10	0.75
4	Phuket 4	21.6	72	3.63	3.13	0.49	6.34	0.00	0.59	1.61	0.64	0.65	0.14	0.00	0.30	0.44	0.35	0.10	0.46	0.29	0.57	1.08	1.22	0.20	0.29	0.10	0.89
5	Phuket 5	21.6	72	3.06	2.54	0.52	4.84	0.00	0.51	1.35	0.51	0.54	0.15	0.00	0.16	0.35	0.38	0.09	0.48	0.34	0.61	1.08	1.13	0.21	0.26	0.10	0.84
6	Phuket 6	21.6	72	4.12	3.46	0.66	5.22	0.07	0.60	1.70	0.81	0.80	0.14	0.00	0.27	0.56	0.52	0.07	0.35	0.26	0.64	3.79	1.47	0.30	0.51	0.11	1.20
7	Phuket 7	21.6	72	3.61	2.87	0.74	3.89	0.00	0.69	1.19	0.70	0.80	0.23	0.00	0.29	0.47	0.51	0.09	0.45	0.00	0.67	5.41	1.40	0.82	0.33	0.12	1.04
8	Phuket 8	21.6	72	3.09	2.49	0.60	4.12	0.05	0.48	1.21	0.55	0.64	0.16	0.00	0.20	0.38	0.44	0.09	0.50	0.29	0.53	3.62	1.57	0.31	0.26	0.11	0.85
9	Phuket 9	21.6	72	3.17	2.31	0.86	2.69	0.00	0.47	1.26	0.59	0.68	0.18	0.00	0.00	0.25	0.68	0.08	0.44	0.27	0.55	5.36	1.90	0.40	0.39	0.14	1.26
10	Phuket 10	21.6	72	4.28	3.27	1.01	3.23	0.00	0.56	1.77	0.93	0.83	0.18	0.00	0.00	1.01	0.83	0.09	0.38	0.62	0.69	3.93	1.57	0.43	0.33	0.12	1.13
11	Phuket 11	21.6	72	3.63	3.01	0.62	4.83	0.03	0.57	1.51	0.66	0.70	0.15	0.00	0.23	0.44	0.47	0.09	0.38	0.26	0.41	1.01	0.72	0.20	0.20	0.06	0.75
12	Phuket 12	21.6	72	3.26	2.84	0.42	6.78	0.10	0.56	1.54	0.49	0.44	0.13	0.00	0.16	0.36	0.28	0.10	0.45	0.52	0.61	1.35	1.31	0.24	0.18	0.11	0.86
13	Phuket 13	21.6	72	2.81	2.24	0.58	3.89	0.03	0.44	1.24	0.53	0.45	0.13	0.00	0.00	0.26	0.45	0.09	0.48	0.51	0.49	1.54	1.22	0.20	0.17	0.11	1.01
14	Phuket 14	21.6	72	2.11	1.83	0.28	6.41	0.00	0.45	0.96	0.34	0.26	0.09	0.00	0.07	0.26	0.19	0.08	0.38	0.32	0.40	0.84	0.65	0.23	0.17	0.08	1.03
15	Phuket 15	21.6	72	2.44	2.06	0.38	5.36	0.00	0.41	1.25	0.37	0.34	0.07	0.00	0.03	0.41	0.31	0.11	0.78	0.38	0.57	1.73	1.95	0.00	0.17	0.18	1.03
16	Phuket 16	21.6	72	2.84	2.28	0.56	4.04	0.01	0.52	1.22	0.52	0.44	0.13	0.00	0.00	0.41	0.44	0.08	0.47	0.00	0.53	3.49	1.98	0.00	0.22	0.16	1.03
17	Phuket 17	21.6	72	2.93	2.49	0.44	5.72	0.13	0.52	1.24	0.52	0.39	0.13	0.00	0.08	0.39	0.31	0.09	0.69	0.26	0.61	2.31	1.72	0.00	0.18	0.14	0.90
18	Phuket 18	21.6	72	6.35	5.48	0.87	6.28	0.00	0.82	2.90	0.95	1.59	0.09	0.00	0.81	1.68	0.79	0.09	0.50	0.57	0.50	0.50	1.40	0.21	0.19	0.11	0.97
19	Phuket 19	21.6	72	2.48	2.14	0.34	6.24	0.02	0.51	1.03	0.44	0.35	0.13	0.00	0.15	0.31	0.21	0.08	0.66	0.26	0.67	4.45	2.29	0.21	0.23	0.23	1.11
20	Phuket 20	21.6	72	2.77	2.36	0.41	5.72	0.03	0.48	1.17	0.52	0.46	0.12	0.00	0.16	0.33	0.30	0.10	0.42	0.57	0.60	1.51	1.03	0.23	0.19	0.10	0.97
21	Phuket 21	21.6	72	1.97	1.63	0.34	4.75	0.00	0.44	0.83	0.31	0.27	0.12	0.00	0.05	0.24	0.22	0.08	0.64	0.33	0.56	2.19	1.35	0.22	0.21	0.14	0.90
22	Phuket 22	21.6	72	2.17	1.75	0.42	4.18	0.00	0.40	0.98	0.31	0.37	0.10	0.00	0.05	0.32	0.31	0.10	0.58	0.40	0.57	1.31	1.25	0.21	0.17	0.12	0.95
23	Phuket 23	21.6	72	1.62	1.45	0.17	8.30	0.01	0.31	0.94	0.19	0.14	0.03	0.00	0.00	0.18	0.14	0.12	0.40	0.73	0.53	0.39	1.04	0.21	0.18	0.11	0.94

24	Phuket 24	21.6	72	2.63	2.13	0.50	4.27	0.01	0.43	1.16	0.45	0.47	0.13	0.00	0.09	0.31	0.37	0.10	0.57	0.29	0.56	1.43	1.33	0.21	0.17	0.12	0.79
25	Phuket 25	21.6	72	1.77	1.67	0.10	16.88	0.00	0.31	1.16	0.20	0.10	0.00	0.00	0.00	0.10	0.10	0.08	0.37	0.28	0.30	0.38	0.99	0.00	0.16	0.11	0.94
26	Phuket 26	21.6	72	1.77	1.55	0.23	6.82	0.00	0.28	1.02	0.24	0.13	0.10	0.00	0.00	0.23	0.13	0.11	0.41	0.00	0.30	0.44	1.02	0.00	0.15	0.09	0.88
27	Phuket 27	21.6	72	3.64	2.72	0.92	2.94	0.01	0.49	1.06	1.16	0.72	0.20	0.00	0.00	0.42	0.72	0.09	0.68	0.00	0.49	2.29	1.56	0.00	0.21	0.14	0.98
28	Phuket 28	21.6	72	1.60	1.42	0.18	7.87	0.00	0.27	0.94	0.22	0.08	0.10	0.00	0.00	0.18	0.08	0.09	0.40	0.27	0.38	0.62	1.05	0.20	0.15	0.10	0.66
29	Phuket 29	21.6	72	2.72	2.51	0.21	12.00	0.01	0.52	1.30	0.51	0.31	0.08	0.00	0.18	0.31	0.13	0.10	0.82	0.29	0.52	1.57	1.41	0.20	0.19	0.14	0.96
30	Phuket 30	21.6	72	3.38	3.07	0.31	9.78	0.06	0.55	1.79	0.55	0.40	0.04	0.00	0.12	0.44	0.27	0.08	1.44	0.00	0.57	1.64	1.95	0.21	0.39	0.19	1.19
31	Phuket 31	21.6	72	2.57	2.35	0.22	10.63	0.00	0.45	1.45	0.37	0.24	0.06	0.00	0.08	0.30	0.16	0.10	0.93	0.31	0.53	1.87	1.66	0.21	0.20	0.17	1.07
32	Phuket 32	21.6	72	2.97	2.52	0.45	5.62	0.00	0.42	1.49	0.47	0.42	0.16	0.00	0.13	0.27	0.29	0.12	0.52	0.27	0.42	2.31	1.40	0.21	0.16	0.15	0.98
33	Phuket 33	21.6	72	1.27	1.19	0.08	14.57	0.00	0.22	0.84	0.13	0.06	0.02	0.00	0.00	0.08	0.06	0.10	0.65	0.46	0.52	0.64	1.55	0.20	0.18	0.15	0.88
34	Phuket 34	21.6	72	2.77	2.30	0.47	4.95	0.05	0.43	1.13	0.53	0.48	0.15	0.00	0.16	0.41	0.32	0.09	0.70	0.00	0.45	2.77	1.64	0.20	0.22	0.16	0.98
35	Phuket 35	21.6	72	2.72	2.36	0.36	6.53	0.00	0.47	1.26	0.48	0.39	0.11	0.00	0.14	0.35	0.25	0.11	0.73	0.48	0.63	2.59	1.92	0.21	0.23	0.15	0.92
36	Phuket 36	21.6	72	2.82	2.33	0.49	4.71	0.00	0.34	1.49	0.37	0.51	0.11	0.00	0.13	0.33	0.38	0.09	0.51	0.00	0.34	0.92	1.32	0.21	0.16	0.15	0.94
37	Phuket 37	21.6	72	3.04	2.50	0.53	4.67	0.01	0.42	1.22	0.60	0.64	0.15	0.00	0.25	0.58	0.39	0.09	0.41	0.27	0.47	3.04	1.26	0.21	0.19	0.13	0.93
38	Phuket 38	21.6	72	2.81	2.40	0.41	5.80	0.06	0.46	1.38	0.41	0.38	0.11	0.00	0.08	0.49	0.30	0.09	0.42	0.41	0.60	1.55	1.38	0.22	0.16	0.12	0.80
39	Phuket 39	21.6	72	3.53	2.84	0.69	4.10	0.00	0.49	1.47	0.63	0.76	0.18	0.00	0.25	0.60	0.51	0.08	0.41	0.36	0.61	1.80	1.31	0.26	0.19	0.11	0.79
40	Phuket 40	21.6	72	2.85	2.12	0.73	2.89	0.00	0.30	1.19	0.63	0.42	0.31	0.00	0.00	0.73	0.42	0.10	0.51	0.45	0.54	0.88	1.15	0.25	0.17	0.14	0.89
41	Phuket 41	21.6	72	2.82	2.36	0.47	5.06	0.00	0.47	1.24	0.49	0.49	0.13	0.00	0.16	0.62	0.34	0.09	0.61	0.34	0.60	1.44	1.46	0.25	0.21	0.15	0.87
42	Phuket 42	21.6	72	1.94	1.77	0.17	10.48	0.00	0.30	1.17	0.26	0.16	0.05	0.00	0.03	0.20	0.12	0.10	0.64	0.64	0.65	0.89	1.45	0.22	0.17	0.17	0.92
43	Phuket 43	21.6	72	2.44	2.20	0.24	9.24	0.00	0.39	1.37	0.37	0.26	0.05	0.00	0.08	0.32	0.19	0.10	0.68	0.47	0.57	0.97	1.52	0.25	0.18	0.18	0.94
44	Phuket 44	21.6	72	2.08	1.71	0.37	4.59	0.00	0.32	1.11	0.28	0.31	0.06	0.00	0.00	0.37	0.31	0.08	0.65	0.33	0.48	1.20	1.24	0.27	0.25	0.14	0.78
45	Phuket 45	21.6	72	2.71	2.29	0.42	5.47	0.00	0.38	1.17	0.55	0.49	0.12	0.00	0.19	0.41	0.30	0.08	0.39	0.43	0.57	2.38	1.41	0.25	0.18	0.13	0.82
46	Phuket 46	21.6	72	3.59	2.87	0.73	3.94	0.02	0.48	1.45	0.66	0.77	0.22	0.00	0.26	0.67	0.51	0.08	0.42	0.43	0.57	2.07	1.45	0.27	0.20	0.13	0.90
47	Phuket 47	21.6	72	2.08	1.74	0.34	5.17	0.00	0.31	1.09	0.25	0.35	0.08	0.00	0.09	0.43	0.26	0.09	0.44	0.37	0.48	0.63	1.13	0.25	0.16	0.13	0.83
48	Phuket 48	21.9	73	2.21	2.01	0.19	10.32	0.00	0.36	1.12	0.40	0.26	0.06	0.00	0.13	0.33	0.13	0.09	0.64	0.29	0.52	1.64	1.40	0.24	0.16	0.15	0.75
49	Phuket 49	22.2	74	3.28	2.76	0.52	5.30	0.06	0.38	1.43	0.63	0.67	0.11	0.00	0.27	0.64	0.41	0.09	0.35	0.38	0.61	2.32	1.28	0.25	0.20	0.14	0.95
50	Phuket 50	21.6	72	2.56	2.27	0.30	7.65	0.00	0.40	1.17	0.51	0.38	0.11	0.00	0.19	0.49	0.19	0.09	0.58	0.30	0.40	1.78	1.51	0.21	0.16	0.15	0.93
51	Phuket 51	21.6	72	5.33	4.56	0.77	5.94	0.12	0.56	2.44	1.01	1.05	0.15	0.00	0.44	0.80	0.62	0.08	0.35	0.27	0.44	3.97	1.54	0.20	0.31	0.13	1.08
52	Phuket 52	21.6	72	2.61	2.38	0.23	10.23	0.05	0.33	1.76	0.24	0.17	0.06	0.00	0.00	0.23	0.17	0.12	0.52	0.00	0.30	0.53	1.29	0.21	0.17	0.13	0.98
53	Phuket 53	21.6	72	4.48	3.66	0.82	4.47	0.15	0.58	1.75	0.89	0.98	0.15	0.00	0.30	0.65	0.67	0.08	0.32	0.27	0.34	2.50	1.44	0.20	0.26	0.11	0.93
54	Phuket 54	21.6	72	4.25	3.62	0.63	5.71	0.22	0.67	1.78	0.66	0.76	0.16	0.00	0.28	0.58	0.48	0.09	0.37	0.47	0.57	1.71	1.14	0.20	0.26	0.15	0.95
55	Phuket 55	21.6	72	3.42	2.92	0.51	5.77	0.01	0.51	1.49	0.64	0.63	0.15	0.00	0.27	0.59	0.36	0.10	0.41	0.33	0.44	1.57	1.49	0.21	0.17	0.15	1.08
56	Phuket 56	21.6	72	3.96	3.41	0.55	6.17	0.09	0.57	1.85	0.64	0.65	0.16	0.00	0.26	0.52	0.40	0.09	0.52	0.35	0.62	1.86	1.58	0.25	0.28	0.15	0.83
57	Phuket 57	21.6	72	2.09	1.92	0.17	11.00	0.03	0.35	1.18	0.28	0.17	0.08	0.00	0.07	0.24	0.10	0.10	0.45	0.27	0.42	0.59	1.28	0.21	0.18	0.13	0.83
58	Phuket 58	21.6	72	5.22	4.38	0.83	5.27	0.04	0.60	2.30	1.01	1.13	0.13	0.00	0.43	0.81	0.70	0.08	0.45	0.00	0.30	1.80	1.22	0.20	0.28	0.13	0.85
59	Phuket 59	21.6	72	4.19	3.45	0.74	4.63	0.09	0.53	1.75	0.74	0.91	0.17	0.00	0.34	0.59	0.57	0.09	0.40	0.36	0.66	1.84	1.34	0.25	0.25	0.16	0.82
60	Phuket 60	21.6	72	5.77	4.55	1.22	3.75	0.08	0.70	2.05	1.25	1.49	0.20	0.00	0.47	0.94	1.02	0.08	0.37	0.47	0.59	3.96	1.28	0.58	0.49	0.11	0.98
61	Phuket 61	21.6	72	4.68	3.97	0.72	5.54	0.10	0.59	1.98	0.92	0.96	0.13	0.00	0.37	0.72	0.59	0.09	0.44	0.38	0.66	2.58	1.51	0.28	0.37	0.13	0.99
62	Phuket 62	21.6	72	4.15	3.42	0.72	4.75	0.09	0.59	1.56	0.87	0.94	0.10	0.00	0.32	0.60	0.62	0.10	2.47	0.44	0.80	2.57	3.04	0.30	0.32	0.15	1.11
63	Phuket 63	21.6	72	5.79	4.74	1.05	4.50	0.20	0.70	2.16	1.16	1.29	0.28	0.00	0.52	0.67	0.77	0.08	0.56	0.00	0.30	2.71	1.79	0.21	0.28	0.13	1.09
64	Phuket 64	21.6	72	4.47	3.64	0.83	4.38	0.08	0.57	1.65	0.95	1.06	0.16	0.00	0.38	0.65	0.67	0.08	0.43	0.00	0.30	2.38	1.56	0.20	0.29	0.12	0.97
65	Phuket 65	21.6	72	14.80	10.91	3.90	2.80	0.13	1.56	5.34	3.88	3.74	0.16	0.00	0.00	1.76	3.74	0.10	0.33	0.46	0.64	7.72	1.90	0.96	1.58	0.14	1.30

66	Phuket 66	21.6	72	1.17	1.08	0.09	12.40	0.00	0.23	0.73	0.12	0.09	0.00	0.00	0.00	0.05	0.09	0.10	0.32	0.00	0.00	0.33	0.87	0.20	0.00	0.10	0.85
67	Phuket 67	21.6	72	3.95	3.27	0.69	4.76	0.03	0.55	1.52	0.83	0.88	0.15	0.00	0.34	0.45	0.54	0.08	0.67	0.00	0.00	3.85	2.14	0.21	0.36	0.15	1.21
68	Phuket 68	21.6	72	3.92	3.22	0.70	4.57	0.06	0.53	1.54	0.80	0.84	0.15	0.00	0.28	0.47	0.56	0.08	0.33	0.00	0.30	3.49	1.78	0.21	0.24	0.14	0.83
69	Phuket 69	21.6	72	7.58	6.54	1.04	6.28	0.06	0.87	3.09	1.74	1.71	0.11	0.00	0.78	0.87	0.93	0.10	0.40	0.00	0.30	3.83	2.07	0.21	0.37	0.17	1.16
70	Phuket 70	21.6	72	11.16	8.96	2.20	4.08	0.14	1.19	4.00	2.70	3.04	0.10	0.00	0.94	1.94	2.10	0.08	0.37	0.51	0.86	6.45	1.85	1.42	1.14	0.17	1.28
71	Phuket 71	21.6	72	12.54	9.33	3.22	2.90	0.16	1.58	4.22	3.37	2.99	0.22	0.00	0.00	1.53	2.99	0.11	0.40	0.38	1.62	9.21	2.16	2.38	1.24	0.24	1.37
72	Phuket 72	21.6	72	2.40	1.96	0.44	4.49	0.01	0.43	1.12	0.41	0.35	0.09	0.00	0.00	0.16	0.35	0.11	0.49	0.53	0.67	1.50	1.33	0.27	0.20	0.14	1.07
73	Phuket 73	21.6	72	4.86	4.09	0.77	5.33	0.00	0.75	1.71	1.01	1.20	0.19	0.00	0.62	0.62	0.58	0.10	0.63	0.42	1.20	6.91	2.39	0.42	0.36	0.19	1.15
74	Phuket 74	21.6	72	5.26	4.41	0.84	5.23	0.05	0.66	1.97	1.15	1.27	0.15	0.00	0.58	0.73	0.69	0.09	0.32	0.42	0.64	4.26	1.58	0.64	0.58	0.15	1.17
75	Phuket 75	21.6	72	2.91	2.53	0.38	6.69	0.08	0.46	1.27	0.51	0.50	0.09	0.00	0.22	0.26	0.28	0.09	0.38	0.00	0.31	2.06	1.14	0.21	0.21	0.09	0.88