CHAPTER 1

INTRODUCTION

1.1 Air pollution; situation in Asia

Air pollution is contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere. Household combustion devices, motor vehicles, industrial facilities and forest fires are common sources of air pollution. Pollutants of major public health concern include particulate matter, carbon monoxide, ozone, nitrogen dioxide and sulfur dioxide. Outdoor and indoor air pollution can cause respiratory and other diseases, which can be fatal (WHO, 2000).

Urban air pollution, with its long- and short-term impacts on human health, well-being and the environment, has been a widely recognized problem during the last 50 years. Besides deleterious effects on human health, pollution causes serious negative effects on ecosystems (leading to injury to plants and reduction in crop yields), materials and the visibility (Fenger, 1999; Riga-Karandinos, 2005). Many countries and different international organizations such as EPA (Environmental Protection Agency), WHO (World Health Organization), the European Union Air Quality Framework and Daughter Directives, World Bank, etc. published their own standards for this purpose (Lim *et al.*, 2005). Monitoring studies are also of particular importance in this respect in order to improve air quality management efforts, detect long-term air quality trends, and observe the effectiveness of air quality control regulations. If the ambient air quality is unlikely to meet existing air quality standards, local authorities are required to devise, test and implement pollution control policies. In developed countries where more than 75% of all people now live in cities, their economical strength allows for effective pollution prevention and control against the pollutants impacts. Pollution prevention and control concepts in developing countries are also gaining increasing importance under stricter regulations, particularly in recent years (Fang and Chen, 1996; O'Malley, 1999; Bailey and Solomon, 2004; Mao *et al.*, 2005), and there has been a growing concern about urban air quality in terms of the pollutants impacts (Wolf, 2002; Brajer *et al.*, 2006; Oudinet *et al.*, 2006). However, air pollution in many urban areas of the developing countries is still a serious environmental problem, and many cities in the world are exposed to high levels of air pollution.

Air pollution in Asia like other is composed part of world of a mixture of pollutants, including particles and gases emitted in large quantities from many different combustion sources, including cars and industries. Air quality in Asia has deteriorated significantly in recent decades because of rapid industrialization, urbanization, and motorization. According to average air quality levels between 2000 and 2003 summarized by the Clean Air Initiative Network, (Huizenga *et al.*, 2004) most Asian cities cannot comply with the WHO air quality guidelines or the US Environmental Protection Agency standards; exceptions are cities in more developed countries such as Singapore, Taiwan, and Japan. Several Asian cities in China, India, and Vietnam have the highest levels of outdoor air pollution in the world. In addition to comparatively higher air pollution levels, Asian countries have specific emission sources that are different from those in the West. Two-stroke vehicles, combustion of

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lower-quality fuels, and open burning of biomass and solid waste materials together contribute to a larger portion of emissions in many Asian countries. Traffic emission in South Asia is especially different from that in Europe or North America, having the largest motorcycle fleet in the world, under-regulated emission standards of vehicles, and high contents of aromatic hydrocarbons and sulfur in gasoline and diesel oils. The 2-stroke engines of motorcycles are an especially important source of volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxide (NO_x), and PM in Taiwan with 20 million motorcycles. Exposure becomes even worse because of frequent traffic congestion in Asian countries such as China, India, Indonesia, Pakistan, the Philippines, and Thailand. The burning of biomass, including rice straw and garbage as well as forest fire, is also an important emitted source of urban air pollution in South and Southeast Asia. Large cities in this region are often surrounded by agricultural land, and the open burning of agricultural waste may also contribute directly to urban air pollution. The products of biomass burning include CO, carbon dioxide, nitrogen, methane, nonmethane hydrocarbons, methyl chloride, and PM in various size classes (Koppmann et al., 2005). In addition, emissions from manufacturing accident can also contribute significant exposures to residents in industrial areas. Long-range transported air pollution, such as Asian dust storms (ADS) in north Asia and forest fires in South Asia, account for additional exposure to the residents in the affected countries, such as China, Japan, Korea, Taiwan, Indonesia, Malaysia, Thailand, Singapore, and Vietnam (Stockholm Environment Institute, 2008).

Air quality in Bangkok Metropolitan Region (BMR), Thailand, was seriously deteriorated in the early 1990s regarding to airborne particles, carbon monoxide, and

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lead concentrations, especially at monitoring stations near major roadways (PCD, 2004). Gradual improvement of air quality in BMR has been observed after the Asian economic crisis in 1997 partly due to the setback of economic expansion as well as stringent environmental regulations. A World Bank report showed that air quality in BMR was still less serious compare to several Asian cities, for example, Beijing, Jakarta, New Delhi and Manila (World Bank, 2003). However, problems still exist in some urban centers and near traffics, especially high concentrations of particulate matter (PM). Airborne fine particles in recent years have increased and started to exceed the national ambient air quality standards (120 µg/m³ for 24 hours average of PM10) in some monitoring stations in BMR and major cities (PCD, 2004). In 2002, the maximum 24 hours concentration of PM10 was as high as 300 µg/m³ in some monitoring stations in BMR (Chuersuwan *et al.*, 2008).

Chiang Mai Province has been annually facing air pollution during the dry season. This pollution has been recorded as a serious problem for well over 10 years. Recently, the problem has become worse than ever. The fact that, the geographical features of Chiang Mai City's located in the Chiang Mai–Lamphun intermountain basin and is surrounded by high mountain ranges that results in the same air being recirculated, picking up more pollutants every time. Anthropogenic activities including cremation, garbage burning, forest fire, vehicle emission and biomass burning are the main contribution of air pollutants in Chiang Mai City. Chantara et al. (2010) measured PM10 and PM10-bound PAHs in Chiang Mai and Lamphun, Thailand in 2005 to 2006 and found that concentrations of most of carcinogenic PAHs were positively correlated to PM10 concentrations. The highest PAH concentration was found in dry season (December–March). They mentioned that apart from traffic congestion, it was probably due to specific local activities i.e. biomass burning.

Biomass burning, which comprises open vegetation fires and domestic biofuel use, is one of the largest sources of aerosol particles worldwide. Burning of biomass such as wood, leaves, trees, grass and agro-residue are the largest source of air pollution in many rural areas of the developed and developing countries (Koppmann *et al.*, 2005). Globally, biomass burning is estimated to produce CO_2 (40%), CO (32%), PM (20%) and 50% of the highly carcinogenic PAHs produced by all sources. In general, numerous particulates (e.g., polycyclic aromatic hydrocarbons and other organics) and gaseous compounds (e.g., carbon monoxide) and volatile organic compounds) that come from biomass burning are known to be hazardous to human health (Jacobs, 1997 and Torigoe, 2000).

1.2 Particulate Matter

Particles in the form of soot had been recognized as pollution for centuries, and they were until the 1980s registered as a total mass, TSP (Total Suspended Particulate matter). But in practice they are characterized by both size and composition. Since 1990 size fractionation was attempted by measurement of PM10 (particles with diameter less than 10 mm). Unfortunately the major part of PM10 may have a natural origin (sea spray and mineral dust), and it is therefore important also to measure PM2.5 or even PM1.0. The number of small particles can be large, even if their total mass is not significant (Figure 1.1). This became especially important when it appeared that the size of the individual particles was an important parameter in the transport into the respiratory system and thus for the impact on human health. Epidemiological studies have in recent years (Schwartz *et al.*, 1997) shown that

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particles with a size below $2.5 \ \mu m$ have a significant impact on people suffering from respiratory and cardio-pulmonary diseases and on the daily mortality.



Figure 1.1 Mass and number distribution of particles (Schwartz et al., 1997).

It is estimated that in a modern city present levels cause yearly some hundred extra deaths per million inhabitants. Such small particles are particularly associated with car exhaust, especially diesel cars, and are thus a growing problem in urban areas. It can be solved by introducing filters in the exhaust, but so far economic considerations have prevented a large scale effort (Fenger, 2009).

Increased levels of fine particles in the air are linked to health hazards such as heart disease, altered lung function and lung cancer (Manual of Ambient Air Particulate Matter Measurement, 2003). Particulate matter (PM) is still a major problem in almost all Asian countries with concentration exceeding 300 μ g/m³ in many cities. Thus, many ambient air pollutant still flow and affect to human health for a long time. It is reported that the cancer incidence rate and mortality have increased in the recent years. This is especially true for Chiang Mai, where the lung cancer incidence rate is much higher than other places in Thailand. In the last decade Chiang Mai face with haze pollution especially in 2007, reported that the level of PM10 was highest by 383 μ g/m³ in March 14. Trend of PM10 levels in March higher than Thailand PCD standard (24 hours standard, 120 μ g/m³) (Jaikamsueb, 2007).

1.3 Polycyclic aromatic hydrocarbons (PAHs)

1.3.1 Definition and sources

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile and very stable organic compounds consisting of only carbon and hydrogen with a fused ring structure containing at least two benzene rings. PAHs are semi-volatile organic compounds (VOCs) and present in both gas and particulate phases. PAHs are a major group of carcinogens, mutagens and teratogens in the environment. They are products of incomplete combustion released from both natural and anthropogenic sources. In general, there are five major emission sources of PAHs, i.e. domestic, mobile, industrial, agricultural, and natural sources. Furthermore, some cosmic sources of PAHs have also been proposed (Wing and Bada, 1992; Beegle *et al.*, 2001).

The low molecular weight PAHs form dominantly in the gas phase, whilst those with four or more rings are found mainly in the particulate phase (Ravindra *et al.*, 2008; Hanedar *et al.*, 2011). The PAHs recognized as carcinogenic are mostly associated with particulate matter. Atmospheric PAH concentrations are strongly dependent upon the size of airborne particulate matter (PM) (Lodovici *et al.*, 2003). PM10 can deposit and accumulate in the respiratory system and can cause a significant threat to human health. It has been an area of continuous research for, and as evidence of, the risks pertaining to human health, and supplementary to reduce human exposure to these toxic agents (US EPA, 1996b; WHO, 2000).

PAHs exist in environment many forms, only 16 of PAHs were selected by United State Environment Protection Agency (U.S. EPA) in 1976 as priority pollutants (Figure 1.2). They are monitored routinely for regulatory purposes by Agency for Toxic Substances and Disease Registry (ASTDR). Their physical and chemical properties are governed by size (number of carbon atoms) and shape (ring linkage pattern) of each molecule. A summary of some physicochemical properties and estimated carcinogenic potency are given in Table 1.1. The molecular weight (MW) of 16-PAHs was between 128.17 – 278.35 g. The lowest MW was NAP while the highest MW was DBA. Amount of PAHs were shown by water solubility values which was highest in NAP and lowest in IND. The octanol-water partition coefficient (K_{OW}) representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher to log Kow, the more non-polar the compound. Log K_{OW} is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log Kow values are generally inversely related to aqueous solubility and directly proportional to molecular weight (U.S.EPA 2009). The lowest of Log K_{OW} value at 25 °C was NAP while highest was FLA. The octanol-air partition coefficient (K_{OA}) is the ratio of a chemicals concentration in octanol to the concentration in air at equilibrium. It is useful for predicting the partitioning behavior between air and environmental matrices such as soil, vegetation and aerosol particles (Meylan and Howard, 2005). The lowest of Log K_{OW} value at 25 °C was also NAP while highest was BkF. Henry's law, the solubility of a gas in a liquid solution at a constant temperature is proportional to the partial

pressure of the gas above the solution. It used in environmental chemistry and atmospheric physics as a major criterion for describing air-water partitioning of solutes at near ambient conditions. It plays a major role in evaluating the transport of pollutants between atmosphere and aquatic systems, rain water and aerosols (Majer *et al.*, 2008). NAP was highest while DBA was lowest values of Henry's law constant at 25 °C. Furthermore, the carcinogenic potency was set up from The International Agency for Research on Cancer (IARC) and The United States Environment Protection Agency (U.S. EPA). IARC classified 16-PAHs into 3 groups that were consisted of group 3: the compound is not classifiable as to its carcinogenic to human (ANT, FLA, PRY and CHR), group 2A = the compound is probably carcinogenic to human (BkF, BbF and IND). The 7-PAHs (BaA, CHR, BkF, BbF, BaP, IND and DBA) was grouped into the compound is probably carcinogenic (B2).

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่ Copyright[©] by Chiang Mai University All rights reserved Naphthalene (NAP)

Acenaphthylene (ACY)



Acenaphthene (ACE)



Phenanthrene (PHE)

Fluoranthene (FLA)



Benz[a]anthracene (BaA)

Benzo[b]fluoranthene (BbF)



benzo[a]pyrene (BaP)

Dibenz[a,h]anthracene (DBA)

Figure 1.2 Structures of 16-PAHs (U.S. EPA, 1993).

Fluorene (FLU)

Anthracene (ANT)



Pyrene (PYR)



Chrysene (CHR)

Benzo[k]fluoranthene (BkF)



Indeno[1,2,3-cd]pyrene (IND)



Benzo[g,h,i]perylene (BPER)





PAHs	Abbreviation	Molar mass (g)	Water solubility (mg L ⁻¹)	log K _{OW} at 25 °C	log K _{OA} at 25 °C	Henry's law constant	Carcinogenic potency	
						(Pa m ³ mol ⁻¹) at 25 °C	IARC	U.S.EPA
Napthalene	NAP	128.17	31	3.37	5.1	42.6	302	
Acenaphthylene	ACY	152.19	16	4.00	6.4	12.7		
Acenaphthene	ACE	154.21	3.8	3.92	6.3	18.5		
Fluorene	FLU	166.22	1.9	4.18	6.7	9.8		
Phenanthrene	PHE	178.23	1.1	4.46	7.5	4.3		
Anthracene	ANT	178.23	0.04	4.49	7.3	4.45	3	
Fluoranthene	FLA	202.25	0.2	8.90	8.6	1.96	3	
Pyrene	PYR	202.25	0.13	8.80	8.6	1.7	3	
Benzo[a]anthracene	BaA	228.29	0.011	5.80	9.5	1.22	2A	B2
Chrysene	CHR	228.29	0.0019	5.73	10.4	0.53	3	B2
Benzo[b]fluoranthene	BbF	252.31	0.0015	5.78	-	0.05	2B	B2
Benzo[k]fluoranthene	BkF	252.31	0.0008	6.50	11.2	0.04	2B	B2
Benzo[a]pyrene	BaP	252.31	0.0015	6.35	10.8	0.07	2A	B2
Indeno[1,2,3-c,d]pyrene	IND	276.33	0.00019	6.70	V-L	0.029	2B	B2
Dibenzo[a,h]anthracene	DbA	278.35	0.0005	6.50	-	0.0075	2A	B2
Benzo[g,h,i]perylene	BPER	276.33	0.00014	6.63	-	0.031		

IARC classified group 3 = the compound is not classifiable as to its carcinogenic to human,

group 2A = the compound is probably carcinogenic to human,

group 2B = the compound is possibly carcinogenic to human U.S. EPA classified group B2 = the compound is probably carcinogenic

1.3.2 Mechanisms and effects

Many organic materials, such as fossil fuels, have a chemical structure able to form polycyclic aromatic compounds (PAC) under pyrolysis and combustion conditions (Mastral *et al.*, 1995 and Mastral *et al.*, 1996). In fossil fuels, coals have the highest concentrations (White *et al.*, 1980), whereas petroleum and their derived products have the least (Mastral *et al.*, 2000). For example, in coal structure, the dominant component is considered to be a macromolecular three dimensional network composed of aromatic and hydroaromatic units connected by alkylic, ether, and thioether bridges (Mastral *et al.*, 2000). Upon heating, the fuel structure undergoes important physical and chemical changes and a fraction is released into the atmosphere. As a consequence of the thermal process, both the released and the remaining fractions undergo cyclization reactions leading to polycyclic compounds which can exist in the gas as well as in the solid phase, depending on their molecular volume and on the environmental temperature. Biomass generally contains very low quantities of PAH structures (Simoneit *et al.*, 1999). The following PAH formation mechanisms have been suggested in the literature:

(1) Incomplete combustion: the fragments of the mainly aromatic structure of the fuel are emitted and escape unburned.

(2) Pyrolysis and pyrosynthesis: as a consequence of the chemical changes during combustion, reactions such as cyclization of alkyl chains and radical condensation can lead to polycyclic compounds through polymerization reactions, which are favored over oxidation in fuel-rich regions of the flame (Mastral *et al.*, 2000). Considering the fact that biomass usually contains less aromatics, the main mechanism that holds for PAH emissions from biomass is pyrolysis and pyrosynthesis. The mechanisms producing PAH in the combustion process are very complex, but it seems that the chemical reactions in flames proceed via the radicals released during the pyrolysis step which precedes combustion (Mastral et al., 2000a and Mastral et al., 2000b). It is also strongly dependent on the type of biomass and the combustion operating conditions. Different synthesis mechanisms of PAHs have been suggested (Mastral et al., 2000a; Chagger et al., 2000; Badger et al., 1962; Frenklach et al., 1991) and are being questioned by others (Lindstedt et al., 2001) and these mechanisms are still in discussion. For example, it has been shown that one way to produce PAH from smaller C2 species proceeds via the HACA mechanism. In this commonly called HACA mechanism (H-abstraction C₂H₂-addition), PAHs are produced from the acetylene (ethyne) which forms benzene and multi-ringed PAH structures. The addition of acetylene to an aromatic ring, or the formation of an aromatic radical, like phenyl, leads to either bonding of an ethynyl $(-C_2H)$ group with the aromatic ring, or the formation of an additional condensed aromatic ring. Depending on the neighboring ring structure, the newly formed ring can either be a radical, which can grow readily with acetylene, or it may be a molecular species. The latter will have to be "activated" through the H-abstraction reaction to produce a PAH radical species before it can undergo the further growth reaction with acetylene. If the concentrations of aromatic species are sufficiently large, PAH growth through the direct ring-ring condensation is also possible. For example, benzene and phenyl can react to form biphenyl. Through the H-abstraction, a biphenyl radical forms and can react with acetylene to form the three-ring phenanthrene, or it can react with benzene to form a four ring aromatic species (Chagger et al., 2000; Frenklach et al., 1991; Law, 2006). The simplest and earliest PAH formed can, depending on the flue gas

conditions, undergo further pyrolytic reactions to form larger, highly condensed PAH by intermolecular reactions, such as condensation and cyclization. Therefore, the PAH can exist in the gas emitted or be supported on particulate matter (soot), or even give rise to particulate matter, depending on their association. Most three-ring PAHs are present in the gas phase emissions and compounds with four, five, and six or more ring PAHs are associated with flyash in biomass combustion emissions. PAHs are important precursors in the formation of PCDDs/Fs (polychlorinated dibenzofurans and polychlorinated dibenzopdioxin). A simple formation scheme is given in Figure



Figure 1.3 General formation schemes of PAHs, PCDDs, and PCDFs (Changger *et al.*, 1998).

At 800-950 °C during fluidized bed combustion (FBC), the destruction and chemical alteration of PAHs are possible in the presence of oxidants such as OH, O₃, HNO₃ etc. (Manahan, 1991). In practice, at typical FBC combustion temperatures, large molecules (if present) break up during pyrolysis, usually into smaller fragments, but small ones, e.g. of lower hydrocarbons, can yield higher molecular mass products. The PAHs produced in this step (< 850 °C) may be mainly due to incomplete combustion. Above 850 °C, since the synthesis reactions of PAHs formation are endothermic (the enthalpy of formation (H_f) of all the 16 PAHs is positive), more PAHs can be formed at higher temperatures (Lui et al., 2001). As a consequence, the PAHs may be synthesized in the dense fluidized zone or freeboard region of the combustor at higher temperatures. The metals (Fe, Cu) in the particles may also act as catalysts for the synthesis reactions. Excess air, residence time, and air staging are reported to affect PAHs significantly. Oxygen-rich environment helps in reducing PAHs. Air staging provides not only oxygen-rich conditions in the freeboard but also increases the residence time of fuel particles in the system. All these effects increase the efficiency of the system thus leading to lower PAHs (Simoneit, 2002 and Mastral and Callen, 2000). Limestone added for SO₂ emission reduction in FBC system can also affect the PAH emissions. Increasing the Ca/S ratio causes an increase in PAH emissions due to a longer turnover rate of bed material and endothermic limestone decomposition (Mastral et al., 1998 and Mastral et al., 2000c).

It has also been reported that low percentages of excess oxygen favor the highest PAH deposition on particulate matter, while the highest percentages of excess air favor the sweep of PAHs to the gas phase. The highest percentages of excess oxygen seem to minimize possible interactions between PAHs inter-conversion, association and other condensation reactions, giving the lowest hydrocarbons emissions (Mastral and Callen, 2000). Perhaps, it is due to the formation of substituted PAHs and other oxygenated compounds, a consequence of the interaction between oxygen atoms and radicals. In this way, at the lowest percentages of excess oxygen, this interaction between oxygen and radicals should be less favored, and as a result, the PAH amount emitted would be higher. It can be concluded that once combustion efficiency is optimized, PAH emissions are a function of the interactions between radicals emitted by the devolatilization of the pyrolytic process and the combustion variables, combustion temperature, airflow, percentage of excess oxygen. The competition between oxidation and condensation reactions, retrogressive reactions, or the radicals conversion in CO, H, and O by oxidation reactions will determine the PAH formation (Mastral and Callen, 2000 and Mastral *et al.*, 2000c).

1.4. Biomass

1.4.1 Biomass classification

Biomass is a biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material (Mastral and BEC, 2008 and Communities CotE, 2001). Biomass energy resources are diverse and therefore a great need exists for a comprehensive classification system. The motivation for such a system is to predict the behavior of biomass by identifying to which class it belongs.

One approach could be on the basis of basic components namely, cellulose, hemicelluloses, and lignin percentages and their behavior (Figure 1.4). However, such

a system cannot account for possible interactions between the components and has been regarded unreliable (Williams, 1992 and Jenkins *et al.*, 1998). However, some success in predicting biomass behavior during pyrolysis with this classification has been achieved with compensation of minerals' effects taken into account (Williams, 1992). Two classification approaches have been proposed based on the origin of the biomass and their properties (Williams, 1992 and Jenkins *et al.*, 1998). Biomass fuels can be generally divided into four primary classes:

1) Primary residues: By-products of food crops and forest products (wood, straw, cereals, maize etc.).

2) Secondary residues: By-products of biomass processing for production of food products or biomass materials (saw and paper mills, food and beverage industries, fruit seed etc.).

3) Tertiary residues: By-products of used biomass derived commodities (waste and demolition wood etc.).

4) Energy crops. The classification based on properties can be categorized into:

- Wood and woody fuel (hard and soft wood, demolition wood).

- Herbaceous fuels (straw, grasses, stalks etc.).

- Wastes (sewage sludge, refuse-derived fuel (RDF) etc.).

- Derivates (waste from paper and food industries etc.).

- Aquatic (Kelp etc.).

- Energy crops (specifically cultivated for energy purposes).

Because of the diverse nature of biomass fuel, properties in these categories vary in a wide range. For example, apart from energy crops, moisture content can

easily vary with a factor 2 in all the categories. An alternative approach based on the Van Krevelen diagram (plot of H/C versus O/C atomic ratios) has also been suggested (Williams *et al.*, 2001). The premise in this classification is that biomass from altogether different categories (waste, wood) fall in close proximity of each other but have very different properties. Another, more recent, classification that can be used is the European standard for solid biofuels (CEN TC 335) (Communities CotE, 2001). This classification is based on the biofuel origin and source. In the hierarchical classification system, the main origin-based solid biofuel groups are:

- 1. Woody biomass (wood chips, pellets, log wood, saw dust etc.).
- 2. Herbaceous biomass
- 3. Fruit biomass
- 4. Blend and mixtures.

CEN/TC 335 is subdivided in 5 subgroups; WG1 (terminology, definitions and description), WG2 (fuel specification and classes), WG3 (sampling and sample reduction), WG4 (physical and mechanical test), and WG5 (chemical test methods). Because of the diversity of the biomass fuels and therefore their effects during combustion, this article is limited to the biomass materials considered in the first classification approach provided above.

1.4.2 Biomass composition

The components of biomass include cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water, hydrocarbon, ash, and other compounds. The concentration of each class of compound varies depending on species, type of plant tissue, stage of growth, and growing conditions. Cellulose is a linear polysaccharide of β -D glucopyranose units linked with 1–4-glycosidic bonds. Hemicelluloses are

polysaccharides of variable composition including both five and six carbon monosaccharide units. The lignin is an irregular polymer of phenylpropane units (Jenkins et al., 1998 and Schultz and Taylor 1989). Due to the carbohydrate structure, biomass is highly oxygenated with respect to the conventional fossil fuels including hydrocarbon liquids and coals. The bulk composition of biomass in terms of carbon, hydrogen, and oxygen (C, H, and O) does not differ much among different biomass sources. Typical (dry) weight percentages for C, H, and O are 30 to 60%, 5 to 6%, and 30 to 45% respectively. C, H, O shares can be different for typical fuels (Faaij et al., 1998 and Faaij, 2004). Nitrogen, sulfur and chlorine can also be found in quantities usually less than 1 % dry matter, but occasionally well above this. Nitrogen is a micro nutrient for plants, and critical to their growth. Certain inorganic elements can be found in high concentration as well. Relative to coal, biomass generally has less carbon, more oxygen, more silica, chlorine and potassium, less aluminum, iron, titanium and sulfur, and sometimes more calcium. Certain biomass types also contain contaminating species in trace amounts depending upon the source of the fuel. For example, heavy metals (cadmium, lead etc.) are commonly found in woody fuels (especially demolition wood) from paints and atmospheric deposit ion sources. These heavy metals make an important part of the emitted pollutants especially in sewage sludge combustion but are also important for contaminated wood operation and therefore have been treated separately in trace metal emission section.



Figure 1.4 Biomass structure (http://www.lbl.gov/Publications/YOS/Feb/index.html)

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1.5 Sampling artifact

Representative PAHs sample should depict their true levels in ambient air. PAH monitoring is usually performed using high- or low-volume samplers (HVS, LVS) and is complex because of the reactive breakdown of PAHs between the gas and particulate phases. In HVS or LVS the particulate phase is first trapped on a filter and the gaseous phase is trapped on a solid adsorbent (e.g. polyurethane foam) located downstream from the filter. However, these sampling procedures have also been shown to be affected by several sampling artifacts (Kavouras et al., 1999; McMurry, 2000). In the particulate phase, positive artifacts (overestimation of the particle phase concentrations) are mainly due to sorption of gaseous compounds on the filter, while negative artifacts (underestimation of the particle phase concentrations) result from the volatilization of particulate PAH from the filter (McMurry, 2000; Goriaux et al., 2006). Moreover, chemical degradations of PAHs by oxidizing compounds such as nitrogen oxides ($NO_x=NO+NO_2$), hydroxyl radical (OH), halogens, nitric acid (HNO₃), hydrogen peroxide (H_2O_2), and ozone (O_3) may occur during sampling (Pitts et al., 1986; Tsapakis and Stephanou, 2003; Schauer et al., 2003). Very recently Goriaux et al. (2006) reported that the atmospheric PAH concentrations measured using conventional samplers not equipped with an ozone trap can underestimate the PAH concentration by more than 200%. This was especially found when the samples were collected in the vicinity of a point source of particulate PAHs and for highly reactive compounds such as B[a]P.

The importance of the sampling artifacts depends mainly on sampling conditions such as temperature or atmospheric concentrations of PAH and oxidants (Mcdow and Huntzicker, 1990; Mader and Pankow, 2001). To reduce artifacts induced by conventional samplers, denuder sampling devices were developed (Coutant et al., 1992; Coutant et al., 1989; Lane and Gundel, 1996). The denuder sampler systems were designed to trap the gas phase on a solid sorbent coated on the surface of the trap prior to collecting the particulate phase on a filter. This methodology avoids the phenomenon of adsorption of the gas phase on the filter and reduces the desorption artifact by collecting the volatilized fraction on a sorbent cartridge placed downstream from the filter. Finally, the chemical degradation of particulate PAHs may be reduced as the sorbent coated on the denuder tubes can remove the oxidizing species included in the gas phase (Coutant et al., 1988; Tsapakis and Stephanou, 2003). It is interesting to notice, however, that most of the studies on ambient levels of PAHs were carried out (or are still being carried out) using a HVS or LVS and hence it is important to modify these samplers to avoid artifacts bias. Moreover, the collection PM samples by nylon and quartz filters were affected artifact sampling. Volatilization of the collected PM would result in the negative artifact of PAHs mostly occuring in nylon filter. Adsorption of gaseous PAHs onto the collected media would lead to positive artifact of the PAHs mostly occurring in quartz filter. Passive adsorption, as indicated by field blanks, accounts for part of the positive artifact. Turpin et al. (1994) and Subramanian et al. (2004) suggest that quartz-fiber (front and backup) filters might reach equilibrium/saturation within 24 hours.

1.6 Gas Chromatography-Mass Spectrometry (GC-MS) for PAHs analysis

Gas chromatography mass spectrometry (GC-MS) is a method that combines the features of gas chromatography and mass spectrometry to identify different substances within a test sample (Figure 1.5). GC-MS has been widely accepted for chemical identification of volatile and semi-volatile organic compounds in mixtures, drug detection, environmental analysis, explosives investigation, and identification of unknown samples. This makes it ideal for the analysis of the hundreds of relatively low molecular weight compounds found in environmental materials. In order for a compound to be analyzed by GC-MS it must be sufficiently volatile and thermally stable. In addition, functionalized compounds may require chemical modification (derivatization), prior to analysis, to eliminate undesirable adsorption effects that would otherwise affect the quality of the data obtained. Samples are usually analyzed as organic solutions consequently materials of interest (e.g. soils, sediments, tissues etc.) need to be solvent extracted and the extract subjected to various 'wet chemical' techniques before GC-MS analysis is possible.

The sample solution is injected into the GC inlet where it is vaporized and swept onto a chromatographic column by the carrier gas (usually helium). The sample flows through the column and the compounds comprising the mixture of interest are separated by virtue of their relative interaction with the coating of the column (stationary phase) and the carrier gas (mobile phase). The latter part of the column passes through a heated transfer line and ends at the entrance to ion source (Figure 1.6) where compounds eluting from the column are converted to ions.



Figure 1.5 A schematic of GC-MS (http://people.whitman.edu/~dunnivfm/ GC_MS_Ebook/CH2/2_3.html)

The most frequently used method is electron ionization (EI) and the occasionally used alternative is chemical ionization (CI). For EI a beam of electrons ionize the sample molecules resulting in the loss of one electron. A molecule with one electron missing is called the molecular ion and is represented by M^+ (a radical cation). When the resulting peak from this ion is seen in a mass spectrum, it gives the molecular weight of the compound. Due to the large amount of energy imparted to the molecular ion it usually fragments producing further smaller ions with characteristic relative abundances that provide a 'fingerprint' for that molecular structure. This information may be then used to identify compounds of interest and help elucidate the structure of unknown components of mixtures. CI begins with the ionization of methane (or another suitable gas), creating a radical which in turn will ionize the

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sample molecule to produce $[M+H]^+$ molecular ions. CI is a less energetic way of ionizing a molecule hence less fragmentation occurs with CI than with EI, hence CI yields less information about the detailed structure of the molecule, but does yield the molecular ion; sometimes the molecular ion cannot be detected using EI, hence the two methods complement one another. Once ionized a small positive is used to repel the ions out of the ionization chamber.



Figure 1.6 A schematic of an ion source (http://www.bris.ac.uk/nerclsmsf/techniques/gcms.html)

The next component is a mass analyser (filter), which separates the positively charged ions according to various mass related properties depending upon the analyzer used. Several types of analyzer exist: quadrupoles (Figure 1.5), ion traps, magnetic sector, time-of-flight, radio frequency, cyclotron resonance and focusing to name a few. The most common are quadrupoles and ion traps. After the ions are separated they enter a detector the output from which is amplified to boost the signal. The detector sends information to a computer that records all of the data produced, converts the electrical impulses into visual displays and hard copy displays. In addition, the computer also controls the operation of the mass spectrometer. A "library" of known mass spectra, covering several thousand compounds, is stored on a computer. Mass spectrometry (MS) is considered the only definitive analytical detector.



Figure 1.7 A schematic of a quadrupole analyzer (http://www.bris.ac.uk/nerclsmsf/ techniques/gcms.html)

The MS detector can operate in 2 different modes: scanning and selected ion monitoring (SIM). The scanning mode provides a fairly reproducible mass spectral fragmentation pattern ("fingerprint"). Mass spectra are recorded (scanned) at regular intervals (typically 0.5 - 1 per second) during the GC separation and stored in the instrument data system for subsequent qualitative or quantitative evaluation. From such patterns, it is often possible to deduce structural features (mass spectral interpretation) but this requires experience and can be very time-consuming,

particularly as a complex mixture might contain hundreds of components. Such "fingerprints" can also be compared with those stored in a standard database (mass spectral library) and several important databases are currently available in the Facility to assist with problem solving. Although considerable care must be exercised in interpreting the results of such comparisons, this is often a useful technique in helping to identify unknowns, or to quickly eliminate known compounds from further consideration. Although library searching is a very useful and timesaving technique, it is important to remember that such searches do not identify compounds. The additional measurement of the GC retention index, related to the time it takes a component to travel through the column, provides an additional parameter and is becoming increasingly important in identification work. Software is available in the Facility to assist with these measurements. Quantitative work can be performed by integration of selected ion chromatographic peaks. Software is available for this purpose. Selected ion monitoring (SIM) is much more sensitive technique for trace quantitative analysis. Here, instead of scanning a whole spectrum, only a few ions are detected during the GC separation. This can result in as much as a 500-fold increase in sensitivity, at the expense of specificity. Stable isotope-labelled internal standards can be employed. Again, software is available for such analysis. Depending on the analyte, low picogram to nanogram amounts can be measured using this powerful technique (Harper, 2002).

1.6.1 Chromatographic retention

The retention time (t_R) of a peak can be used as means of qualitative identification. The position of the target compound peak plays an important role in GC qualitative analysis. We call the length of time between injection and position of the target compound peak a retention time.



Figure 1.8 Retention time (http://clu-in.org/characterization/technologies/gc.cfm)

a) Resolution (Rs)

The resolution of a column refers to its ability to separate or resolve two solutes. The significance of this term is illustrated in Figure 1.9, which is shown calculation of resolution parameter on the chromatogram of two compounds. Column resolution is defined as

$$Rs = \frac{2[t_{RB} - t_{RA}]}{W_A + W_B}$$

Where; t_R = retention time, W = peak width

The resolution 1.5 gives as essentially complete separation of 2 components with no overlapping where as the resolution equal 1 represents that 2% of peak pair are overlapped, or it mean 98% of peak pair are separated (Skoog and Leary, 1991).



Figure 1.9 The calculation parameters of adjacent peak pair resolution (http:// people.whitman.edu/~dunnivfm/C_MS_Ebook/CH1/1_2.html)

b) Internal standardization method

The highest precision for quantitative chromatography is obtained be use of internal standards (IS) because the uncertainties introduced by sample injection are avoided. In this procedure, a carefully measured quantity of and IS substance is introduced into each standard and sample, and the ratio of analyst to IS peak areas serves as the analytical parameter (Skoog and Leary, 1991). Use the following equation for calculation of analyst to IS ratio.

Peak area ratio = $\frac{Area (analyst)}{Area(IS)}$

For PAHs analysis, deuterated internal standards are selected that are similar in analytical behavior to compounds of interest. 1.7 Geographical background, population and economic structure of Chiang Mai Province

Chiang Mai is the largest in the northern area of Thailand. It is located about 310 meters above sea level and at latitude 17° 15' to 20° 10' N and longitude 98° 5' to 99° 35' E. It is located 700 km² from Bangkok. The valley of Chiang Mai is located on the coast of the river Ping. Chiang Mai is surrounded in the east by Chiang Rai, Lamphun, and Lampang and Mae Hong Sorn in the west. This is surrounded by monumental walls. This area consists of valleys and hills and forests. The province covers an area of 20,107.057 km² (12,566,910 rai), made up of 8,787,656 rai (69.92%) of forest, 1,611,283 rai (12.82%) of agricultural land and 2,167,971 rai (17.25%) of residential and other land (Chiang Mai Office, 2012). Ping River is known to be the support system of Chiang Mai. This is the most important river in this area. It plays a vital role in influencing the geography of Chiang Mai in a positive way. Chiang Mai Province has a total population of 1,670,317 with 819,750 males and 850,567 females. There are approximately 829,400 families and the population density averages 83.24 people per km² in the province. The Chiang Mai Province consists of 24 districts. Muang district or Chiang Mai City, which is central administrative district of the province, covering an area about 166.47 km², has a population of about 240,046 and the population density averages 1446 people per km² (Department of Local Administration, 2008). In relation to the rest of Thailand, Chiang Mai's year round weather is considered to be relatively cool. The annual average temperature is 26.5 °C. The highest temperature is 40.1 °C and the lowest is 10.9 °C. The annual average humidity is 70.2 %. An annual average number of rainy

days are around 89.2 mm, while the total rainfall is around 1,070.2 mm (Northern Meteorological Center, 2009).

The weather of Chiang Mai can be clearly divided into three seasons (hot, rainy and cool). Summers begin at the early March and go on till the end of May. During this period, temperatures range between 17°C and 36°C. During the daytime, the average temperature is around the 30°C. April is the hottest month in the region. By the end of March, the surrounding valley becomes hazy. Sometimes, short and violent storms bring in winds and rains that provide a relief from the dryness. The rainy season lasts between June and October. In this season, the average daytime temperature is about 25°C, with September being the wettest month. The afternoons experience short and intense rainstorms that get cleared by the evening. The period from November to February is the cool season in Chiang Mai.

1.8 Emission of atmospheric PAHs from various sources

Zhang (2009) estimated the global atmospheric emissions of the 16-PAHs listed as the US EPA priority pollutants using reported emission activity and emission factor data for the reference year 2004. The results for 37 countries were compared with other PAH emission inventories. It was estimated that the total global atmospheric emission of these 16 PAHs in 2004 was 520 giga grams per year (Gg/y) with biofuel (56.7%), wildfire (17.0%) and consumer product usage (6.9%) as the major sources. China (114 Gg/y), India (90 Gg/y) and United States (32 Gg/y) were the top three countries with the highest PAH emissions. The PAH sources in the individual countries varied remarkably. For example, biofuel burning was the dominant PAH source in India, wildfire emissions were the dominant PAH source in

Brazil, while consumer products were the major PAH emission source in the United States. In China, in addition to biomass combustion, coke ovens were a significant source of PAHs. Ravindra *et al.* (2008) was found that the level of PAHs 5-7 times higher in January, February and December, in comparison to May, June and August on the border area between Belgium and France. The annual average concentration of the sum of 16 US EPA criteria PAHs was 6.7 ng/m³ and around 63% of it was found to be probably carcinogenic to humans.

Open burning of biomass is a common method for crop and forest residue disposal and land preparation. Burning of agricultural waste, however, is a source of atmospheric PAHs. Godoi et al. (2004) studied the particulate PAHs emission during sugarcane burning and the levels were found to be comparable with some urban centers. Similar results were also reported by Fang et al. (1999). Their study has been conducted in Indonesia and the levels of PAHs varied from 7 to 46 ng/m³. Larkin et al. (1986) estimated that 1.26 million ha of land was burnt in UK during 1884, resulting in emission of 18,000 tons of black smoke. Based on the study of Freeman and Catell (1990), an estimation of 6.3 tons of total particulate PAHs emission was calculated (Wild and Jones, 1995). Jenkins et al. (1996) conducted the emission factor for the 19 PAH species under wind tunnel simulation of open burning for agricultural and forest biomass fuels including cereals grasses, agricultural tree pruning, and fir and pine wood. PAHs varied from 5 to 683 mg/kg, depending mainly on burning condition and to a lesser extent on fuel type. The total PAH emission rates increases with increasing of particulate matter emission rate and decreasing of combustion efficiency. The higher PAHs emissions were found at higher wind speed lower flaming rate, and smoldering of wood fuels. However, the PAHs emission estimated

from of open burning was found highest with significant content of phenanthrene (Kakareka and Kukharchyk, 2003). Hays *et al.* (2005) simulated the agricultural fires of surface residuals of rice and wheat and found that n-alkane, PAHs, and lignan dimmer molecules predominate in the organic carbon fraction of the PM2.5 emissions. Kumata *et al.* (2006) also estimated that biomass burning contributes 17–45% of PAHs burden of fine particles in Tokyo and the increase in the biomass–PAH accounts for approximately 27% and 22% of winter-time elevation of 3–4 ring PAHs and 5–6 ring PAHs, respectively.

The emission characteristics, sources, sampling and analysis methods of PAHs in the Asian countries (Thailand, Malaysia, China, Korea, Japan and Taiwan) during 1999-2004 was summarized by Chang, et al. The main PAH sources are traffic exhausts (ACY, FLA, FLU, PHE, PYR, CHR, BeP (benzo[e]pyrene)) and industrial emissions (BaP, BaA, PER (perylene), BeP, COR (coronene) and CYC (cyclopenta[c,d]pyrene)). PAH concentrations are highest in traffic areas, followed by the urban sites, and lowest in rural sites. Meteorological conditions, such as temperature, wind speed and humidity, strongly affect PAH concentrations at all sampling sites. The results indicate that Taiwan has a more serious problem than any other Asian country, especially at traffic sites (Chang, 2006).

The seasonal variations of different sources in different regions of China and the spatial distribution of the major sources in different seasons were also achieved. The PAHs emissions were larger in the winter than in the summer, with a difference of about 1.3-folds between the months with the largest and the smallest emissions. Residential solid fuel combustion dominated the pattern of seasonal variation with the winter-time emissions as much as 1.6 times as that in the summer, while the emissions

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from wild fires and open fire straw burning was mainly concentrated during the spring and summer (Zhang and Tao, 2008).

In a previous study carried out in Bangkok for example, it was found that traffic police officers working on the roads were exposed to PAHs at a mean level of 72.79 ng/m³, while those working in the office were exposed at a mean level of 6.88 ng/m³ (Ruchirawat *et al.*, 2002). Bangkok street vendors are also exposed to high levels, with cloth vendors exposed to a mean level of 19.64 ng/m³, and grilled meat vendors exposed to a mean level of 29.12 ng/m³ (Ruchirawat *et al.*, 2005). Boonyatumanond *et al.* (2008) collected samples of roadside air, automobile exhaust soot, tires, asphalt, and used engine oil in a tropical Asian mega-city, Bangkok, Thailand, and analyzed them for PAHs and hopanes. Total PAHs had the following order: gasoline powered vehicle soot (2600±2900 µg/g; n=4) > diesel-powered vehicle soot (115±245 µg/g; n=7) \approx roadside aerosols (101±35 µg/g; n=5) \approx used engine oil (97±65 µg/g; n=4) \approx tire wear particles (82±41 µg/g; n=5) > asphalt (2.3±1.6 µg/g; n=3) > street dust (1.1±0.8 µg/g; n=10).

Chantara and Sangchan (2009) reported the PM10 and PAHs concentrations collected from Chiang Mai city, Thailand. The mean 24 hours PM10 levels in a suburban area, a community area, and two traffic-congested areas were found to be in the ranges of 15–54 µg/m³, 23–60 µg/m³, and 67–144 µg/m³, respectively. The mean total concentrations of the 16 PAHs in the PM10 samples were in the ranges 2.7–8.4 ng/m³, 3.9–9.1 ng/m³, and 7.6–16.6 ng/m³, respectively. The amount of PM10 was fairly well correlated with particle-bound PAH concentrations. Temporal variation clearly affected the PM10 concentration but it was not so clear in the case of particle-bound PAHs. The average benzo(a)pyrene-equivalent (BaPE) carcinogenic power

values showed that community areas had a better air quality than traffic-congested areas. The diagnostic ratios revealed that diesel engine emissions might be the main source of PAHs in the ambient air of these areas (Chantara and Sangchan 2009).

Understanding the contributions of the various emission sources is critical to appropriately managing PAH levels in the environment. The sources of PAHs to ambient air in Baltimore, Maryland, were determined by using three source apportionment methods, principal component analysis with multiple linear regression, UNMIX, and positive matrix factorization. Determining the source apportionment through multiple techniques mitigates weaknesses in individual methods and strengthens the overlapping conclusions. Overall source contributions compare well among methods. Vehicles, both diesel and gasoline, contribute on average 16-26%, coal 28-36%, oil 15-23%, and wood and other having the greatest disparity of 23-35% of the total (gas- plus particle-phase) PAHs. Seasonal trend were found for both coal and oil. Coal was dominated PAH source during the summer while oil dominated during the winter. Positive matrix factorization was the only method to segregate diesel from gasoline sources. These methods indicate the number and relative strength of PAH sources to the ambient urban atmosphere. As with all source apportionment techniques, these methods require the user to objectively interpret the resulting source profiles (Larsen and Baker, 2003; Galarneau, 2008).

The influence of moisture content on PAHs emission during rice straw burning was studied in open burning which was carried out in different moisture contents. The 10 EPA priority PAHs compounds plus naphthacene and perylene were analyzed by means of GC-MS. Total particulate PAHs emission varied between 1 and 38 mg/kg for 12 species-specific PAHs. Experimental results showed that water has a

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depression effect on PAHs emission during rice straw burning. The lowest emission of total particulate PAHs was obtained when rice straw with 15% moisture content was burned. 11 species-specific PAHs showed the lowest emissions within 10±20% moisture content exclusive of naphthacene. In addition, higher emission was observed for intermediate molecular weight compounds such as fluoranthene, pyrene, benz[a]anthracene and chrysene, and relatively lower emission for heavier molecular weight compounds such as perylene, benzo[a]pyrene and dibenz[ah]anthracene (Korenaga *et al.*, 2001).

1.9 Chamber for burning experiment

Chamber in various types and patterns were constructed in many studies for burning experiment. A new state-of-the-art indoor environmental chamber was designed for atmospheric chemical mechanism evaluation at low reactant concentrations under well-controlled environmental conditions which was studied about atmospheric processes leading to the formation of ozone and secondary organic aerosol (Cartera *et al.*, 2005). The deposition rate of aerosol particles (diameter between 0.03 and 5 mm) on rough surfaces of wallpapers, wall-plasters, and two types of carpets inside was investigated in a test chamber (Hussein *et al.*, 2009). Moreover, a controlled chamber used for estimation of emissions from various types of garden biomasses namely grass, leaves, twigs and mixtures of these three in India by Kannan *et al.*, 2005. It was found that the particulate emission (1.51 g/kg) was lowest from grass. The particle size distribution indicates that the emission contains 10% of fine particulates (2.5 mm) and significant quantity (70%) of respirable fraction (10 mm). On the other hand leaves, though generating 32.3 g/kg particulate matter contained major portion in non-respirable range (around 40%). CO_2 emission from leaves (1064.6 g/kg) and twigs (897.3 g/kg) are significantly lower than the emission from mixture (1423 g/kg) of equal proportion of these two. Similar trend is followed in case of carbon monoxide and nitrogen oxides emissions (Kannan *et al.*, 2005).

The particle size was distributed in the smoke emissions of two common agricultural waste residues (biofuels) in California. Almond prunings and rice straw was studied by Keshtkar and Ashbaugh, 2007. The residues were burnt in a combustion chamber designed specifically for this purpose, and the smoke emissions were collected on 10-stage MOUDI impactors for analysis of PAH and total particle mass. The results, in units of emission factors, showed that combustion temperature is an important factor in determining the smoke particle PAH composition. Total PAH emissions from rice straw burns were 18.6 mg/ kg of fuel, while the emissions from almond prunings were lower at 8.03 mg/kg. The less volatile five- and six-ring PAH was predominately on smaller particles where it condensed in the early stages of combustion while the more volatile three- and four-ring PAH formed on larger particles as the smoke cooled.

Recently number of experiment of biomass burning in a chamber is still limited. Moreover, there was no data of PAHs emitted from burning of local biomass in Northern Thailand. In dry season, air pollution from open burning is a serious issue in Chiang Mai province. This study purposes to provide reliable data and information concerning biomass burning and its PAHs emission.

1.10 Research Objectives

- 1. To determine PM10-bound PAHs from burning of different biomass types.
- 2. To calculate emission rates and emission factors of PM10-bound PAHs from biomass burning.
- 3. To estimate PAHs profiles from burning of different biomass types.
- 4. To find out possible sources of PAHs in Chiang Mai province using source apportionment model.

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