

**Ph.D. Dissertation**

**Influence of Biomass Burning on Characterization  
of Atmospheric Polycyclic Aromatic Hydrocarbons  
and their Nitro Derivatives in Chiang Mai, Thailand**

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Atmospheric Polycyclic Aromatic Hydrocarbons and their  
Nitro Derivatives in Chiang Mai, Thailand**

タイ・チェンマイにおける大気中多環芳香族炭化水素と  
そのニトロ誘導体の特性解析とバイオマス燃焼の影響

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## List of Abbreviations

Ant	Anthracene
AP	Aminopyrene
APAH	Aminopolycyclic aromatic hydrocarbon
AQM	Air quality monitoring
ASR	Age standardized rate
BaA	Benz[ <i>a</i> ]anthracene
BaP	Benzo[ <i>a</i> ]pyrene
BbF	Benzo[ <i>b</i> ]fluoranthene
BghiPe	Benzo[ <i>ghi</i> ]perylene
BkF	Benzo[ <i>k</i> ]fluoranthene
BSTFA	<i>N,O</i> -Bis(trimethylsilyl) trifluoroacetamide
Chr	Chrysene
CL	Chemiluminescence
CMPHO	Chiangmai Provincial Public Health Office
DAP	Diaminopyrene
DBA	Dibenz[ <i>a,h</i> ]anthracene
DCM	Dichloromethane
DHHS	The Department of Health and Human Services
DMSO	Dimethyl sulfoxide
DNP	Dinitropyrene
FL	Fluorescence
Flu	Fluoranthene
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IARC	The International Agency for Research on Cancer
IDP	Indeno[1,2,3- <i>cd</i> ]pyrene
LG	Levogluconan
MS	Mass Spectrometry
NA	Nitroanthracene
NBaA	Nitrobenz[ <i>a</i> ]anthracene
NBaP	Nitrobenzo[ <i>a</i> ]pyrene
NC	Nitrochrysene

NF	Nitrofluorene
NFR	Nitrofluoranthene
NP	Nitropyrene
NPAH	Nitropolycyclic aromatic hydrocarbon
NPer	Nitroperylene
NPh	Nitrophenanthrene
NPL	The National Priorities List
NTP	Nitrotriphenylene
PAH	Polycyclic aromatic hydrocarbon
PCD	Pollution Control Department
PM	Particulate matter
Pyr	Pyrene
rev.	Revertants
SD	Standard deviation
TCPO	<i>bis</i> (2,4,6-trichlorophenyl)oxalate
TEFs	Toxic equivalent factors
TEOM	Tapered element oscillating microbalance
TMCS	Trimethylchlorosilane
TSP	Total suspended particulate matter
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compounds



## Abstract

Chiang Mai and several other provinces in northern Thailand have been annually facing air pollution problems during the dry season. The levels of airborne particulate matter (PM) increase in the season and often exceed the standard level in Thailand. Biomass burning is expected as a main contributor to the high PM concentrations. PM contains many inorganic and organic hazardous compounds. Among them, polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are of great concern because of their toxicity (carcinogenicity or mutagenicity) to human. However, the contribution of biomass burning to PAHs and especially NPAHs remains unclear. This study reports atmospheric levels and distribution profiles of PAHs and NPAHs in Chiang Mai, Thailand. Ten PAHs, 19 NPAHs, and levoglucosan, a marker for biomass burning, were quantified in total suspended particulates collected in Chiang Mai during the dry, transition, and wet seasons in 2010. PAHs and NPAHs were analyzed by HPLC with fluorescence and chemiluminescence detections, respectively. In addition, LG was analyzed by GC-MS after derivatization with a silylating reagent. The concentrations of PAHs and NPAHs in the dry season were significantly higher than those in the wet season. The [Benzo[*a*]pyrene (BaP)]–[benzo[*ghi*]perylene (BghiPe)] ratio, as an indicator of traffic, and the correlations of PAHs and NPAHs with LG showed that biomass burning significantly contributes to air pollution in the dry season. We proposed 9-nitroanthracene (9-NA) as a marker of biomass burning and the [9-NA]–[1-nitropyrene (1-NP)] ratio as a new indicator for assessing the contribution of biomass burning. The analysis using the markers indicated that biomass burning was a major source of PAHs and NPAHs in the dry season, whereas vehicle exhaust was the main contributor in the wet season. The high carcinogenic risks in the dry season correlate with more harmful air conditions during this season. Thus, it is important to control biomass burning to reduce air-pollution-related health risks during the dry season in northern Thailand. These results should be useful in controlling and managing air pollution in Thailand.

# Chapter 1

## Introduction

### 1.1. Background information

Air pollution, both indoors and outdoors, is a major environmental health problem affecting everyone in developed and developing countries alike. Air pollution occurs when the air contains gases, dust, fumes or odor in amounts that could be harmful to the health or comfort of humans and animals or could cause damage to plants and buildings. The substances that cause air pollution are called pollutants. There are two types of air pollutants. Primary air pollutants are emitted directly from the sources such as carbon monoxide (CO) and sulfur dioxide (SO<sub>2</sub>). Secondary air pollutants are formed by chemical or physical transformations in the atmosphere such as ozone (O<sub>3</sub>), nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>).

United States Environmental Protection Agency (US EPA) has established air quality standards for six common air pollutants to protect public health and the environment. These pollutants include carbon monoxide, ozone, lead, nitrogen dioxide, sulfur dioxide and particulate matter.

#### 1.1.1. Particulate matter (PM)

One of the most serious pollutants is PM. PM is a complex mixture of solid and liquid particles that are suspended in air. These particles typically consist of a mixture of inorganic and organic chemicals including carbon, sulfates, nitrates, metals, acids, and semi-volatile compounds.

Air quality standards for PM in the United States were expressed some decades ago in terms of the mass of total suspended particulate matter (TSP) which represent the sum of all the suspended particles in the atmosphere. The standard was then changed to mass of suspended PM less than 10 µm in size, commonly called PM<sub>10</sub>, and was more recently was modified to PM less than 2.5 µm in diameter, PM<sub>2.5</sub>. Particle size distributions of atmospheric PM and chemical compounds in PM are very important with regard to the influence of PM on human health, because particle size controls the deposition behavior of PM in respiratory organ. Coarse particles are mainly deposited in the extrathoracic region, while PM<sub>2.5</sub> can reach the pulmonary alveoli (Kawanaka *et al.*, 2008). PM<sub>2.5</sub> has greater numbers and greater surface area than PM<sub>10</sub> of the same mass, and is generally considered to be more toxic.

Numerous studies have found associations between exposure to PM and adverse health effects (Brunekreef and Holgate, 2002; Bernstein *et al.*, 2004; Rojas-Martinez *et al.*, 2007; Sehlstedt *et al.*, 2007). The health effects of PM are likely to depend on several factors, including the size and composition of the particles, the level and duration of exposure, and age and sensitivity of the exposed person. Symptoms of exposure may include a sore throat, persistent cough, burning eyes, wheezing, shortness of breath and tightness of chest. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases as well as lung cancer. Turner *et al.* (2011) observed a total of 1,100 lung cancer deaths during the 26-year follow-up period. Each 10  $\mu\text{g}/\text{m}^3$  increase in PM<sub>2.5</sub> concentrations was associated with a 15-27% increase in lung cancer mortality.

### ***1.1.2. Toxicity of polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs)***

PM contains many inorganic and organic species, many of which can adversely affect human health. Among them, polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are of great concern because of their toxicity (carcinogenicity or mutagenicity) to humans (Ames *et al.*, 1975). PAHs are a group of organic compounds that consist of two or more benzene rings fused together in a variety of ways as linear, angled or clustered structures. NPAHs are nitro-derivatives of PAHs, which contain two or more fused aromatic rings and one or more nitro groups. They are ubiquitous environmental pollutants and form by the incomplete combustion of organic materials. The major sources to the environment include fossil fuel, coal, wood, and industrial processes. PAHs are emitted directly from combustion sources whereas NPAHs are both primary emitted and secondarily formed by gas phase reactions in the atmosphere (Albinet *et al.*, 2008b).

The International Agency for Research on Cancer (IARC) has classified benzo[*a*]pyrene (BaP) in Group 1 (carcinogenic to humans), 1-nitropyrene (1-NP) in Group 2A (probably carcinogenic to humans) and 1,3-, 1,6- and 1,8-dinitropyrene (1,3-, 1,6- and 1,8-DNP) in Group 2B (possibly carcinogenic to humans) (IARC, 2013). PAH derivatives such as hydroxylated PAHs (OHPAHs) and quinoid PAHs (PAHQs) also have estrogenic/antiestrogenic or antiandrogenic activities (Kizu *et al.*, 2000; Hayakawa *et al.*, 2011).

PAHs are classified as carcinogenic materials by many organizations including US EPA, IARC, and the Department of Health and Human Services (DHHS). Table 1.1 shows the

carcinogen classification of 16 priority PAHs by the IARC, compared to classifications by the US EPA and DHHS. Many toxicity studies reported that BaP has the highest carcinogenic potency with long-term persistency in the environment. Schulte *et al.*, (1994) found a significant increase in all lung tumors and a dose-dependent increase in malignant lung tumors for mice exposed to PAH-enriched exhausts containing BaP of 0.05 or 0.09 mg/m<sup>3</sup>. In general, PAHs with high molecular weights are often more carcinogenic than those with low molecular weights (Yang *et al.*, 2005).

**Table 1.1.** Sixteen priority PAHs were classified by IARC in comparing those by the DHHS and the US EPA.

PAHs	No. of ring	US EPA	IARC	DHHS
Naphthalene	2		2B	
Acenaphthylene	3	Not classifiable		
Acenaphthene	3		3	
Fluorene	3	Not classifiable	3	
Phenanthrene	3	Not classifiable	3	
Anthracene	3	Not classifiable	3	
Fluoranthene	4	Not classifiable	3	
Pyrene	4	Not classifiable	3	
Chrysene	4	Probably carcinogen	2B	
Benz[a]anthracene	4	Probably carcinogen	2B	Animal carcinogen
Benzo[b]fluoranthene	5	Probably carcinogen	2B	Animal carcinogen
Benzo[k]fluoranthene	5	Probably carcinogen	2B	
Benzo[a]pyrene	5	Probably carcinogen	1	Animal carcinogen
Dibenz[a,h]anthracene	5	Probably carcinogen	2A	Animal carcinogen
Benzo[ghi]perylene	6	Not classifiable	3	
Indeno[1,2,3-cd]pyrene	6	Probably carcinogen	2B	Animal carcinogen

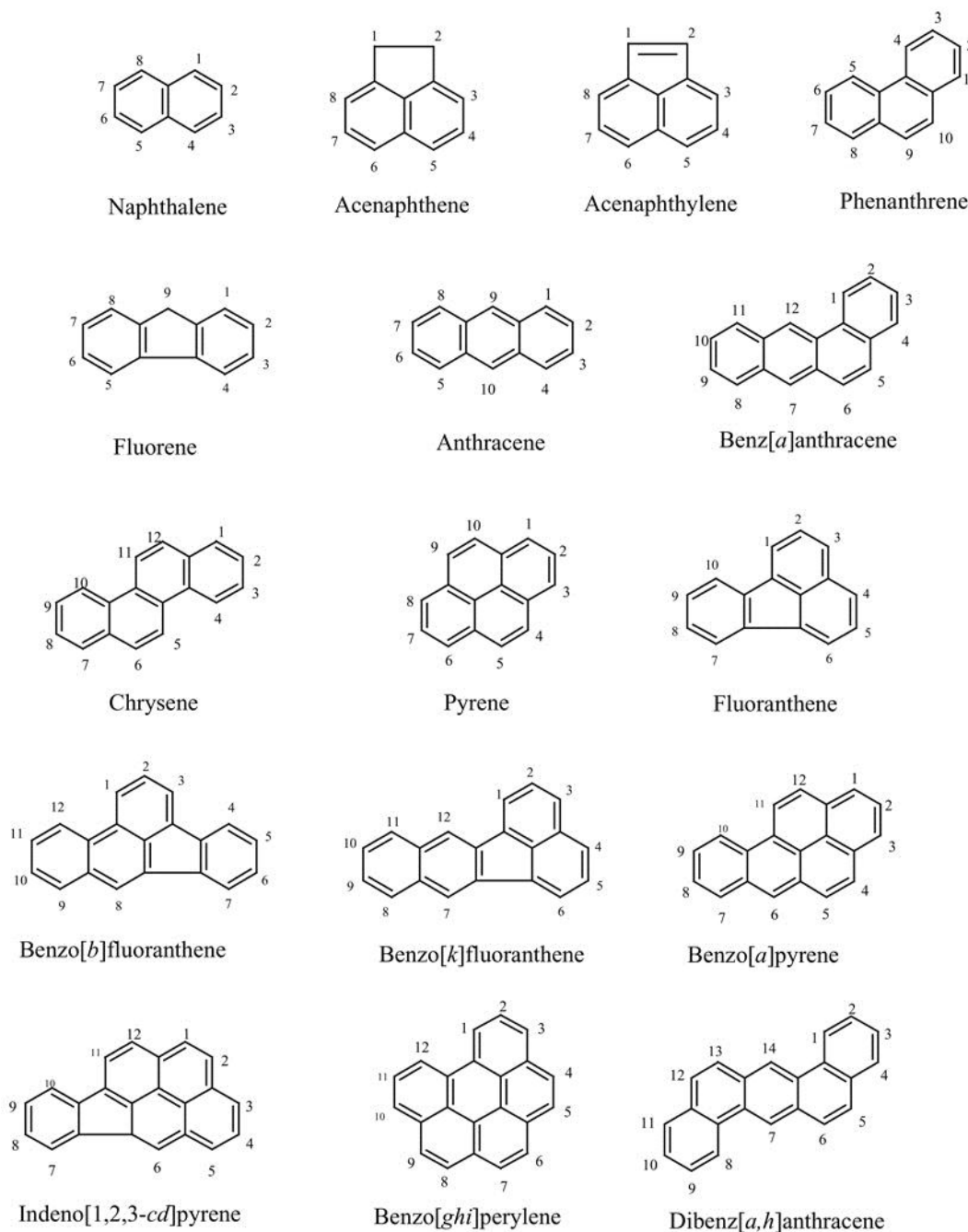
[http://cdn.intechopen.com/pdfs/11767/InTech-Sources\\_distribution\\_and\\_toxicity\\_of\\_polyaromatic\\_hydrocarbons\\_pahs\\_in\\_particulate\\_matter.pdf](http://cdn.intechopen.com/pdfs/11767/InTech-Sources_distribution_and_toxicity_of_polyaromatic_hydrocarbons_pahs_in_particulate_matter.pdf)

IARC classification: Group 1 (carcinogenic), 2A (probably carcinogenic), 2B (possibly carcinogenic), 3 (not classifiable).

### 1.1.3. Sources, formation and properties of PAHs

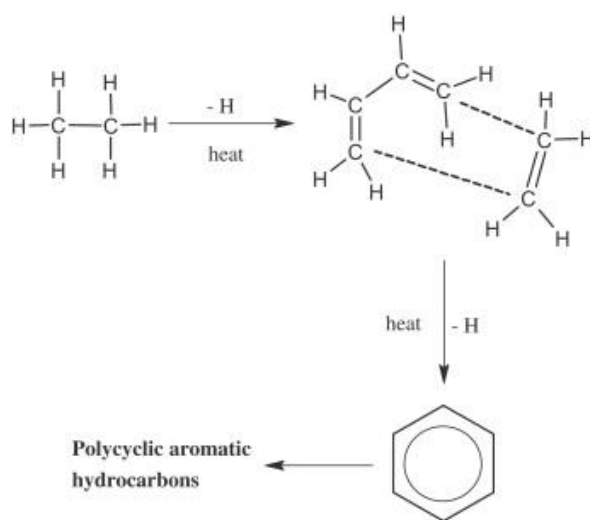
PAHs are emitted to the environment through natural processes (e.g. volcanoes and forest fires) and anthropogenic sources (e.g. burning of wood, vehicles and factories) (Chang *et al.*, 2006 and Ravindra *et al.*, 2008). There are more than 100 different PAHs. PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds. US EPA has designed 16 PAH compounds as priority pollutants (Fig.

1.1). These 16 PAHs were chosen to be included in the priority list because (1) more information is available on these than on the others; (2) they are suspected to be more harmful than some of the others, and they exhibit harmful effects that are representative of the PAHs in general; (3) there is a greater chance for exposure to these PAHs than to the others; and (4) of all the PAHs analyzed, these were the PAHs identified at the highest concentrations at the National Priorities List (NPL) hazardous waste site.



**Fig. 1.1.** Chemical structure of US EPA 16 PAHs.

PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Pyrosynthesis and pyrolysis are two main mechanisms that can explain the formation of PAHs (Ravindra *et al.*, 2008). Low hydrocarbons form PAHs by pyrosynthesis. When the temperature exceeds 500 °C, carbon-hydrogen and carbon-carbon bond are broken to form free radicals. These radicals combine to acetylene which further condenses with aromatic ring structures, which are resistant to thermal degradation. Fig. 1.2 illustrates the formation of such rings starting with ethane. The tendency of hydrocarbons to form PAH structure by pyrosynthesis varies in the order—aromatics > cycloolefins > olefins > paraffins (Manahan, 1994). The types of PAHs produced in pyrolysis considerably with temperature. At high temperature and under anaerobic conditions, as in cooking process, the products are relatively simple mixture of low molecular weight PAHs lacking alkyl substituents. At moderate temperature, the product mixtures are more complex containing substantial amounts of alkyl-substituted and unsubstituted PAHs. At low temperature, methyl and other alkyl-substituted polyarenes become predominant products (Harvey, 1998).



**Fig. 1.2.** Pyrosynthesis of PAHs starting with ethane (Ravindra *et al.*, 2008).

The movement of PAHs in the environment depends on properties such as their solubility in water and their volatility. PAHs have low solubility in water (Table 1.2) as expected from their nonpolar character. These decrease dramatically in going from the 2- and 3-ring PAHs (e.g., naphthalene, with a solubility of 31 mg/L) through the 4-ring semi-volatile compounds (e.g., fluoranthene, with a solubility of 0.26 mg/L) to 5-ring PAHs (BaP, with a solubility of only 0.0038 mg/L). The partitioning of semi-volatile PAHs between gas and particle phases

depends on their vapor pressure (Table 1.2) and the ambient temperature (Tsapakakis and Stephanou, 2005). PAHs with two or three rings, which have relatively high vapor pressure, are mainly associated with the gas phase. Four ring PAHs exist in both the gas and particle phases whereas PAHs with five rings or more, which have low vapor pressure, are mostly bound to particle.

**Table 1.2.** Physical-chemical characteristics of some PAHs.

PAH	M.W. (g/mol)	Vapor pressure		Solubility (mg/L)	Log $K_{ow}$
		P (Pa)	$P_L^o$ (Pa)		
Naphthalene	128.2	10.4	36.8	31	3.37
Acenaphthylene	152.2	$9 \times 10^{-1}$	4.1	16.1	4.00
Acenaphthene	154.2	$3 \times 10^{-1}$	1.5	3.80	4.00
Fluorene	166.2	$9 \times 10^{-2}$	$7.2 \times 10^{-1}$	1.90	4.18
Phenanthrene	178.2	$2 \times 10^{-2}$	$1.1 \times 10^{-1}$	1.10	4.57
Anthracene	178.2	$1 \times 10^{-3}$	$7.78 \times 10^{-2}$	0.045	4.54
Fluoranthene	202.3	$1.23 \times 10^{-3}$	$8.72 \times 10^{-3}$	0.26	5.22
Pyrene	202.3	$6.0 \times 10^{-4}$	$1.19 \times 10^{-2}$	0.132	5.18
Chrysene	228.3	$5.7 \times 10^{-7}$	$1.07 \times 10^{-4}$	$2 \times 10^{-3}$	5.75
Benz[a]anthracene	228.3	$2.80 \times 10^{-5}$	$6.06 \times 10^{-4}$	0.011	5.91
Benzo[b]fluoranthene	252.3	-	-	0.0015	5.80
Benzo[k]fluoranthene	252.3	$5.2 \times 10^{-8}$	$4.12 \times 10^{-6}$	0.0008	6.00
Benzo[a]pyrene	252.3	$7.0 \times 10^{-7}$	$2.13 \times 10^{-5}$	0.0038	6.04
Dibenz[a,h]anthracene	278.4	$3.7 \times 10^{-10}$	$9.2 \times 10^{-8}$	0.0006	6.75
Benzo[ghi]perylene	276.3	-	$2.25 \times 10^{-5}$	0.00026	6.50

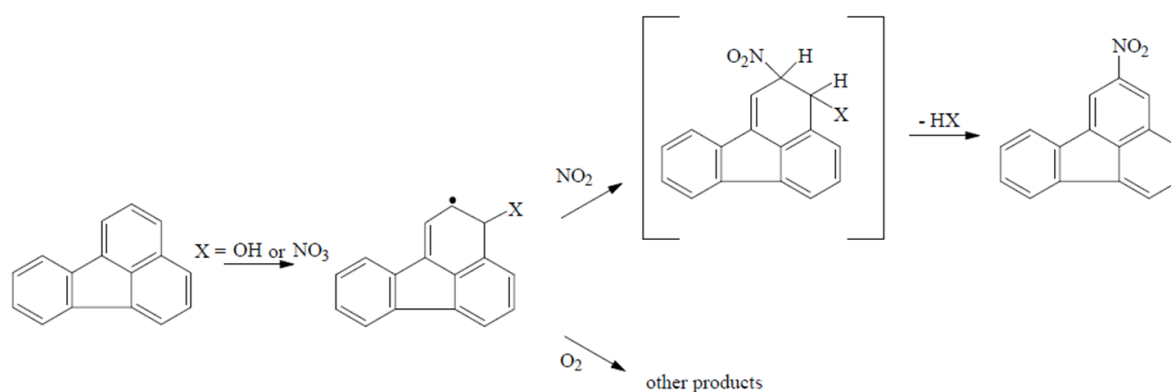
P is Vapor Pressure,  $P_L^o$  is Subcooled Liquid Vapor Pressures, Log  $K_{ow}$  is Logarithm of Octanol/Water Partition Coefficient (Pitts and Pitts, 2000).

#### ***1.1.4. Sources, formation and properties of NPAHs***

NPAHs occur in the environment as a mixture together with parent PAHs and hundreds of other organic compounds. The ambient concentrations of NPAHs are usually much lower than those of PAHs. NPAHs are present in the atmosphere from primary sources and gas-phase reactions of the parent PAHs in the atmosphere. NPAHs are emitted from various primary combustion sources such as diesel exhaust (Paputa-Peck *et al.*, 1983; Schuetzle *et al.*, 1982), gasoline exhaust (Gibson, 1982), coal combustion (Hattori *et al.*, 2007; Tang *et al.*, 2005, 2011) and biomass burning (Ding *et al.*, 2012; Shen *et al.*, 2012).

NPAHs directly emitted by combustion sources are formed via electrophilic nitration of PAHs in the presence of nitrogen dioxide ( $\text{NO}_2$ ) (Nielsen, 1984). The most abundant NPAH directly emitted from diesel exhaust is 1-nitropyrene (Paputa-Peck *et al.*, 1983; Bamford *et al.*, 2003b). Other NPAHs such as 9-nitroanthracene (Paputa-Peck *et al.*, 1983; Bamford *et al.*, 2003b), 3-nitrofluoranthene and 7-nitrobenz[*a*]anthracene (Pitts and Pitts, 2000; Bamford *et al.*, 2003b), 6-nitrochrysene, 6-nitrobenzo[*a*]pyrene (Kawanaka *et al.*, 2008; Zwirner-Baier and Neumann, 1999) and 1,3-, 1,6- and 1,8-dinitropyrene (Bamford *et al.*, 2003b) were also detected in diesel exhaust.

In contrast, gas phase reactions of the parent PAHs are initiated by hydroxyl (OH) radicals during the day and by nitrate ( $\text{NO}_3$ ) radicals in the presence of  $\text{NO}_x$  during the night (Arey *et al.*, 1986; Atkinson and Arey, 1994). The radical initiated reactions are postulated to proceed through initial addition of either the OH radical or the  $\text{NO}_3$  radical to the position with the highest electron density in the PAH molecule (e.g., the one position for pyrene and the three positions of fluoranthene) (Fig. 1.3). This is followed by the addition of  $\text{NO}_2$  at the *ortho*-position and subsequent loss of water or nitric acid to form 2-nitrofluoranthene (2-NFR) or 2-nitropyrene (2-NP) (Arey *et al.*, 1986). These two NPAHs have not been identified in diesel exhaust or other combustion products. In addition to gas phase reactions, laboratory studies have reported NPAH production via heterogeneous reactions (Pitts *et al.*, 1985; Kamens *et al.*, 1990).



**Fig. 1.3.** Gas phase reaction of 2-NFR.

NPAH are more hydrophilic and have lower vapor pressure than their parent PAHs. A part of NPAHs are also volatile or semi-volatile organic compounds. NPAHs with two aromatic rings were detected only in the vapor phase, and three-ring NPAHs were found in both the



gas and particle phases in the atmosphere. On the other hand, NPAHs with four or more rings were mainly distributed in particle phase (Dimashki *et al.*, 2000).

The increased attention to NPAHs, particularly in the environmental analytical community, is due to their persistence in the environment and higher mutagenic and carcinogenic properties of certain compounds compared to their parent PAHs (Lewtas *et al.*, 1990; Durant *et al.*, 1996). Although at lower concentrations compared to PAHs, in recent years it has become well-established that certain NPAHs exhibit high direct-acting mutagenic potency in a microbial mutagenicity bioassays (Pitts *et al.*, 1978) and in a forward mutation assay based on human cells (Durant *et al.*, 1996). Furthermore, NPAHs can account for a significant fraction of the direct-acting mutagenic compounds present in extracts of ambient PM (Wang *et al.*, 1980; Pitts *et al.*, 1982), and their persistence in the particle phase may result in human exposure through inhalation. These concerns have stimulated research into the primary sources, fate, and transport of these contaminants in the atmosphere.

#### ***1.1.5. Biomass burning***

Biomass burning is the largest source of primary PM and the second largest source of trace gases (e.g. NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>) in the global atmosphere (Yokelson *et al.*, 2011). In addition, it entails the emissions of volatile organic compounds (VOC) and PAHs, many of which are toxic and some known or suspected carcinogens. Biomass burning aerosol may have a significant impact on regional air quality, visibility, cloud processes, human health, global and regional climate (Adler *et al.*, 2011).

The wood combustion process can be summarized briefly as follows. When heating wood, its constituents start to be hydrolyzed, oxidized, dehydrated, and pyrolyzed with increasing temperature to form combustible volatiles, tarry substances, and highly reactive carbonaceous char (Shafizadeh, 1984). At the ignition temperature of the volatiles and tarry substances, exothermic reactions known as combustion begin (Skaar, 1984). Resinous compounds and decomposition products of cellulose, hemicelluloses, and lignin, together with water vapor are stripped off, and then undergo both partial to complete combustion in the flaming zone. During the flaming combustion, char formation continues until the combustible volatile flux drops below the minimum level required for the propagation of a flame. During the smoldering process, enough heat is produced to propagate the charring process as well as the release of additional volatile wood decomposition products.

Total global PAH emission was estimated to be 520 Gg in 2004, among which 80% was from developing countries and 73.7% was from biofuel and wildfire (Zhang and Tao, 2009).

Forest fires are the major type of biomass burning in Southeast Asia (Chang and Song, 2010). It has caused severe concerns about health effects due to the high PAH content (Simoneit, 2002). Therefore, it is important to assess the level of PAHs and their derivatives from biomass burning.

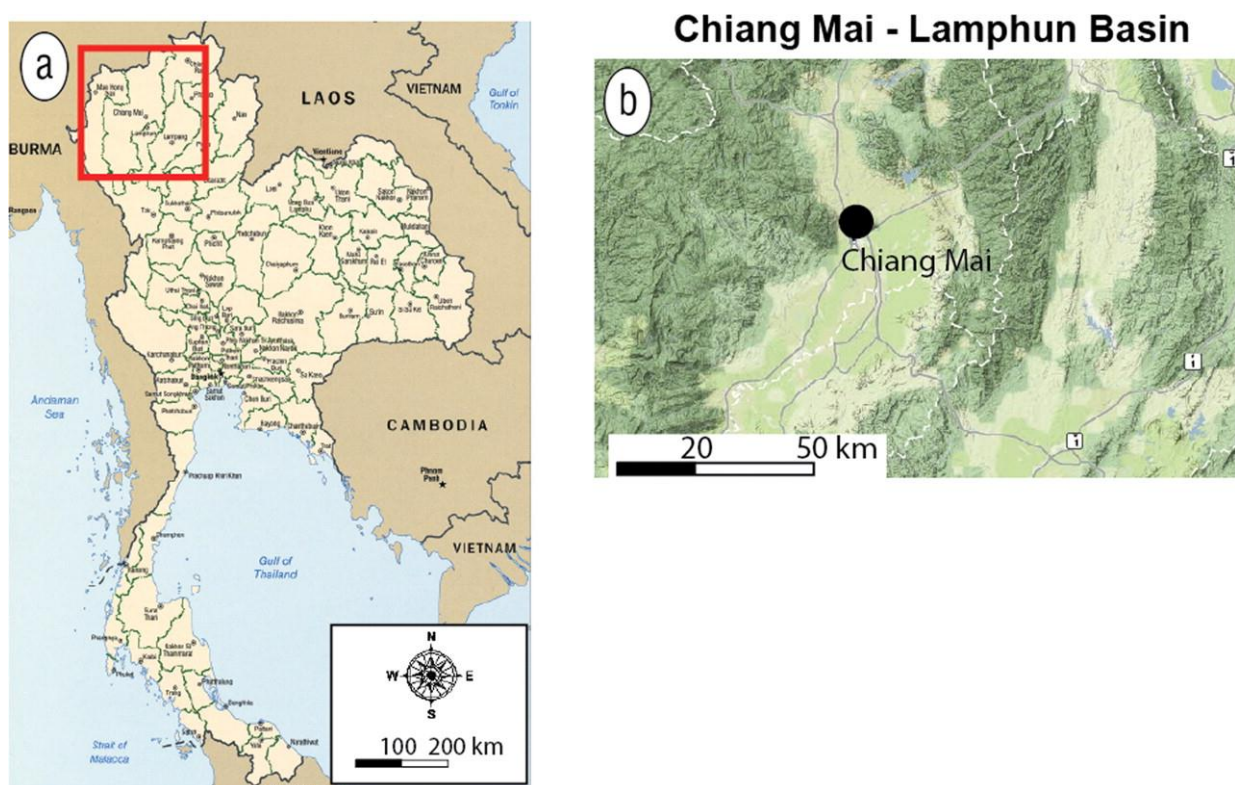
Water-soluble potassium is a common inorganic tracer for biomass burning source (Duan *et al.*, 2004), but it has also contributions from sea salt and soil dust. In recent year, levoglucosan (1,6-Anhydro- $\beta$ -D-glucose, LG) are increasingly employed as a marker of biomass burning (Puxbaum *et al.*, 2007; Wang *et al.*, 2007; Lanz *et al.*, 2008). LG originates from the pyrolysis of cellulose and hemicelluloses, the main building material of wood, at temperatures higher than 300°C (Zhang *et al.*, 2008). LG has been considered as an excellent tracer of biomass-burning sources (Puxbaum *et al.*, 2007; Mochida *et al.*, 2010). LG is emitted in large quantities; is stable in the atmosphere; and is specific to the thermal breakdown of cellulose.

## **1.2. Air pollution in Thailand**

Emission of air pollutants in the Southeast Asia region has been rapidly increasing, resulting from population growth, rapidly economic development, and the associated systems of energy consumption and production. The potential for trans-boundary air pollution problems in the region is also greatly due to high emissions and the proximity of many of the major industrial and urban centers such as Bangkok, Hanoi, Kuala Lumpur, Singapore and Jakarta (He *et al.*, 2010). In addition, biomass burning in Southeast Asia occurs in a vast region including Thailand, Vietnam, Indonesia, Malaysia, Philippines, Singapore, Taiwan, Myanmar, Laos and Cambodia (Reid *et al.*, 2013). This biomass burning produces high levels of haze, especially in the dry season (Reid *et al.*, 2013; He *et al.*, 2010). Northern Thailand has been facing air pollution in the dry season almost every year (Chantara, 2012).

Bangkok is the capital and the most populous city of Thailand. The severe air pollution in Bangkok is mainly due to vehicles and factories. Bangkok is situated in the plain and near the sea promoting air pollutants dispersion. Northern Thailand, especially Chiang Mai has also suffered badly from air pollution due to biomass burning during dry season. Chiang Mai (18°47' N and 98°59' E) is the largest city in northern Thailand with a population of more than 1.6 million. It is located in the Chiang Mai–Lamphun basin at a height of 310 m above sea level and covers an area of approximately 20,107 km<sup>2</sup> (Fig. 1.4). The geographical and meteorological conditions contribute to the high levels of PM in the air of Chiang Mai (Chantara, 2012; Wiriya *et al.*, 2013). Chiang Mai is located in basin and is surrounded by

mountain resulting non-dispersion and accumulation of air pollutants. Haze problem in Chiang Mai has been classified as “serious” and “urgent” by Thai governments since 2003. Recently, the problem has become worse than ever that affects to human health, environment as well as economy. In the city, the PM<sub>10</sub> concentration increases at the beginning of the dry season (December), peaks in March, and decreases by the end of April (Pengchai *et al.*, 2009). During the dry season of the past several years, the daily average concentrations of PM<sub>10</sub> often exceeded the Thai ambient air quality standard of 120 µg/m<sup>3</sup> (Table 1.3). More importantly, many consecutive days with high PM<sub>10</sub> level resulted in haze-related health threats to the residents from February to April every year (Chantara, 2012). Not only biomass burning but also vehicle emissions was expected as the main contributions to the critical levels of air pollutants in Chiang Mai. The Public Health Ministry of Thailand has reported increased respiratory diseases and cardiovascular problems in people living in this area (Pengchai *et al.*, 2009). A research carried out in Bangkok, Chiang Mai, and Tokyo has revealed that the levels of carcinogenic PAHs in Chiang Mai were higher than those in Tokyo and Bangkok (Matsushita *et al.*, 1987).

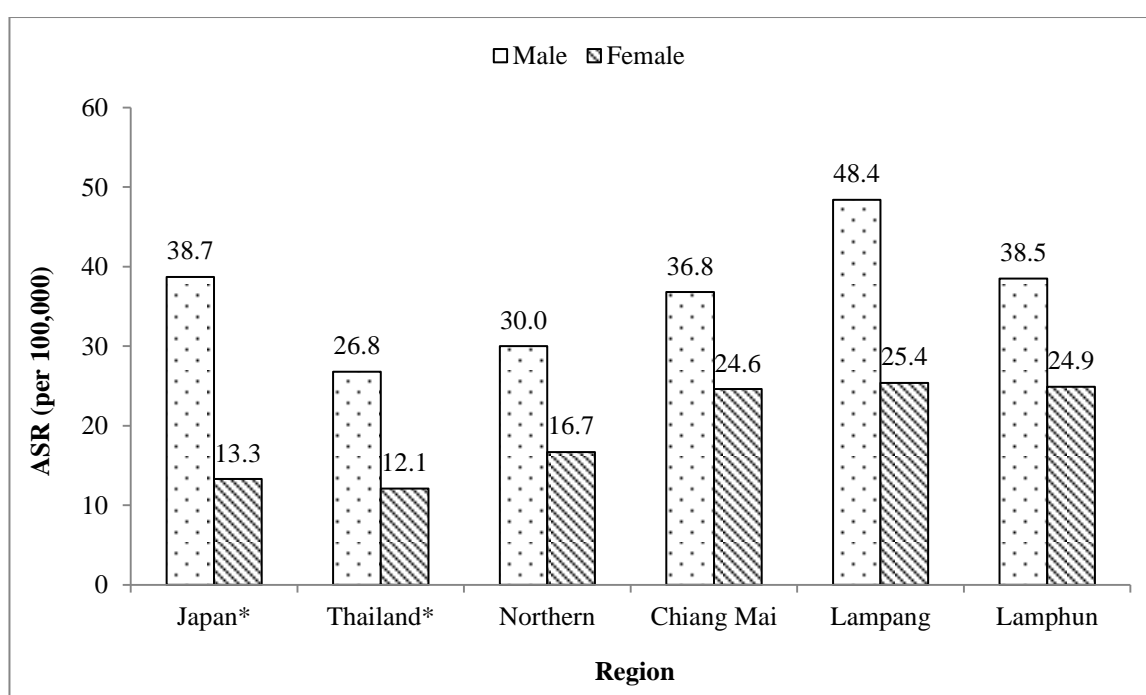


**Fig. 1.4.** Map of Chiang Mai and Chiang Mai – Lamphun basin.

**Table 1.3.** The highest level of PM<sub>10</sub> in Chiang Mai Province.

Year	Air quality monitoring station	
	Provincial Hall (suburban)	Yupparaj Wittayalai School (downtown)
2001	143.0	151.5
2005	198.8	206.9
2006	248.8	237.0
2007	317.0	396.4
2008	142.2	178.9
2009	196.2	219.0
2010	274.8	291.1

<http://aqnis.pcd.go.th/data/yearly>



**Fig. 1.5.** ASRs of lung cancer by region in northern Thailand, 2003-2007, compared to Japan.

\*The incidence is in 2008.

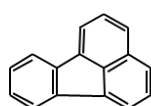
The highest incidence of lung cancer has been recognized in the Northern Thailand (Wiwatanadate, 2011). During 2003-2007, the total number of new lung cancers was 15,604 cases, 9,603 in males and 6,001 in females. The Age standardized rates (ASRs) of lung cancer in northern region were higher than those in the entire Thailand (Fig. 1.5). In

particular, Lampang, Lamphun and Chiang Mai were the three highest provinces in this region. The ASR in males of Japan was comparable with those of Chiang Mai and Lamphun but was lower than Lampang. However, the ASRs in females of three provinces are higher than that of Japan. Although smoking is the major cause of lung cancer, this factor alone could not explain the high incidence in northern Thailand. Wiwatanadate (2011) postulated that indoor radon and air pollution might be the other risk factors. Therefore, it is important to assess air pollution and know the level of air pollutants in Chiang Mai.

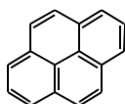
### **1.3. Purpose of this study**

Chiang Mai and several other provinces in northern Thailand have been annually facing air pollution problems during the dry season. In the season, biomass burning was expected as the main contributors to the critical levels of air pollutants. However, the contribution of biomass burning to PAHs and especially NPAHs remains unclear. This study reports atmospheric levels and distribution profiles of PAHs and NPAHs in Chiang Mai, Thailand, and discusses their possible emission sources and health risks. The results are expected to facilitate air pollution management in northern Thailand.

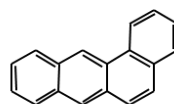
Since the recognized carcinogenic PAHs and NPAHs are mostly associated with particle phase, only particle-bound PAHs and NPAHs were selected for analysis in this study. The structures of 10 PAHs targeted for analysis by this research are shown in Fig. 1.6. In addition, Fig. 1.7 shows the structures of targeted 19 NPAHs.



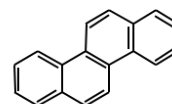
**fluoranthene  
(Flu)**



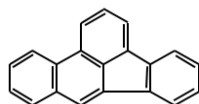
**pyrene  
(Pyr)**



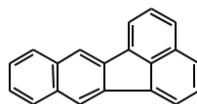
**benz[a]anthracene  
(BaA)**



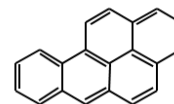
**chrysene  
(Chr)**



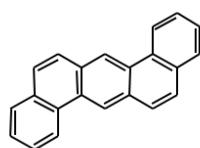
**benzo[b]fluoranthene  
(BbF)**



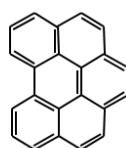
**benzo[k]fluoranthene  
(BkF)**



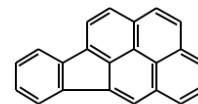
**benzo[a]pyrene  
(BaP)**



**dibenz[a,h]anthracene  
(DBA)**

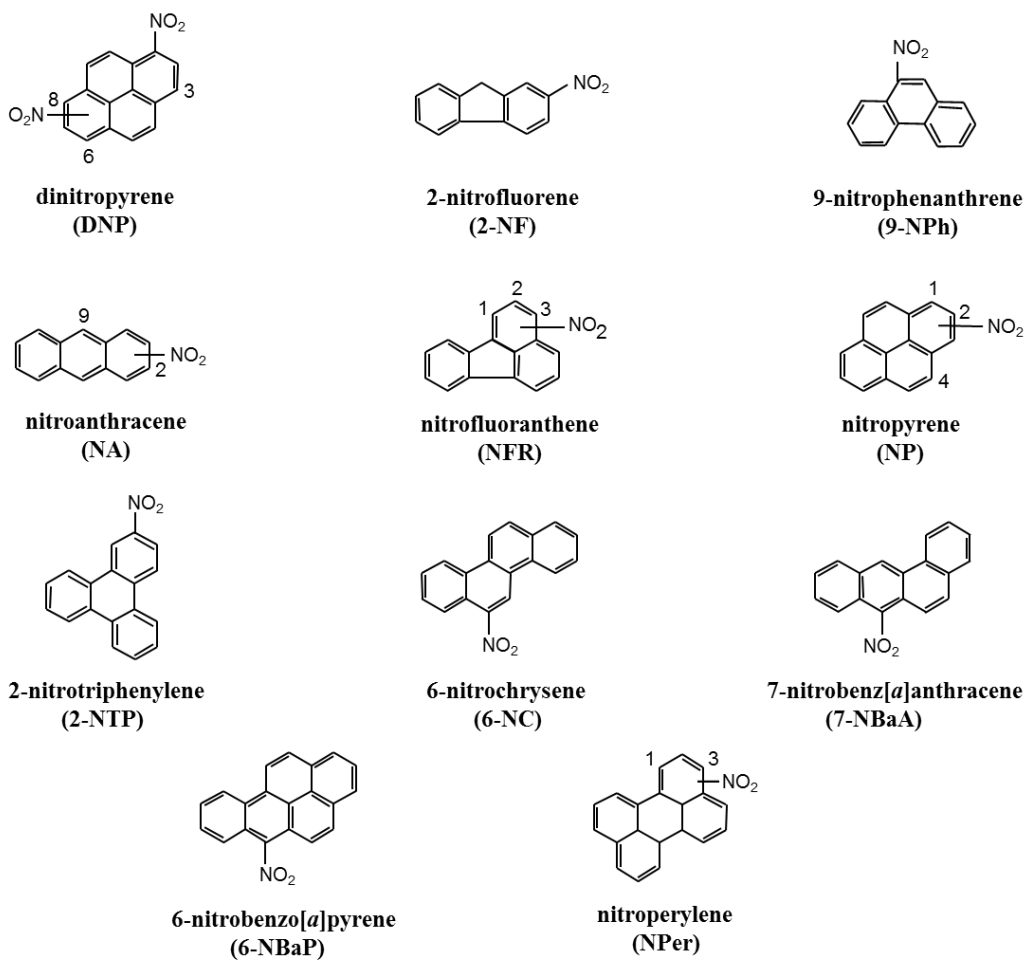


**benzo[ghi]perylene  
(BghiPe)**



**indeno[1,2,3-cd]pyrene  
(IDP)**

**Fig. 1.6.** The structures of targeted 10 PAHs in this research.



**Fig. 1.7.** The structures of targeted 19 NPAHs in this research.

## Chapter 2

### **Influence of Biomass Burning on the Levels of Atmospheric Polycyclic Aromatic Hydrocarbons and their Nitro Derivatives in Chiang Mai, Thailand**

Air quality in Chiang Mai has become a major concern and has been steadily deteriorating over the past ten years, especially in the dry season. A large amount of PM containing hazardous chemicals was emitted to the atmosphere. The most severe PM pollution was observed in March 2007, with the highest concentration of  $383 \mu\text{g}/\text{m}^3$  on March 14, exceeding the 24 h average standard level in Thailand ( $120 \mu\text{g}/\text{m}^3$ ). The number of patients with respiratory problems recorded in 23 Chiang Mai public hospitals was significantly larger in March 2007 than that in March 2006 and March 2008 (CMPHO, 2008).

In recent years, increasing attention has been paid to PAHs and NPAHs because of their toxicity (carcinogenicity or mutagenicity) to humans (Ames *et al.*, 1975). Atmospheric PAH levels and their sources in Thailand were reported in several previous studies. In Bangkok, vehicle emissions were identified as the major source of PAHs in urban areas (Kim Oanh *et al.*, 2000; Boonyatumanond *et al.*, 2007). In Chiang Mai, nearly all studies found PAHs in the ambient air of urban areas, and the diagnostic ratios revealed that vehicle emissions might be the main source of PAHs (Chantara and Sangchan, 2009; Pengchai *et al.*, 2009).

Although NPAHs are generally present at low concentrations in the atmosphere compared to their parent PAHs (Feilberg *et al.*, 2001; Bamford and Baker, 2003a), they have been recognized as direct-acting mutagens and carcinogens, which are more toxic than their parent PAHs (Durant *et al.*, 1996; Albinet *et al.*, 2008a). Thus, the analysis of NPAHs in emission sources and in ambient air is important. Atmospheric NPAHs have been reported in Europe (Dimashki *et al.*, 2000; Feilberg *et al.*, 2001), USA (Zielinska *et al.*, 1989; Bamford and Baker, 2003a), and East Asia (Tang *et al.*, 2005; Hayakawa *et al.*, 2007). However, few studies have been conducted in Southeast Asia, Singapore (Ang *et al.*, 1987), and Vietnam (Hien *et al.*, 2007; Pham *et al.*, 2012). To the best of our knowledge, there have been no reports on atmospheric NPAH concentrations in Thailand.

The purpose of this study is to investigate the occurrence and profiles of PAHs and NPAHs in Chiang Mai, to understand the emission sources and to assess health risks. Chiang Mai should be a representative sampling site to assess the air pollution in northern Thailand that



has similar geography and situation. The results are expected to facilitate air pollution management in northern Thailand.

## **2.1. Methods**

### ***2.1.1. Sampling***

PM samples were collected at the rooftop of a nine-story building at the Faculty of Science in Chiang Mai University (ca. 32 m in height). The sampling location as a representative sampling site to assess the general air pollution in Chiang Mai was chosen by avoiding the direct effects of particular sources such as vehicle exhaust and biomass burning. The site is about 4 km away from the downtown area, is far from roads with heavy traffic and is surrounded by student housing (Fig. C). According to the Chiang Mai Provincial Land Transport Office, the average number of registered gasoline and diesel engine vehicles in Chiang Mai in 2010 was 5,069,466 (78.5%) and 1,391,066 (21.5%), respectively. Total suspended particulates (TSP) were collected using quartz fiber filters (2500QAT-UP, Pall, NY, USA) and a high-volume air sampler (Model HV700F, Sibata Sci. Tech., Saitama, Japan) at a flow rate of 700 L/min for 23 h (Fig. 2.1). We collected samples for seven consecutive days during the dry season [Feb 24–March 2, March 24–30, and April 24–30], the transition period (May 17–23), and the wet season [Aug 21–27 and Sept 8–14] of 2010. For the wet season, there were 6 and 7 rainy days in Aug and Sept, respectively. The filters were equilibrated in desiccators at room temperature for at least 24 h and weighed before and after sample collection. The filters were stored at  $-20^{\circ}\text{C}$  for six months until analyzed.



**Fig. 2.1.** High volume air sampler.

### 2.1.2. Reagents

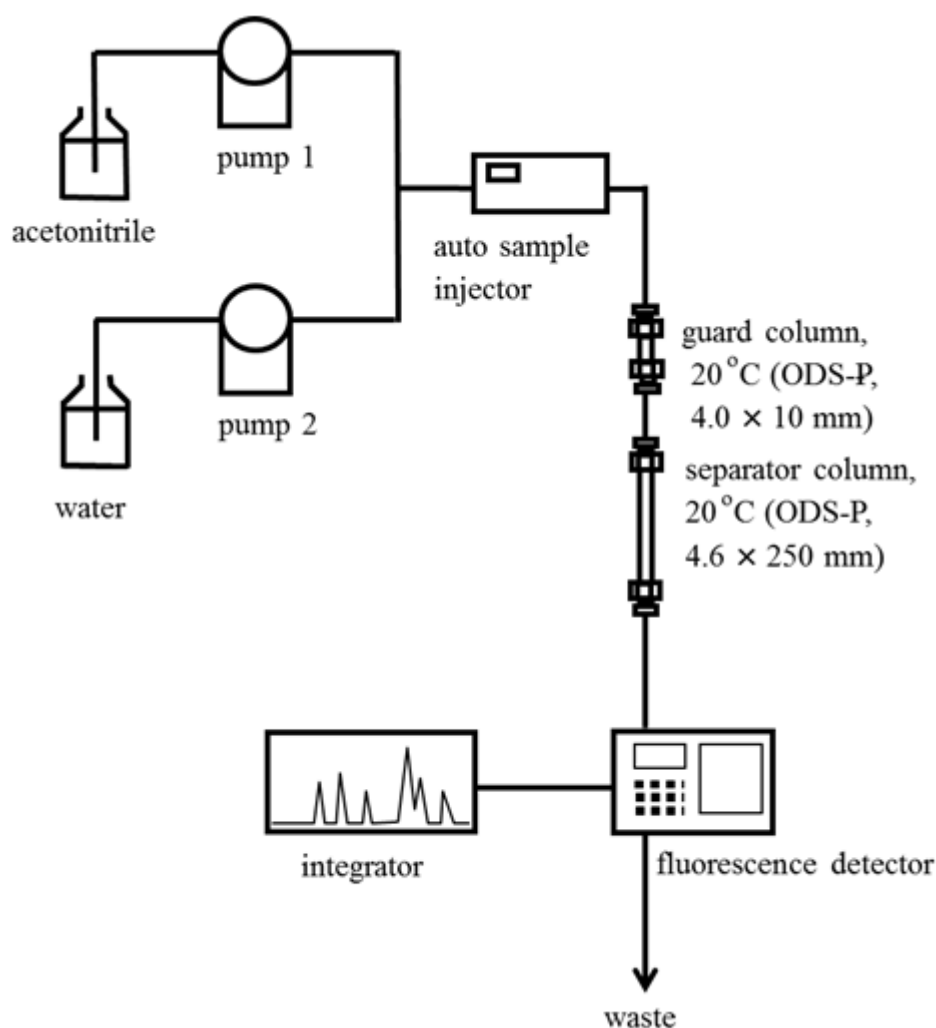
The EPA 610 PAH mixture including fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, dibenz[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe), and indeno[1,2,3-*cd*]pyrene (IDP) was purchased from Sigma–Aldrich (St. Louis, MO, USA). 2-Nitrofluorene (2-NF); 2- and 9-nitroanthracene (2- and 9-NA); 1-, 2-, and 4-nitropyrene (1-, 2-, and 4-NP); 2-nitrotriphenylene (2-NTP); 2- and 3-nitrofluoranthene (2- and 3-NFR); 3-nitroperylene (3-NPer); 1,3- and 1,6-dinitropyrene (1,3- and 1,6-DNP); and LG and *N,O*-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) as a silylating agent were also supplied by Sigma–Aldrich. 1,8-Dinitropyrene (DNP), 1-nitrofluoranthene (1-NFR), 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 6-nitrobenzo[*a*]pyrene (6-NBaP), and 1-nitroperylene (1-NPer) were obtained from Chiron AS (Trondheim, Norway). 9-Nitrophenanthrene (9-NPh) was purchased from AccuStandard, Inc. (New Haven, CT, USA). Two deuterated PAHs (BaA-*d*<sub>12</sub> and BaP-*d*<sub>12</sub>), 6-nitrochrysene-*d*<sub>11</sub> (6-NC-*d*<sub>11</sub>), and LG-<sup>13</sup>C<sub>6</sub> were obtained from the Cambridge Isotope Lab. Inc. (Andover, MA, USA). All solvents and other chemicals were high performance liquid chromatography (HPLC) or analytical-reagent grade.

### 2.1.3. Sample preparation

A quarter of the filter samples was thoroughly cut into small pieces and placed in a flask. After adding the internal standard (BaA- $d_{12}$ , BaP- $d_{12}$ , 6-NC- $d_{11}$ , and LG- $^{13}\text{C}_6$ ) to correct analytical variability, the cut filters were ultrasonically extracted twice with 40 mL of dichloromethane (DCM) for 20 min. The extract was passed through a filter paper. After adding 100  $\mu\text{L}$  of dimethyl sulfoxide (DMSO) into the combined extract, centrifugal evaporation was carried out until the DCM was completely evaporated. The resulting DMSO solution was mixed with 900  $\mu\text{L}$  of ethanol, and the solution was then filtered through a membrane filter (HLC-DISK 3 with pore size of 0.45  $\mu\text{m}$ , Kanto Chemical Co., Inc., Tokyo, Japan). A 20  $\mu\text{L}$  and 100  $\mu\text{L}$  aliquot of the filtered solution was subjected to HPLC for detecting PAHs and NPAHs, respectively. For LG analysis using GC-MS, the derivatization of LG was carried out according to a reported method with minor modifications (Hsu *et al.*, 2007). An adequate volume (10  $\mu\text{L}$ ) of the ethanol extract was evaporated to dryness, and then the residue was derivatized by adding 10  $\mu\text{L}$  of pyridine, 10  $\mu\text{L}$  of 1,4-dithioerythritol (5 mM), 20  $\mu\text{L}$  of silylating agents and 50  $\mu\text{L}$  of toluene. The reaction mixture was heated at 80°C for 60 min. After cooling, 10  $\mu\text{L}$  of 1-phenyldodecane (0.1 mM) as a syringe spike was added to the derivatized solution.

### 2.1.4. Analysis

The 10 PAHs were determined by using HPLC with fluorescence detection (HPLC-FL) without modification (Toriba *et al.*, 2003). The system consisted of two HPLC pumps (LC-10A), a fluorescence detector (RF-10A), a system controller (SCL-10A), a degasser (DGU-14A), an auto sample injector (SIL-10A) and a column oven (CTO-10AS) (all from Shimadzu, Kyoto, Japan). PAHs were separated using a guard column (Inertsil ODS-P, 10  $\times$  4.0 mm i.d., 5 $\mu\text{m}$ , GL Sciences, Tokyo, Japan) and an analytical column (Inertsil ODS-P, 250  $\times$  4.6 mm i.d., 5 $\mu\text{m}$ , GL Sciences) with acetonitrile/water gradient and fluorescence detection (Fig. 2.2).



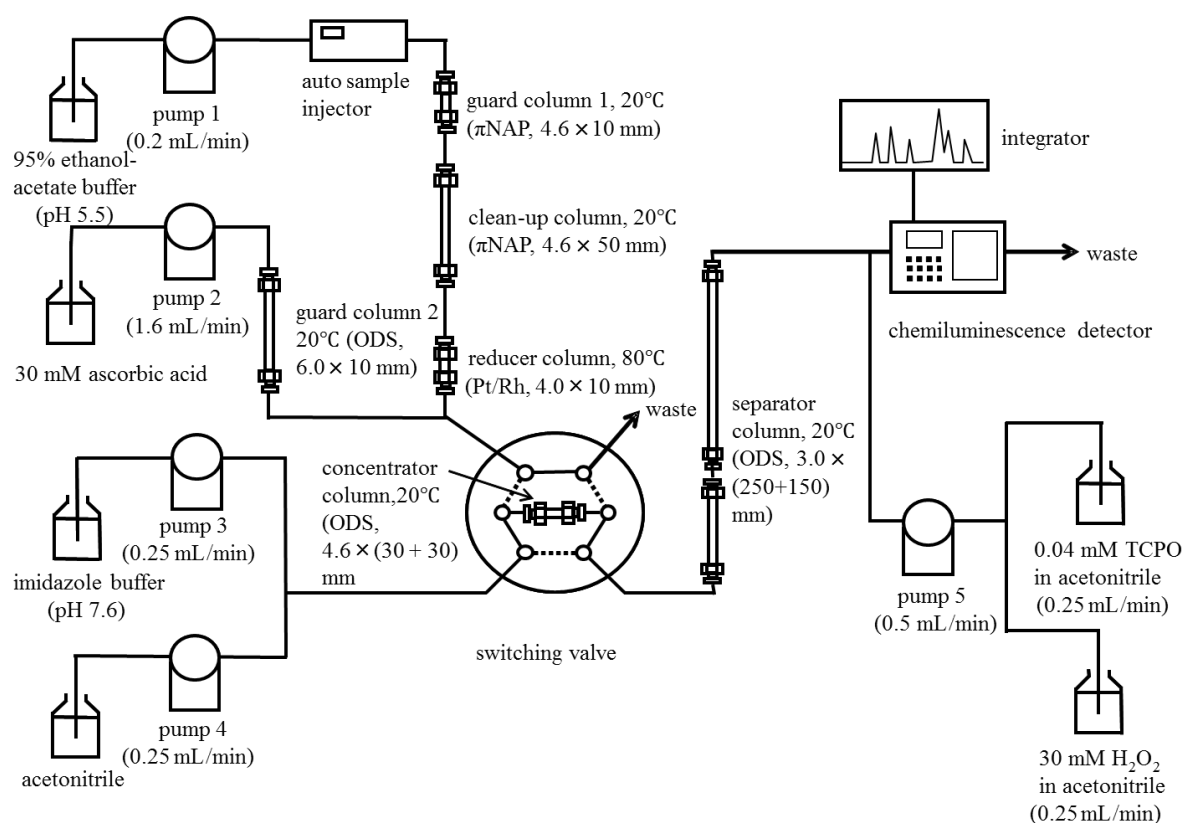
**Fig. 2.2.** HPLC-FL system for PAHs analysis.

The 19 NPAHs were analyzed using HPLC with chemiluminescence (CL) detection. The system consists of five HPLC pumps (LC-20AD), a system controller (CBM-20A), a degasser (DGU-20A5), an auto sample injector (SIL-20AC), a column oven (CTO-20AC) (all from Shimadzu, Kyoto, Japan), and a CL detector (S-3400, Soma Optics Ltd., Tokyo, Japan). The NPAHs were purified using a clean-up column (Cosmosil  $\pi$ NAP, 50 mm  $\times$  4.6 mm i.d. 5 $\mu$ m, Nacalai Tesque, Kyoto, Japan) with its guard column (10 mm  $\times$  4.6 mm i.d.), and were then reduced to their amino derivatives by using a reduction column (NPPak-RS, 10 mm  $\times$  4.0 mm i.d. JASCO, Tokyo, Japan) under 80°C. The mobile phase in the clean-up and reduction columns was acetate buffer (pH 5.5)–ethanol (5/95, v/v) at a flow rate of 0.2 mL/min. Only a fraction of the amino derivatives was trapped on the concentration column (Spheri-5 RP-18, 30 mm  $\times$  4.6 mm i.d. 5  $\mu$ m, Perkin Elmer, MA, USA) by using a switching

valve. The concentrated fraction was applied to two separation columns (Cosmosil 5C<sub>18</sub>-MS-II, 150 mm × 3.0 mm i.d. 5 μm and Cosmosil 5C<sub>18</sub>-AR-II, 250 mm × 3.0 mm i.d. 5 μm, both from Nacalai Tesque) in tandem. All columns, except for the reduction column, were maintained at 20°C. The mobile phase in the separation columns was a gradient elution of 10 mM imidazole buffer (pH 7.6) and acetonitrile at a flow rate of 0.5 mL/min. The eluted fraction from the separation columns was mixed with the CL reagents and detected by the CL detector. The CL reagent solutions were acetonitrile solutions containing 0.02 mM *bis*(2,4,6-trichlorophenyl)oxalate and 15 mM hydrogen peroxide at a flow rate of 0.5 mL/min (Fig. 2.3).

The HPLC system was carried out by using the procedure described in a previous study with some modifications (Tang *et al.*, 2005). To improve selectivity for NPAHs, the clean-up column was changed from a basic column with octadecyl silica (ODS) to the column (πNAP) with naphthylethyl group bonded silica. Ethanol percentage in the mobile phase for the clean-up and reduction column increased with the change of the clean-up column. The combination of a monomeric ODS column (Cosmosil 5C<sub>18</sub>-MS-II) and a polymeric ODS column (Cosmosil 5C<sub>18</sub>-AR-II) enabled us to separate 2-NFR and 2-NP. To decrease acetonitrile consumption, we used the separation columns with smaller internal diameter than the previous paper and decreased the flow rates of the mobile phase for the separation columns and of the CL reagent.

LG analysis was carried out according to a reported method with minor modifications (Hsu *et al.*, 2007). The derivatized samples were applied to gas chromatography coupled with mass spectrometry (GC-MS). The Agilent 6890N Network Gas Chromatograph was fitted with a DB-5MS column (30 m × 250 μm i.d., 0.25 μm film thickness). The Agilent 5975B inert MSD mass spectrometer was operated in electron impact mode (EI). Helium was used as the carrier gas, at a flow rate 1.0 mL/min. The injector temperature was set at 250°C. The column temperature was programmed as follows: initial temperature of 70°C, hold for 1 min, ramp at 20.0°C/min to 300°C, hold for 2 min. The MS ion source temperature was set at 230°C. The derivatized LG was injected 1 μL, under splitless mode. LG quantification was performed in selected ion monitoring mode (SIM), with specific fragment ions at *m/z* 333.



**Fig. 2.3.** HPLC-CL system for NPAHs analysis.

**Table 2.1.** Meteorological parameters, and concentrations of collected PM and forest fires.

	Meteorological conditions <sup>a, b</sup>					TSP <sup>a</sup>	Forest fire <sup>c</sup>	
	Temperature (°C)	Pressure (hPa)	Relative humidity (%)	Wind speed (km/h)	Precipitation (mm)	(µg/m <sup>3</sup> )	Frequency (time)	Burned area (km <sup>2</sup> )
Feb	25.5 ± 0.4	1013.6 ± 1.4	43.6 ± 3.9	18.8 ± 3.6	0.0 ± 0.0	93.5 ± 19.6	991	11.50
March	28.2 ± 0.7	1013.9 ± 2.0	51.0 ± 5.4	30.2 ± 13.9	0.0 ± 0.0	125.0 ± 37.6	659	7.05
April	30.8 ± 0.7	1013.0 ± 1.0	51.4 ± 3.3	38.7 ± 16.3	0.5 ± 0.9	80.8 ± 9.4	371	4.31
May	30.6 ± 0.8	1010.2 ± 1.1	60.0 ± 4.3	28.3 ± 5.9	0.3 ± 0.7	27.5 ± 5.5	14	0.11
Aug	26.8 ± 1.0	1009.4 ± 1.3	82.3 ± 7.1	20.4 ± 5.9	12.7 ± 15.0	25.1 ± 6.4	No data <sup>d</sup>	No data
Sept	26.8 ± 1.7	1010.4 ± 1.1	81.6 ± 7.2	29.9 ± 7.4	15.9 ± 13.7	22.0 ± 5.1	No data	No data

<sup>a</sup> All meteorological and TSP data represent mean ± SD during the sampling period (7 days/month).

<sup>b</sup> Data from the Northern Meteorological Center; <http://www.cmmet.tmd.go.th/index1.php>

<sup>c</sup> Monthly forest fires in Chiang Mai and Lamphun in 2010: Data from the Protected Area Regional Office 16, Natural Park, Wildlife and Plant Conservation Department, Thailand.  
<http://www.fca16.com/upload/files/forestfire/09022556.pdf>

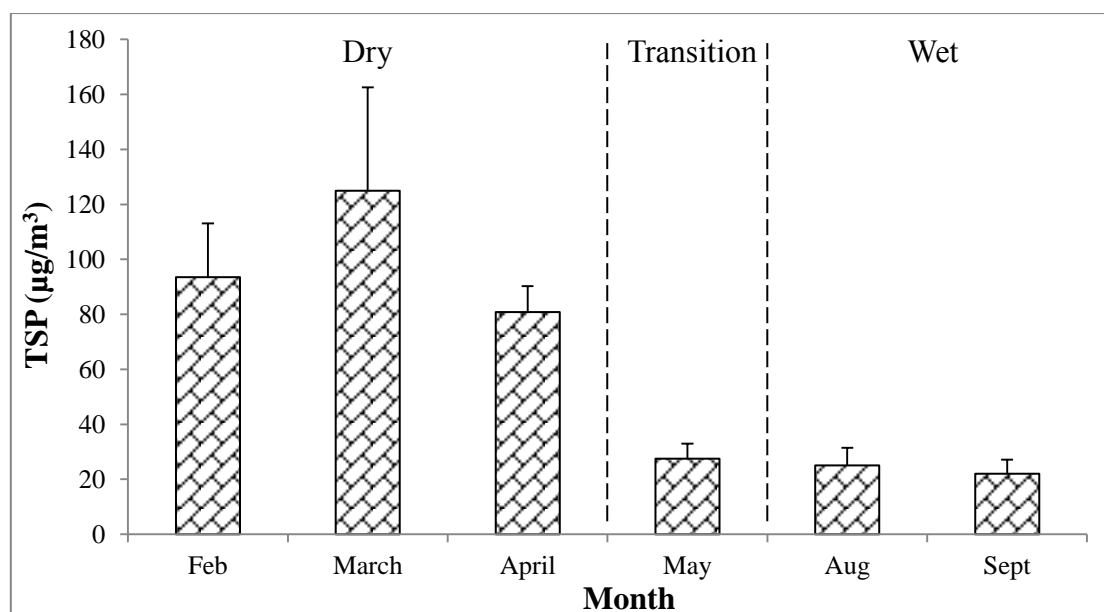
<sup>d</sup> It means almost 0.

## 2.2. Results and discussion

### 2.2.1. Ambient concentrations of TSP

Meteorological conditions during the sampling period (7 days/month) and the concentrations of the collected TSP are shown in Table 2.1. As shown in Table 2.1 and Fig. 2.4, the TSP concentrations in the dry season (Feb–April) were considerably higher than those in the wet season (Aug–Sept), which is in agreement with previous study in Chiang Mai (Pengchai *et al.*, 2009). This distinctly high concentration of PM in the dry season has been recognized as a unique seasonal pattern in northern Thailand. The TSP concentrations of this study were correlated with real-time PM<sub>10</sub> at Provincial Hall in suburban ( $r = 0.888$ ,  $p < 0.01$ ) and Yupparaj Wittayalai School in downtown ( $r = 0.900$ ,  $p < 0.01$ ) sites from the Pollution Control Department (PCD), Ministry of Natural Resources and Environment, Thailand (Fig. C.). The PM<sub>10</sub> concentrations during the 7-day sampling period at the PCD monitoring sites showed similar transition of the concentrations to their monthly PM<sub>10</sub> data (Table C). Therefore, the chosen sampling site can be used to assess the general air quality in Chiang Mai. The elevated PM concentrations during the dry season are attributed to (a) extensive biomass burning due to forest fires and agricultural activities under dry climate conditions, (b) stable meteorological conditions, and (c) the geographical features of Chiang Mai-Lamphun basin surrounded by mountains (Fig. C) (Chantara, 2012). In 2010, the frequency of forest fires and the burned area in Chiang Mai and Lumphun were particularly high in the dry season (Table 2.1). Although farmers burn agricultural debris to prepare the land for cultivation after harvesting, a research concerning biomass open burning using remote sensing data indicated that the amount of burned biomass from forest fires in Thailand (58,880,000 tons) was significantly higher than that from agricultural burning (866,368 tons) (Garivait, 2008). Emission inventory conducted by the Pollution Control Department for the city of Chiang Mai (Muang district) in 2000 showed that 700 tons of the total PM were emitted, of which 89% came from forest fires, 5.4% from solid waste burning, 2.6% from mobile sources, 2.3% from agriculture residue field burning, 0.08% from industry and 0.56% from other sources (Kim Oanh and Leelasakultum, 2011). The stagnant air resulting from high air pressure, calm winds, and a vertical temperature inversion, as well as low levels of precipitation, is responsible for the scarce dispersion and prolonged suspension of PM containing atmospheric pollutants in the atmosphere. The basin architecture also promotes the accumulation of PM during the dry season.





**Fig. 2.4.** Monthly concentration of TSP (mean  $\pm$  SD).

### 2.2.2. Ambient concentrations of PAHs

In this study, we focused on 10 PAHs that have four to six rings and are distributed mostly in the particle phase, and on the 16 PAHs identified as priority pollutants by US EPA. The mean concentrations of the total and individual PAHs in the TSP samples are shown in Table 2.2. As shown in Fig. 2.5, a clear seasonal variation in PAH concentrations was observed over the study period, with significantly higher concentrations in the dry season (Feb > March > April) than in the wet season (Aug and Sept). The total atmospheric PAH concentrations in Chiang Mai were lower than those measured in Bangkok, Thailand (Boonyatumanond *et al.*, 2007), and Ho Chi Minh City and Hanoi, Vietnam (Hien *et al.*, 2007; Pham *et al.*, 2012) (Table D). The chosen sampling site was located in a suburban area and was away from public roadways, whereas the previously reported sampling sites were located in urban areas with high traffic density, resulting in sampling sites closer to PAH sources than this study.

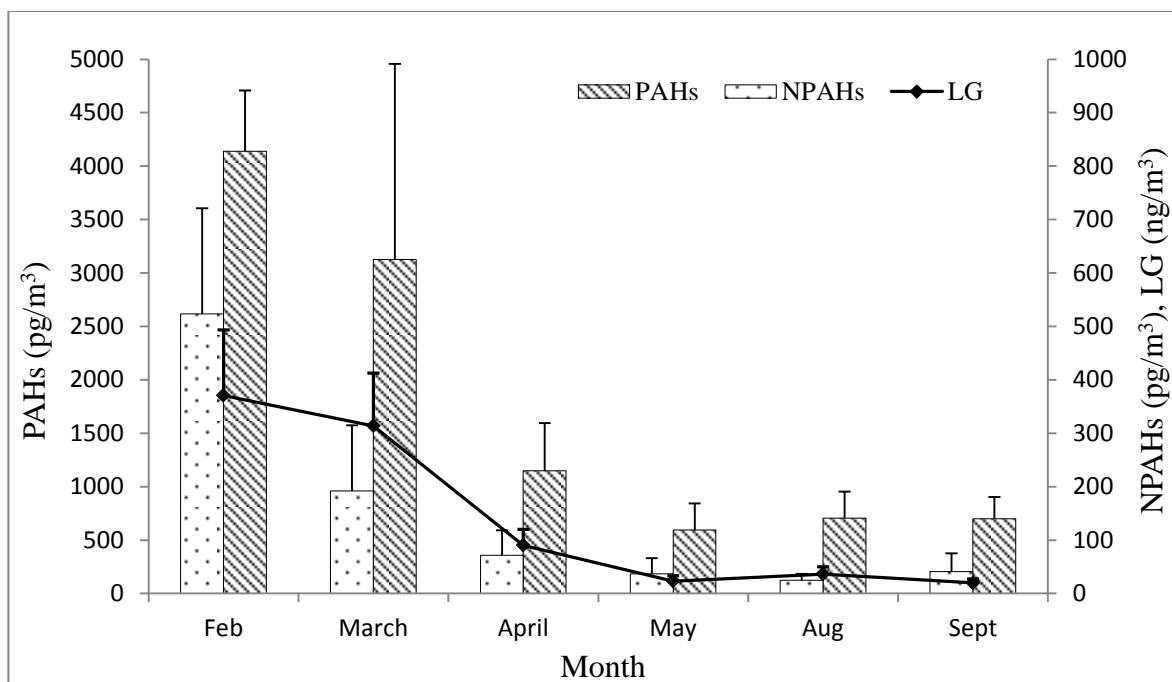
**Table 2.2.** Concentrations (mean  $\pm$  SD) of LG, PAHs, and NPAHs in the dry, transition, and wet seasons.

Compound	Dry season			Transition	Wet season	
	Feb (n = 7)	March (n = 7)	April (n = 7)	May (n = 7)	Aug (n = 7)	Sept (n = 7)
<b>LG (ng/m<sup>3</sup>)</b>	<b>370.8<math>\pm</math>122.4</b>	<b>313.9<math>\pm</math>98.5</b>	<b>90.3 <math>\pm</math> 29.7</b>	<b>23.2 <math>\pm</math> 10.1</b>	<b>36.2 <math>\pm</math> 13.8</b>	<b>20.0 <math>\pm</math> 7.0</b>
<b>PAHs</b> (ng/m <sup>3</sup> )						
Flu	0.24 $\pm$ 0.05	0.20 $\pm$ 0.11	0.07 $\pm$ 0.03	0.03 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01
Pyr	0.31 $\pm$ 0.05	0.27 $\pm$ 0.13	0.12 $\pm$ 0.06	0.04 $\pm$ 0.01	0.04 $\pm$ 0.01	0.03 $\pm$ 0.01
BaA	0.14 $\pm$ 0.01	0.12 $\pm$ 0.06	0.05 $\pm$ 0.02	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.02 $\pm$ 0.00
Chr	0.35 $\pm$ 0.06	0.29 $\pm$ 0.17	0.10 $\pm$ 0.05	0.04 $\pm$ 0.01	0.03 $\pm$ 0.01	0.03 $\pm$ 0.01
BbF	0.71 $\pm$ 0.12	0.50 $\pm$ 0.35	0.15 $\pm$ 0.06	0.08 $\pm$ 0.04	0.09 $\pm$ 0.03	0.08 $\pm$ 0.02
BkF	0.37 $\pm$ 0.06	0.25 $\pm$ 0.16	0.08 $\pm$ 0.03	0.04 $\pm$ 0.02	0.05 $\pm$ 0.02	0.05 $\pm$ 0.01
BaP	0.61 $\pm$ 0.08	0.45 $\pm$ 0.33	0.14 $\pm$ 0.05	0.07 $\pm$ 0.03	0.08 $\pm$ 0.04	0.07 $\pm$ 0.02
DBA	0.03 $\pm$ 0.01	0.03 $\pm$ 0.02	0.01 $\pm$ 0.00	<LOQ	<LOQ	<LOQ
BghiPe	0.65 $\pm$ 0.12	0.57 $\pm$ 0.25	0.25 $\pm$ 0.10	0.17 $\pm$ 0.08	0.20 $\pm$ 0.08	0.23 $\pm$ 0.08
IDP	0.71 $\pm$ 0.14	0.47 $\pm$ 0.29	0.17 $\pm$ 0.07	0.10 $\pm$ 0.05	0.16 $\pm$ 0.07	0.17 $\pm$ 0.07
<b>Total PAHs</b>	<b>4.14<math>\pm</math>0.57</b>	<b>3.13<math>\pm</math>1.83</b>	<b>1.15<math>\pm</math>0.45</b>	<b>0.60<math>\pm</math>0.25</b>	<b>0.70<math>\pm</math>0.25</b>	<b>0.70<math>\pm</math>0.20</b>
<b>NPAHs</b> (pg/m <sup>3</sup> )						
1,3-DNP	0.037 $\pm$ 0.011	0.015 $\pm$ 0.013	0.008 $\pm$ 0.004	0.009 $\pm$ 0.006	0.022 $\pm$ 0.013	0.015 $\pm$ 0.008
1,6-DNP	0.109 $\pm$ 0.045	0.067 $\pm$ 0.042	0.042 $\pm$ 0.026	0.062 $\pm$ 0.038	0.047 $\pm$ 0.038	0.058 $\pm$ 0.023
1,8-DNP	0.121 $\pm$ 0.037	0.030 $\pm$ 0.028	0.021 $\pm$ 0.006	0.046 $\pm$ 0.022	0.088 $\pm$ 0.037	0.042 $\pm$ 0.007
2-NF	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.
9-NPh	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2-NA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
9-NA	249.4 $\pm$ 92.2	92.0 $\pm$ 65.0	23.7 $\pm$ 15.2	9.4 $\pm$ 10.3	6.6 $\pm$ 3.3	9.3 $\pm$ 9.3
2-NFR	164.1 $\pm$ 63.5	59.4 $\pm$ 38.5	29.2 $\pm$ 19.1	14.1 $\pm$ 8.3	7.6 $\pm$ 5.6	9.7 $\pm$ 7.7
2-NP	62.5 $\pm$ 25.7	20.8 $\pm$ 12.8	7.1 $\pm$ 5.5	6.2 $\pm$ 8.1	2.7 $\pm$ 1.8	10.6 $\pm$ 10.8
4-NP	1.7 $\pm$ 0.6	0.9 $\pm$ 0.5	0.5 $\pm$ 0.4	0.1 $\pm$ 0.1	<LOQ	0.2 $\pm$ 0.2
3-NFR	1.2 $\pm$ 0.7	2.4 $\pm$ 0.8	1.6 $\pm$ 1.1	0.2 $\pm$ 0.2	0.1 $\pm$ 0.0	0.6 $\pm$ 0.7
1-NP	10.0 $\pm$ 2.7	4.2 $\pm$ 1.4	3.3 $\pm$ 1.7	2.6 $\pm$ 1.4	2.4 $\pm$ 0.8	4.7 $\pm$ 2.1
1-NFR	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2-NTP	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.
6-NC	2.3 $\pm$ 1.1	1.8 $\pm$ 0.8	1.3 $\pm$ 0.3	1.2 $\pm$ 0.5	3.1 $\pm$ 1.5	1.9 $\pm$ 1.2
7-NBaA	28.9 $\pm$ 24.3	8.7 $\pm$ 5.6	4.4 $\pm$ 4.6	2.5 $\pm$ 3.4	1.3 $\pm$ 0.5	2.6 $\pm$ 3.6
3-NPer	1.2 $\pm$ 0.7	0.9 $\pm$ 0.6	0.3 $\pm$ 0.1	0.2 $\pm$ 0.2	0.2 $\pm$ 0.1	0.3 $\pm$ 0.1
6-NBaP	2.0 $\pm$ 1.6	0.9 $\pm$ 0.7	0.4 $\pm$ 0.1	0.4 $\pm$ 0.4	0.5 $\pm$ 0.2	0.6 $\pm$ 0.2
1-NPer	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
<b>Total NPAHs</b>	<b>523.5<math>\pm</math>197.4</b>	<b>192.0<math>\pm</math>122.9</b>	<b>71.6<math>\pm</math>46.8</b>	<b>36.9<math>\pm</math>30.4</b>	<b>24.7<math>\pm</math>12.3</b>	<b>40.6<math>\pm</math>33.7</b>

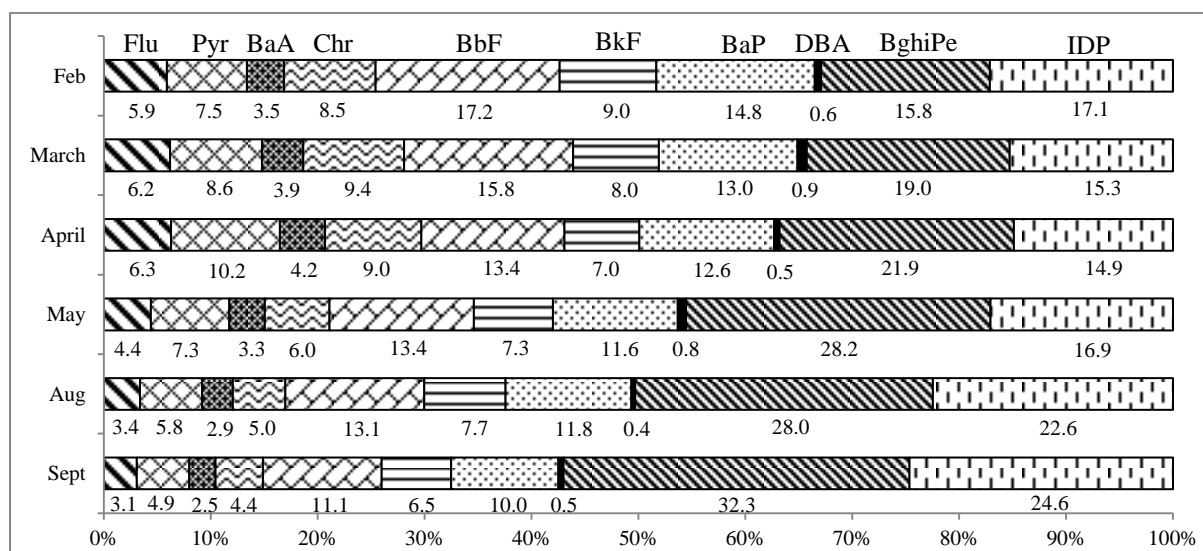
<LOQ = less than limit of quantification.

N.D. = not detected.

N.Q. = not quantified, small peaks of 2-NF and 2-NTP were detected but not quantified because of the presence of interfering peaks.

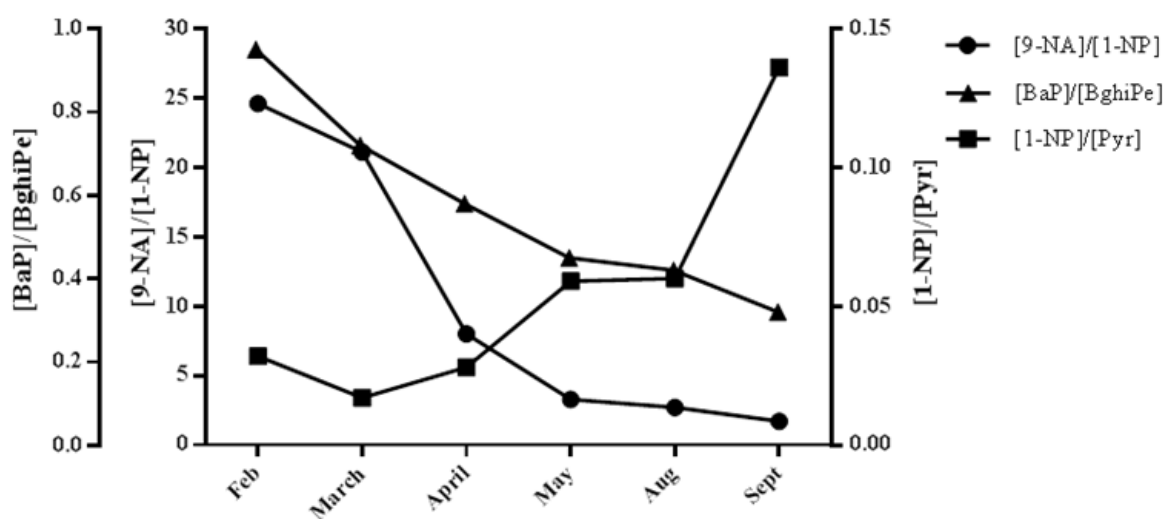


**Fig. 2.5.** Monthly concentrations (mean  $\pm$  SD) of PAHs, NPAHs, and LG. Each bar represents the mean concentrations of the total PAHs or NPAHs; [PAHs] = [Flu] + [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [DBA] + [BghiPe] + [IDP], [NPAHs] = [1,3-DNP] + [1,6-DNP] + [1,8-DNP] + [9-NA] + [2-NFR] + [2-NP] + [4-NP] + [3-NFR] + [1-NP] + [6-NC] + [7-NBaA] + [3-NPer] + [6-NBaP]. The line plot connects the mean concentrations of LG.



**Fig. 2.6.** Monthly composition profiles of PAHs. The numbers under the bars denote the percentage of each compound in the total concentration.

The proportion of each PAH to the total PAH concentrations was calculated monthly to show the seasonal variations in the PAH profiles (Fig. 2.6). The proportions of PAHs having five and six rings, especially BbF, BaP, BghiPe, and IDP, were high. Several PAHs have been proposed as tracers to distinguish the miscellaneous combustion sources. BaP is a tracer for biomass burning, whereas BghiPe and IDP are tracers for vehicle exhaust (Kulkarni and Venkataraman, 2000). In Fig. 2.6, the increase in BaP in the dry season and that in BghiPe and IDP in the wet season suggest increased contribution of biomass burning in the dry season and vehicle exhaust in the wet season, respectively. The high proportion of BghiPe and IDP is common in Southeast Asian countries such as Thailand (Kim Oanh *et al.*, 2000, Chantara and Sangchan, 2009), Vietnam (Hien *et al.*, 2007 and Pham *et al.*, 2012), and Malaysia (Omar *et al.*, 2002), presumably because of the contribution of gasoline engine vehicles (Miguel *et al.*, 1998; Boonyatumanond *et al.*, 2007). The concentration ratios of PAHs are characteristic of combustion sources. The [BaP]/[BghiPe] value ( $<0.6$ ) indicates the predominant contribution of traffic emissions (Pandey *et al.*, 1999). The ratios in the wet season (0.32–0.42) were within the range of the traffic emission indicators, whereas the increase in the ratio in the dry season (0.58–0.95) suggests the increased contribution of source(s) other than traffic emissions (Fig. 2.7).

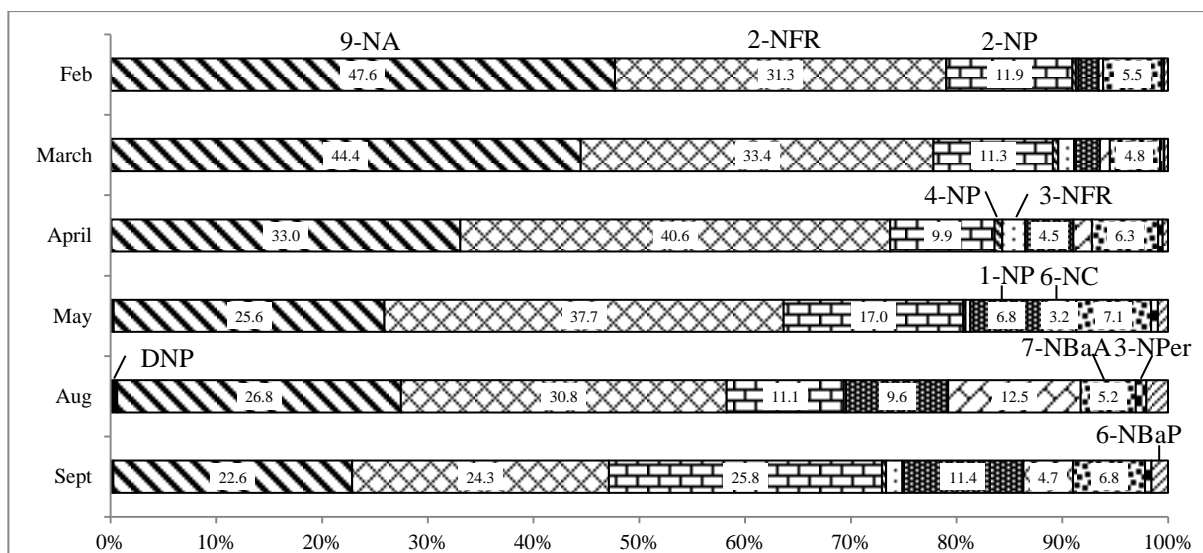


**Fig. 2.7.** Monthly diagnostic ratios of [9-NA]–[1-NP], [1-NP]–[Pyr], and [BaP]–[BghiPe].

### 2.2.3. Ambient concentrations of NPAHs

The total NPAH and PAH concentrations have similar trends, with significantly higher concentrations in the dry season than in the wet season (Table 2.2, Fig. 2.5). Moreover, the total NPAH concentration was one order of magnitude lower than the total PAHs each month. The NPAH profiles in the dry and wet seasons are shown in Fig. 2.8. Overall, 9-NA, 2-NFR, and 2-NP were abundant in the determined 19 NPAHs in both seasons, accounting for 72.7%–90.9% of the total NPAH concentrations each month. Among the NPAHs—except 2-NFR and 2-NP, which represent secondary formation of NPAHs in the atmosphere (Arey *et al.*, 1986; Atkinson and Arey, 1994)—9-NA was the most abundant and mainly originated from incomplete combustion of organic materials, especially in the dry season. The proportion of 9-NA in the dry season is much higher than in other studies conducted in Asian cities such as Kanazawa, Japan (Hayakawa *et al.*, 2007); Hanoi (Pham *et al.*, 2012); and Fushun, China (Hayakawa *et al.*, 2007). Several reports have suggested the generation of 9-NA from diesel exhaust (Pitts *et al.*, 1982; Paputa-Peck *et al.*, 1983). The extremely high concentration and proportion of 9-NA to the other NPAHs have not been observed even at a road side and is specific for Chiang Mai in dry season. This might indicate another source of 9-NA such as biomass burning in addition to diesel exhaust.

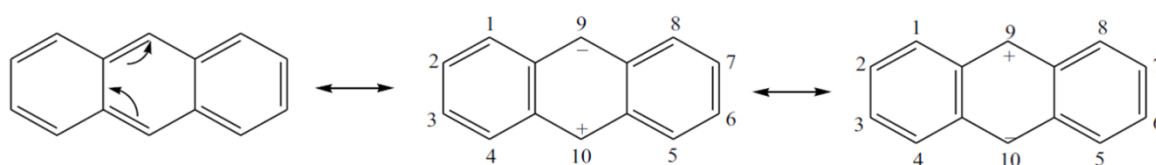
1-NP, 6-NC, 7-NBaA, and 6-NBaP are directly emitted from vehicles, especially diesel engines (Murahashi *et al.*, 1999; Bamford *et al.*, 2003b). In particular, 1-NP is present in diesel exhaust and is one of the most abundant NPAHs in the atmosphere, and therefore has been proposed as a chemical marker for diesel exhaust (Paputa-Peck *et al.*, 1983; Bamford *et al.*, 2003b). The annual concentration of 1-NP in Chiang Mai ( $4.6 \pm 2.8$  pg/m<sup>3</sup>) is remarkably lower than that in urban Hanoi, which also has high traffic density (43.3–120.7 pg/m<sup>3</sup>, Pham *et al.*, 2012). Because the sampling site was located in a suburban area far from roads with heavy traffic, the contribution of diesel exhaust may be relatively small. Nevertheless, the percentage of 1-NP, 6-NC, and 6-NBaP increased in the wet season (Fig. 2.8), suggesting that the contribution of vehicle exhaust increased in the wet season.



**Fig. 2.8.** Monthly composition profiles NPAHs. The numbers in the bars denote the percentage of each compound in the total concentration.

On the other hand, the unexpected high concentrations of 9-NA in the dry season were obviously different from the distinct behavior of NPAHs derived from vehicle exhaust (Table 2.2 and Fig. 2.8). It seems likely that 9-NA can be produced by biomass burning. This hypothesis is supported by finding NPAHs emitted from wood combustion. 9-NA was observed in the combustion of all types of wood (Shen *et al.*, 2012). Furthermore, Ding *et al.* (2012) reported one of the highest concentrations of 9-NA in NPAHs in particulate phase collected in rural Chinese homes that use biomass (firewood and corn residue) as fuel. Therefore, 9-NA is likely correlated with biomass burning, probably because of the low temperatures in biomass combustion and the high reactivity of PAH nitration. PAH formation with different number of aromatic rings depends on the reaction temperature. Usually, low reaction temperature favors the formation of low molecular weight PAHs, whereas high reaction temperature promotes the formation of high molecular weight PAHs (Dong and Huttinger, 2002; Mai *et al.*, 2003). The combustion temperature in wood stoves (500–600°C) is much lower than in diesel engines (2700–3000°C). Anthracene (Ant) which has 3 rings may be produced in higher levels in biomass combustion, and as a result, produce more 9-NA. Higher Ant concentrations in wood-burning exhaust than in diesel exhaust were observed by Khalili *et al.* (1995) and Cochran *et al.* (2012). Further, smoldering combustion emitted 2 times more Ant than flaming combustion (Jenkins *et al.*, 1996). Nielsen (1984) investigated the nitration reactivity of PAHs which the relative reactivity of anthanthrene was set at 100,000. The most reactive positions in Ant are the meso positions (C-9 and C-10) and

the relative reactivity of Ant (1,200) is higher than those of BaP (1,100), Pyr (27), Chr (6.3), BaA (4.5), phenanthrene (<2), and Flu (<0.4). Due to the following resonance of Ant (Fig. 2.9), the electron density at C-9 or C-10 is higher than the other positions and thus, C-9 and C-10 positions are more easily to be oxidized than other positions. The high nitration reactivity of Ant at position 9 may accelerate the preferential generation of 9-NA under the lower-temperature combustion of biomass relative to other sources. Clearly, the mechanism of NPAH formation from biomass burning needs to be studied in more detail.



**Fig. 2.9.** Resonant structures of Ant.

#### 2.2.4. PAH and NPAH correlation with LG

To identify the contribution of biomass burning to air pollutants, LG has been considered as a good tracer of biomass-burning sources (Puxbaum *et al.*, 2007; Mochida *et al.*, 2010). The correlation coefficients of PAHs and NPAHs with LG in the dry and wet seasons were calculated to discuss the major sources of PAHs and NPAHs, and are shown in Table 2.3. The strong correlation of PAHs and NPAHs with LG in the dry season suggested that biomass burning is the major contributor of PAHs and NPAHs. In particular, among NPAHs, 9-NA showed the highest correlation coefficient with LG, suggesting generation from biomass burning. The significant correlation among the individual and total PAHs and NPAHs and between PAHs and NPAHs in the dry season also suggests the existence of a common source (Table 2.4 and 2.5). Although the concentrations of NPAHs per weight unit for vehicle exhaust particulates are higher than those for biomass-burning particulates (Yang *et al.*, 2010; Cochran *et al.*, 2012), massive biomass burning can be a major source of NPAHs at this site. On the other hand, poor correlations of PAHs and NPAHs with LG were observed in wet season (Table 2.3, 2.4 and 2.5), suggesting a decrease of the contribution of biomass burning.

**Table 2.3.** Correlation coefficients of PAHs and NPAHs with LG in the dry and wet seasons.

	Dry	Wet
Flu	0.812**	0.509
Pyr	0.838**	0.630*
BaA	0.869**	0.641*
Chr	0.877**	0.446
BbF	0.898**	0.464
BkF	0.895**	0.513
BaP	0.876**	0.606*
DBA	0.867**	−0.243
BghiPe	0.921**	0.292
IDP	0.915**	0.313
∑PAHs	0.910**	0.458
1,3-DNP	0.706**	0.236
1,6-DNP	0.738**	−0.142
1,8-DNP	0.539*	0.692**
9-NA	0.850**	0.152
2-NFR	0.802**	0.131
2-NP	0.801**	−0.026
4-NP	0.662**	−0.114
3-NFR	0.167	−0.090
1-NP	0.688**	−0.252
6-NC	0.490*	0.278
7-NBaA	0.605**	0.044
3-NPer	0.767**	0.185
6-NBaP	0.653**	−0.103
∑NPAHs	0.829**	0.084

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).



**Table 2.4.** Correlation coefficients among the concentrations of individual and total PAHs and NPAHs and between PAHs and NPAHs in the dry season.

	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	DBA	BghiPe	IDP	ΣPAHs	1,3-DNP	1,6-DNP	1,8-DNP	9-NA	2-NFR	2-NP	4-NP	3-NFR	1-NP	6-NC	7-NBaA	3-NPer	6-NBaP	ΣNPAHs	LG
Flu	1.00																									
Pyr	.991**	1.00																								
BaA	.938**	.961**	1.00																							
Chr	.958**	.975**	.977**	1.00																						
BbF	.889**	.905**	.923**	.960**	1.00																					
BkF	.868**	.887**	.919**	.948**	.994**	1.00																				
BaP	.917**	.926**	.944**	.963**	.971**	.966**	1.00																			
DBA	.833**	.852**	.869**	.911**	.932**	.899**	.892**	1.00																		
BghiPe	.874**	.906**	.934**	.951**	.966**	.957**	.964**	.926**	1.00																	
IDP	.858**	.872**	.900**	.934**	.985**	.986**	.958**	.888**	.955**	1.00																
ΣPAHs	.927**	.943**	.957**	.982**	.991**	.985**	.987**	.921**	.979**	.979**	1.00															
1,3-DNP	.725**	.706**	.701**	.745**	.801**	.807**	.723**	.652**	.693**	.839**	.778**	1.00														
1,6-DNP	.806**	.821**	.825**	.834**	.773**	.763**	.773**	.660**	.765**	.807**	.807**	.823**	1.00													
1,8-DNP	.550**	.526*	.555**	.542*	.630**	.651**	.555**	.451*	.494*	.672**	.599**	.896**	.651**	1.00												
9-NA	.715**	.733**	.796**	.810**	.862**	.891**	.814**	.699**	.810**	.908**	.852**	.882**	.820**	.744**	1.00											
2-NFR	.692**	.709**	.748**	.761**	.797**	.816**	.732**	.631**	.738**	.851**	.790**	.916**	.878**	.803**	.964**	1.00										
2-NP	.628**	.657**	.741**	.750**	.816**	.858**	.766**	.632**	.770**	.864**	.800**	.823**	.754**	.687**	.983**	.933**	1.00									
4-NP	.468*	.512*	.627**	.557**	.542*	.594**	.501*	.384	.565**	.611**	.565**	.618**	.673**	.560**	.807**	.808**	.822**	1.00								
3-NFR	.162	.231	.193	.169	.040	-.011	.006	.189	.183	.007	.084	-.150	.217	-.247	-.109	.008	-.154	.139	1.00							
1-NP	.604**	.628**	.689**	.665**	.679**	.718**	.622**	.470*	.634**	.741**	.683**	.837**	.831**	.774**	.914**	.956**	.902**	.898**	.045	1.00						
6-NC	.691**	.672**	.595**	.632**	.581**	.547*	.524*	.508*	.494*	.575**	.587**	.764**	.761**	.692**	.549**	.667**	.434*	.326	.218	.609**	1.00					
7-NBaA	.336	.393	.533*	.531*	.614**	.670**	.562**	.455*	.610**	.668**	.590**	.585**	.557**	.440*	.820**	.737**	.895**	.754**	-.172	.733**	.111	1.00				
3-NPer	.664**	.695**	.766**	.797**	.837**	.847**	.840**	.749**	.854**	.842**	.835**	.629**	.703**	.392	.814**	.712**	.825**	.542*	-.052	.623**	.341	.803**	1.00			
6-NBaP	.434*	.476*	.601**	.615**	.696**	.737**	.676**	.557**	.699**	.741**	.679**	.601**	.598**	.412	.821**	.713**	.880**	.652**	-.218	.667**	.143	.963**	.911**	1.00		
ΣNPAHs	.685**	.708**	.774**	.785**	.836**	.866**	.781**	.666**	.786**	.887**	.825**	.883**	.832**	.749**	.996**	.978**	.985**	.827**	-.078	.936**	.554**	.836**	.801**	.823**	1.00	
LG	.812**	.838**	.869**	.877**	.898**	.895**	.876**	.867**	.921**	.915**	.910**	.706**	.738**	.539*	.850**	.802**	.801**	.662**	.167	.688**	.490*	.605**	.767**	.653**	.829**	1.00

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

**Table 2.5.** Correlation coefficients among the concentrations of individual and total PAHs and NPAHs and between PAHs and NPAHs in the wet season.

	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	DBA	BghiPe	IDP	ΣPAHs	1,3-DNP	1,6-DNP	1,8-DNP	9-NA	2-NFR	2-NP	4-NP	3-NFR	1-NP	6-NC	7-NBaA	3-NPer	6-NBaP	ΣNPAHs	LG
Flu	1.00																									
Pyr	.965**	1.00																								
BaA	.951**	.966**	1.00																							
Chr	.949**	.913**	.960**	1.00																						
BbF	.776**	.847**	.772**	.718**	1.00																					
BkF	.762**	.836**	.775**	.705**	.984**	1.00																				
BaP	.787**	.855**	.825**	.716**	.915**	.951**	1.00																			
DBA	-.052	-.168	-.171	-.130	-.043	.055	.047	1.00																		
BghiPe	.428	.491	.440	.322	.719**	.764**	.795**	.323	1.00																	
IDP	.458	.533*	.497	.383	.652*	.663**	.690**	-.161	.717**	1.00																
ΣPAHs	.693**	.762**	.715**	.608*	.895**	.918**	.935**	.056	.900**	.862**	1.00															
1,3-DNP	.336	.476	.432	.379	.642*	.633*	.610*	-.172	.427	.242	.496	1.00														
1,6-DNP	.309	.315	.290	.325	.466	.440	.449	.094	.421	.115	.383	.794**	1.00													
1,8-DNP	.439	.587*	.557*	.416	.661**	.652*	.686**	-.370	.344	.300	.511	.742**	.367	1.00												
9-NA	.357	.303	.254	.218	.342	.361	.337	.648*	.468	.008	.328	-.011	.160	-.028	1.00											
2-NFR	.453	.481	.368	.310	.583*	.560*	.504	.365	.634*	.263	.552*	.306	.375	.154	.862**	1.00										
2-NP	.092	.069	.002	-.063	.190	.202	.187	.579*	.544*	.144	.311	-.157	.050	-.235	.884**	.831**	1.00									
4-NP	.014	-.026	-.075	-.118	.035	.045	.036	.573*	.402	.022	.160	-.255	-.013	-.364	.857**	.774**	.980**	1.00								
3-NFR	-.017	-.050	-.128	-.193	.107	.125	.107	.571*	.551*	.238	.299	-.326	-.096	-.367	.737**	.674**	.944**	.912**	1.00							
1-NP	.375	.217	.202	.267	.207	.167	.199	.484	.371	.044	.251	-.129	.329	-.250	.741**	.673**	.719**	.721**	.633*	1.00						
6-NC	.460	.581*	.514	.473	.634*	.636*	.612*	-.071	.348	.135	.448	.929**	.713**	.679**	.161	.437	-.060	-.128	-.285	-.034	1.00					
7-NBaA	.169	.158	.076	.014	.227	.255	.214	.629*	.476	.102	.297	-.126	-.029	-.199	.917**	.853**	.948**	.937**	.858**	.626*	.054	1.00				
3-NPer	.364	.468	.303	.224	.669**	.646*	.554*	.189	.684**	.304	.598*	.505	.446	.320	.622*	.887**	.646*	.547*	.541*	.391	.572*	.652*	1.00			
6-NBaP	.070	.123	-.003	-.062	.457	.484	.419	.516	.737**	.290	.514	.364	.487	.044	.612*	.753**	.730**	.636*	.697**	.445	.360	.670**	.834**	1.00		
ΣNPAHs	.320	.304	.221	.166	.396	.401	.369	.567*	.580*	.145	.422	.064	.216	-.029	.961**	.946**	.945**	.909**	.814**	.746**	.211	.953**	.759**	.738**	1.00	
LG	.509	.630*	.641*	.446	.464	.513	.606*	-.243	.292	.313	.458	.236	-.142	.692**	.152	.131	-.026	-.114	-.090	-.252	.278	.044	.185	-.103	.084	1.00

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

### 2.2.5. Evaluation of emission sources by diagnostic ratios using NPAHs

The concentration ratios of PAHs and NPAHs can be used to compare combustion sources. Tang *et al.* (2005) proposed the [1-NP]/[Pyr] ratio, as an indicator of vehicle contribution, and coal combustion to atmospheric PAHs and NPAHs. The [1-NP]/[Pyr] ratio for coal stove (0.001) was much smaller than that for diesel exhaust (0.36). As shown in Fig. 2.7, the [1-NP]/[Pyr] values in this study are lower in the dry season than in the wet season. This suggests that the contribution of vehicle exhaust in the dry season is low and increases with the wet season approaching. The ratios in the dry season were similar to those in Chinese cities where the contribution of coal burning predominates, i.e., Fushun (0.013) and Shenyang (0.012) (Hayakawa *et al.*, 2007; Tang *et al.*, 2011). The ratios should decrease because of the high contribution of PAHs from biomass burning in Chiang Mai as well as coal burning in Chinese cities.

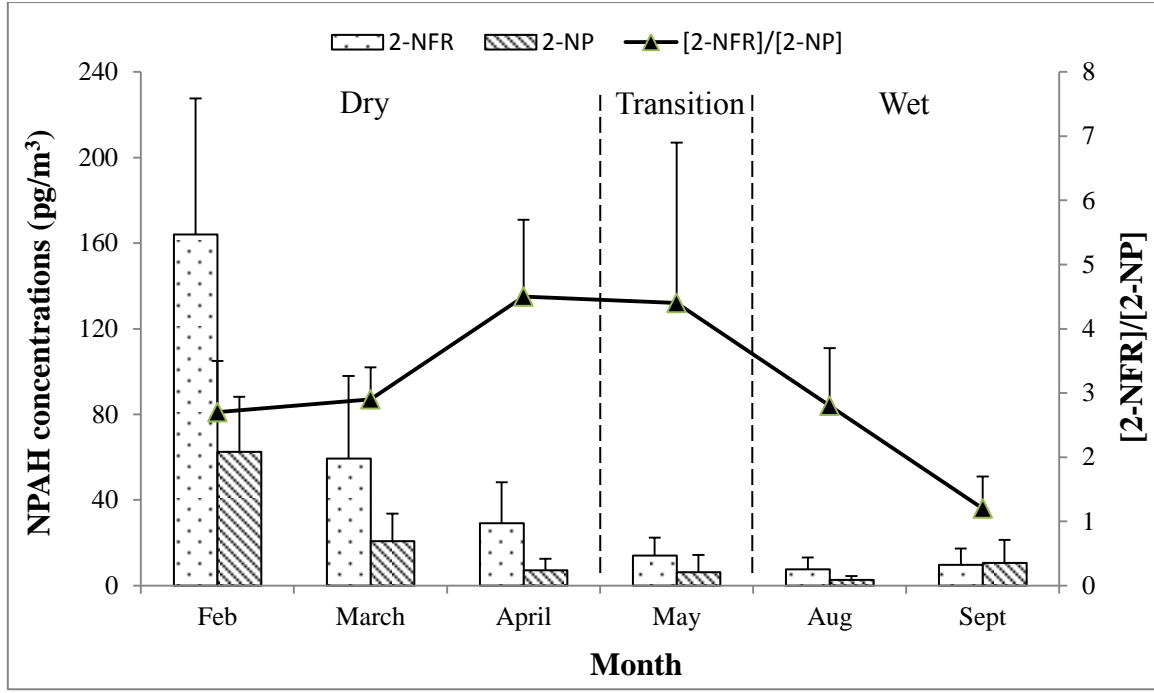
Generation of large amounts of 9-NA from biomass burning was observed in this study. We proposed the [9-NA]/[1-NP] value as an indicator to distinguish biomass burning from vehicle exhaust. The significant correlation between the [9-NA]/[1-NP] values and LG concentrations ( $r = 0.933$ ;  $p < 0.01$ ) indicated that the proposed ratio should be a good indicator for biomass burning. The transition of the ratio was clearly opposite to that of the [1-NP]/[Pyr] values (Fig. 2.7). The high [9-NA]/[1-NP] and low [1-NP]/[Pyr] values in Feb and March were strongly influenced by biomass burning, whereas the opposite pattern in Sept was strongly influenced by vehicle exhaust. On the other hand, the concentrations of LG in PM<sub>10</sub> samples collected during the haze episode ranged from 200 – 600 ng/m<sup>3</sup> (Fraser and Lakshmanan, 2000). In this study, the LG levels in Feb and March exceeded 200 ng/m<sup>3</sup> (Fig. 2.5 and Table 2.2). Although forest fires were still observed in April (Table 2.1), Feb and March were judged to be strongly affected by biomass burning. Therefore, we propose that a [9-NA]/[1-NP] value of more than 10 indicates strong contributions from biomass burning.

The low [9-NA]/[1-NP] and high [1-NP]/[Pyr] values in Sept (1.70/0.136) were remarkably similar to those in Asian cities such as Kanazawa (0.08/0.141) and Hanoi (0.17/0.145), which are highly affected by vehicle exhaust (Hayakawa *et al.*, 2007; Pham *et al.*, 2012). Chinese cities with predominant contributions from coal burning showed [9-NA]/[1-NP] less than 10 and low [1-NP]/[Pyr] values, i.e., Fushun (3.67/0.013) and Shenyang (6.30/0.012) (Hayakawa *et al.*, 2007; Tang *et al.*, 2011). The profile of Chiang Mai with low [1-NP]/[Pyr] values in the dry season was clearly distinguished from coal burning

using the [9-NA]/[1-NP] values. The [9-NA]/[1-NP] ratio in addition to [1-NP]/[Pyr] ratio should be useful for evaluating the contribution of biomass burning.

#### **2.2.6. Secondary formation of NPAHs**

2-NFR and 2-NP form in the atmosphere through secondary gas-phase reactions of parent PAHs with OH radicals in the presence of NO<sub>2</sub> during daytime. OH radicals form via the photolysis of O<sub>3</sub> during the day (Arey *et al.*, 1986; Atkinson and Arey, 1994). 2-NFR can also form by the gas-phase reaction of Flu with NO<sub>3</sub> radicals at night, because the radicals are rapidly photolyzed during the day (Arey *et al.*, 1986; Atkinson and Arey, 1994). The average concentrations of 2-NFR and 2-NP in the dry season were higher than those in the wet season (Table 2.2, Fig. 2.10), and were abundant in all seasons, accounting for ca. 50% of the total NPAH concentrations each month (Fig. 2.8). This result indicates that the formation of gaseous 2-NFR and 2-NP was prominent in the dry season. The prolonged lack of air convection and precipitation in the dry season could facilitate the photochemical formation of 2-NFR and 2-NP. Moreover, the Flu and Pyr concentrations as reactants were higher in the dry season than in the wet season (Table 2.2). The [2-NFR]/[2-NP] ratio has been used to evaluate the formation of NPAHs by daytime OH- or nighttime NO<sub>3</sub>-initiated reactions (Zielinska *et al.*, 1989). A ratio close to 10 indicates the dominance of daytime OH radical reactions, while a ratio closer to 100 indicates the dominance of nighttime NO<sub>3</sub> radical reactions. The monthly ratios obtained in this study were all in the range 0.7–7.9. This suggests the predominance of OH-radical-initiated formation at the sampling site.



**Fig. 2.10.** Monthly concentration of 2-NFR, 2-NP and [2-NFR]/[2-NP] ratio.

## 2.2.7. Health risk assessment

### 2.2.7.1. Carcinogenic risk

Carcinogenic risk was estimated using toxic equivalent factors (TEFs) according to the procedure by Albinet *et al.* (2008a), and was calculated as shown in Eq. (1).

$$\text{Carcinogenic risk} = [\sum[\text{PAH}]_i \text{TEF}_{\text{PAH}i} + \sum[\text{NPAH}]_i \text{TEF}_{\text{NPAH}i}] \times \text{UR}_{\text{BaP}} \quad (1)$$

where  $[\text{PAH}]_i$  and  $[\text{NPAH}]_i$  are the atmospheric concentrations of individual PAHs and NPAHs in nanogram per cubic meter.  $\text{TEF}_{\text{PAH}i}$  and  $\text{TEF}_{\text{NPAH}i}$  are the TEFs of individual PAHs and NPAHs, respectively (Table 2.6). The TEFs of PAHs and NPAHs were normalized to BaP, which was used as reference compound.  $\text{UR}_{\text{BaP}}$  is the inhalation cancer unit risk factor of BaP ( $1.1 \times 10^{-6} (\text{ng}/\text{m}^3)^{-1}$ ). The carcinogenic risk calculated using eight PAHs and five NPAHs is shown in Fig. 2.11. The carcinogenic risks in Feb were 6.2 times higher than the average risk in the wet season, indicating more harmful air conditions in the dry season than in the wet season. The risks are comparable with those observed in Maurienne, France (Albinet *et al.*, 2008a), which is a heavy-duty international traffic area.

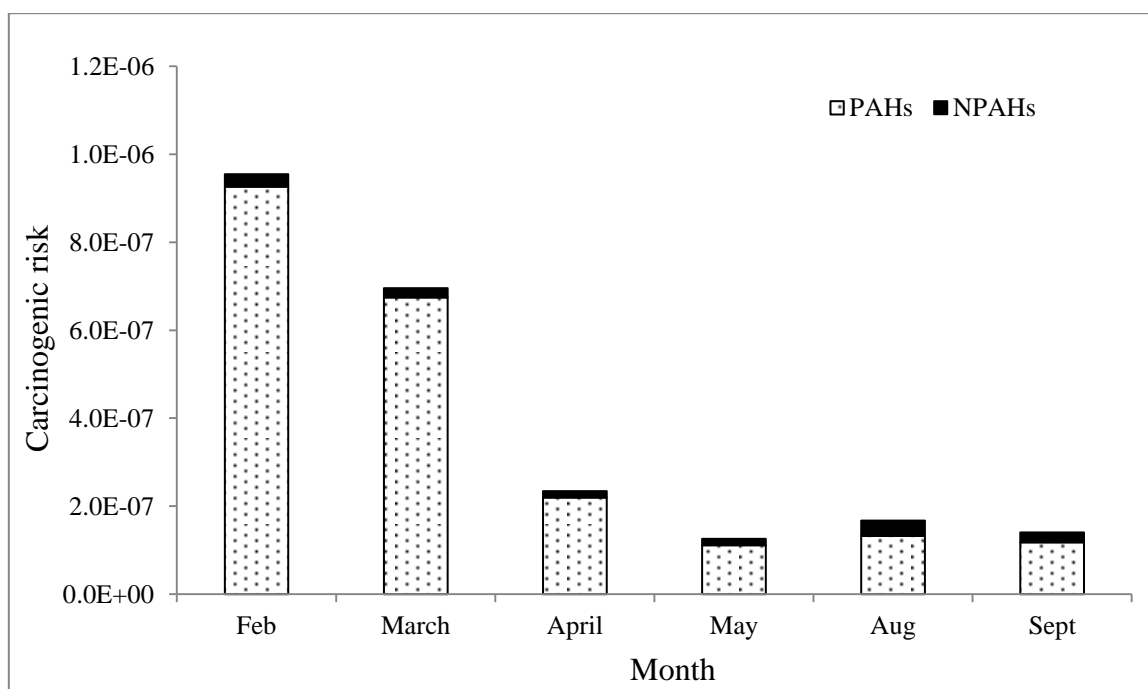
Although the atmospheric concentrations of NPAHs were lower than those of PAHs and the risks were calculated using only five NPAHs, the risk from NPAHs is 21% of the total risk in Aug. Since the direct-acting mutagenicity of individual NPAHs, especially secondary

NPAHs other than the five compounds, is not negligible (Murahashi *et al.*, 1999; Yang *et al.*, 2010), the risks would be higher than the presented values.

**Table 2.6.** PAH and NPAH toxic equivalent factors (TEFs).

Compounds	TEFs
PAHs	
BaA	0.1
Chr	0.01
BbF	0.1
BkF	0.1
BaP	1
DBA	1
BghiPe	0.01
IDP	0.1
NPAHs	
1-NP	0.1
4-NP	0.1
6-NC	10
1,6-DNP	10
1,8-DNP	0.1

Data from Albinet *et al.* (2008a).



**Fig. 2.11.** Total carcinogenic risk calculated from the atmospheric concentrations of eight PAHs and five NPAHs.

### 2.2.7.2. Mutagenicity

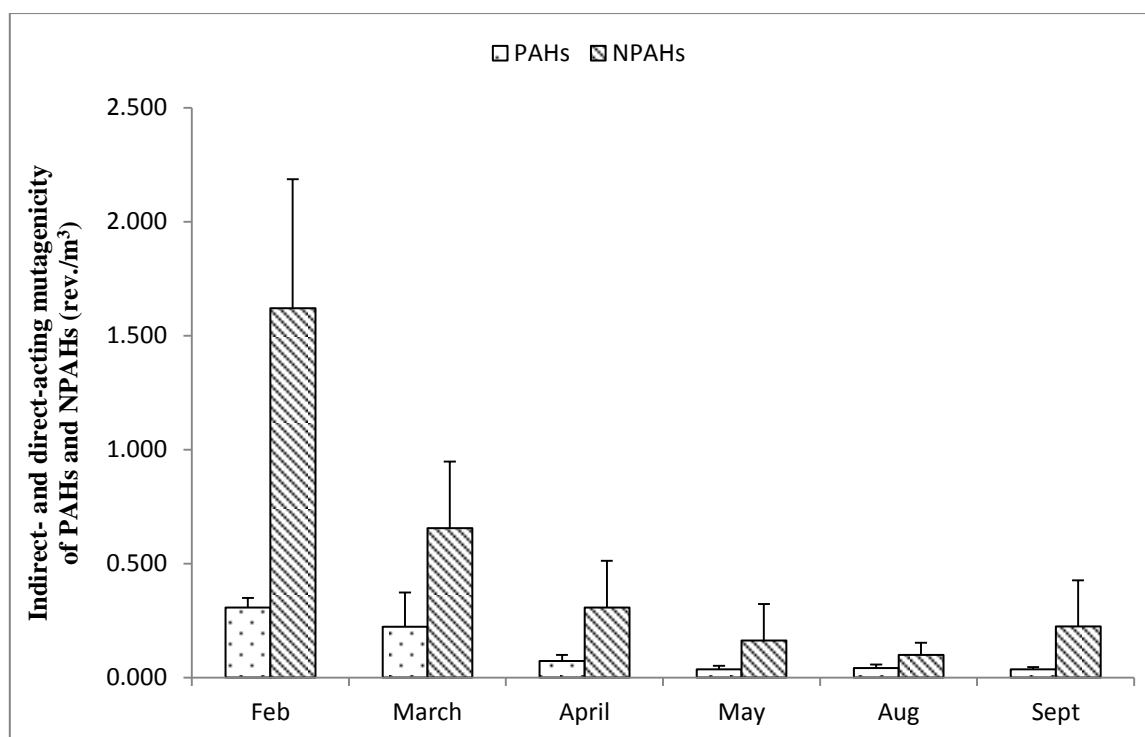
We calculate relative mutagenicity from the atmospheric concentrations using the indirect-acting mutagenicity of individual PAHs and the direct-acting mutagenicity of individual NPAHs in our previous papers (Yang *et al.*, 2010, Murahashi *et al.*, 1999) as shown in Table 2.7. Both indirect- and direct-acting of mutagenicity were higher in dry season than those in wet season (Fig. 2.12) that corresponded to carcinogenic risk. These results confirmed that ambient air in dry season was more harmful than in wet season.

**Table 2.7.** Indirect and direct-acting mutagenicity of PAHs and NPAHs.

Compounds	Mutagenicity
Indirect-acting mutagenicity of PAHs	(rev./nmol) <sup>a</sup>
Flu	10
Pyr	<1
BaA	10
Chr	<1
BbF	34
BkF	15
BaP	64
DBA	20
BghiPe	1
IDP	3
Direct-acting mutagenicity of NPAHs	(rev./pmol) <sup>a, b</sup>
1,3-DNP	48
1,6-DNP	7
1,8-DNP	116
9-NA	<0.1
1-NP	0.3
2-NP	3
4-NP	37
3-NFR	7
2-NTP	26
7-NBaA	<0.1
6-NC	<0.1
6-NBaP	<0.1
1-NPer	<0.1
3-NPer	<0.1
2-NFR <sup>b</sup>	0.57 <sup>b</sup>

<sup>a</sup>Data from Yang *et al.* (2010).

<sup>b</sup>Data from Murahashi *et al.* (1999).



**Fig. 2.12.** Monthly indirect-acting mutagenicity of PAHs and direct-acting mutagenicity of NPAHs calculated from the atmospheric concentrations of all PAHs and NPAHs.

Although the total NPAH concentration was one order of magnitude lower than the total PAHs each month, the direct-acting mutagenicity of NPAHs showed higher than the indirect-acting mutagenicity of PAHs. This suggests that NPAHs make up a significant portion of the overall mutagenicity of TSP in Chiang Mai. Therefore, the determination of NPAH levels in ambient air is important for health risk assessment.

The results suggest that it is important to control biomass burning to reduce air-pollution-related health risks during the dry season. The Thai government is encouraging the people to stop unnecessary burning, causing a forest fire and is asking for ASEAN countries' cooperation to control forest fires along border areas. Scientists should provide the results to the government for policy planning.



### 2.3. Conclusions

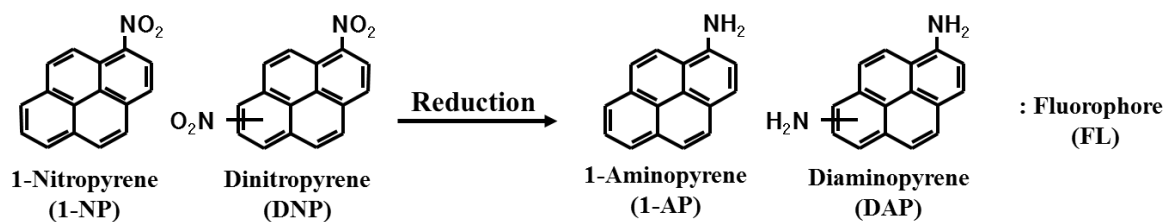
In recent years, high haze levels during the dry season have been affecting Northern Thailand. The high PM concentrations in the dry season are due to massive biomass burning, stable meteorological conditions, and the basin geomorphology of the region. In addition to PAHs, this study reports for the first time the NPAH levels and distribution profiles of ambient air in Chiang Mai. The most severe PAH and NPAH contaminations occur in the dry season, and biomass burning is the major source of PAHs and NPAHs. 9-NA is the most abundant NPAH in the dry season, suggesting strong contribution from biomass burning. We propose 9-NA as a marker of biomass burning and the [9-NA]–[1-NP] ratio as a suitable indicator for identifying the contribution of biomass burning. It is apparently important to control biomass burning to reduce air-pollution-related health risks during the dry season. These results should be useful in controlling and managing air pollution in Thailand.

## Appendix

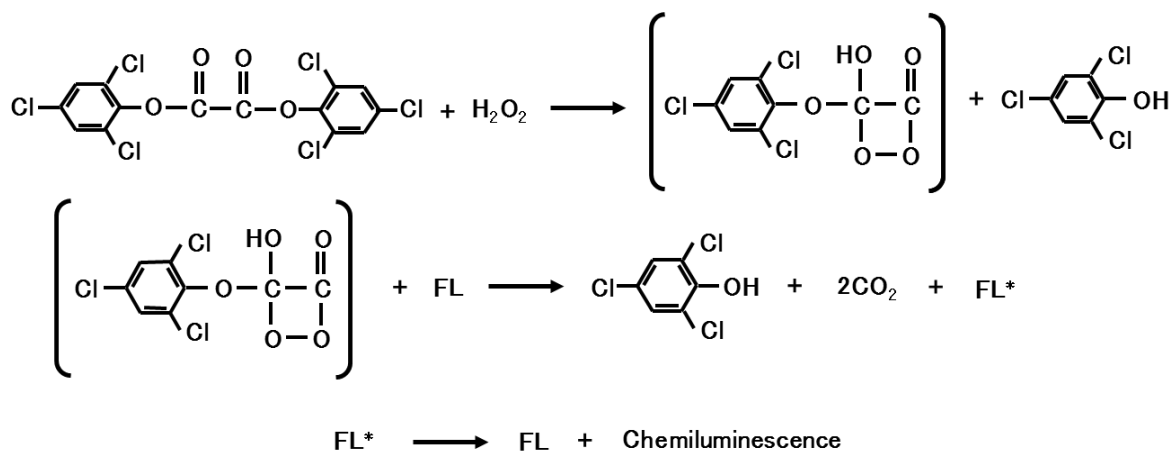
### Appendix A: PAHs and NPAHs analysis

In this study, PAHs were analyzed using HPLC with fluorescence (FL) detection. NPAHs do not have fluorescent properties. NPAHs were reduced to aminopolycyclic aromatic hydrocarbons (APAHs) (Fig. A) which are not only intensely fluorescent but also highly sensitive to peroxyoxalate-chemiluminescence method. Therefore, NPAHs were determined using HPLC with chemiluminescence (CL) detection (Hayakawa *et al.*, 2006). This detection approach is based on reaction between corresponding amino derivatives of NPAHs (fluorophore) with a mixture of bis(2,4,6-trichlorophenyl)oxalate (TCPO) and hydrogen peroxide, as shown in Fig. A. TCPO-H<sub>2</sub>O<sub>2</sub> chemiluminescence is the most sensitive HPLC detection technique in NPAHs analysis. The detection limits are typically 1-2 orders of magnitude lower than those which can be achieved in the same chromatographic system using fluorescence detection. Moreover, the high degree of selectivity allows the direct determination of NPAHs in complex matrices with minimum sample preparation. The high sensitivity of detection is due to a combination of high efficiencies in the excitation step and high chemiluminescence quantum yields. As no light source is used, a low background is obtained (Cvacka *et al.*, 1998).

## 1. Reduction



## 2. Chemiluminescence reaction



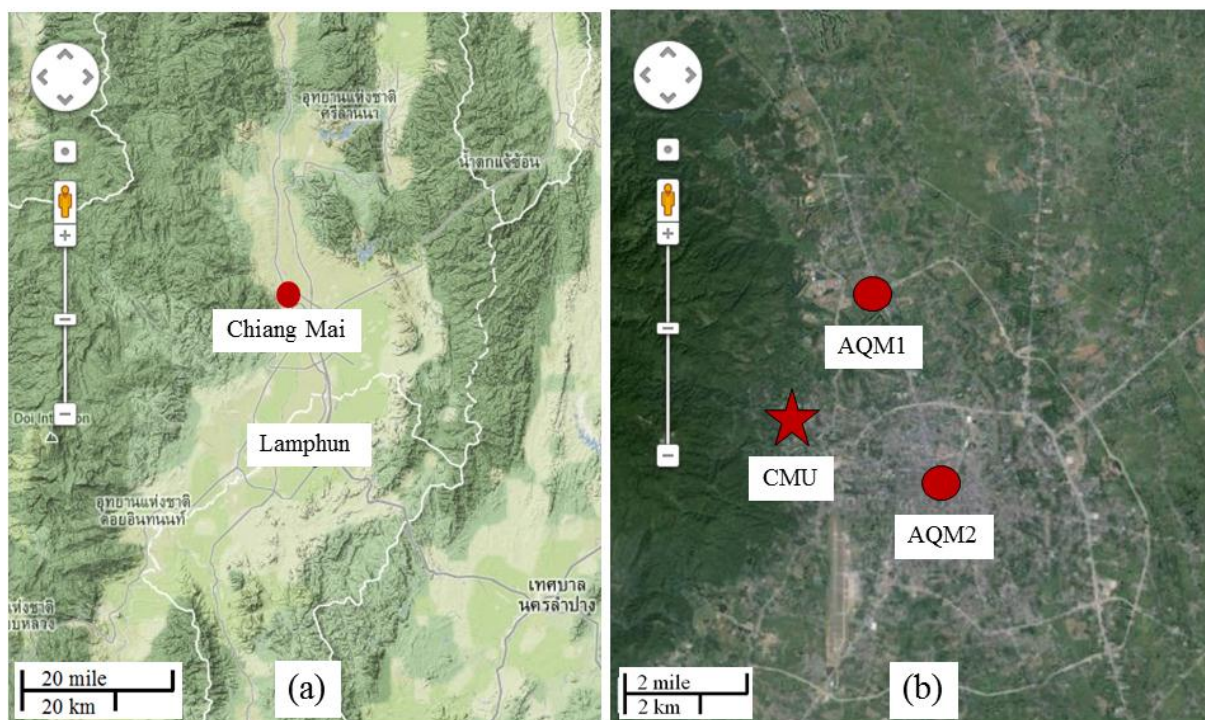
**Fig. A.** Reduction and Chemiluminescence reactions for NPAH analysis.

## **Appendix B: Levoglucosan analysis**

In this study, LG was analyzed by GC-MS after derivatization with a silylating agent. Silylation involves the replacement of an acidic hydrogen (or an active hydrogen) on the compound with an alkylsilyl group. Hence, silylation derivatization achieves compounds that are generally less polar, more volatile, and have increased thermal stability. TMS derivatizations typically require a base such as triethylamine or pyridine to catalyze the reaction.

## Appendix C: PM<sub>10</sub> monitoring at the Air Quality Monitoring (AQM) stations

Ambient PM<sub>10</sub> concentrations have been monitored at the Air Quality Monitoring (AQM) stations set up by the Pollution Control Department (PCD) of Thailand. There are two AQM stations in Chiang Mai which are located at Provincial Hall (suburban) and Yupparaj Wittayalai School (downtown). PM<sub>10</sub> were measured with the tapered element oscillating microbalance (TEOM) detector which utilizes an inertial mass weighing principle. Locations of our sampling site and two AQM sites by PCD were shown in Fig. C. Monthly average PM<sub>10</sub> and average PM<sub>10</sub> during the 7-day sampling period were shown in Table C.



**Fig. C.** Locations of (a) Chiang Mai-Lamphun basin and (b) sampling site (CMU) and the Air Quality Monitoring (AQM) sites (AQM1 : suburban; AQM2 : downtown) by PCD.

**Table C.** Comparison between monthly PM<sub>10</sub> and average PM<sub>10</sub> during the 7-day sampling period in 2010 by PCD.

Month	Average PM <sub>10</sub> concentration (µg/m <sup>3</sup> )			
	Provincial Hall		Yupparaj Wittayalai School	
	Monthly <sup>a</sup>	The 7-day period <sup>b</sup>	Monthly <sup>a</sup>	The 7-day period <sup>b</sup>
Feb	67.4	91.4	77.6	102.3
March	111.6	101.1	120.2	111.1
April	102.0	62.2	106.6	66.6
May	35.4	19.6	40.8	25.8
Aug	17.7	16.6	23.1	23.6
Sept	18.7	18.6	23.6	22.5

<sup>a</sup> Monthly PM<sub>10</sub> indicates average PM<sub>10</sub> concentration in each month.

<sup>b</sup> The 7-day sampling period indicates average PM<sub>10</sub> concentration during the period corresponding to our sampling day (Feb 24–March 2, March 24–30, April 24–30, May 17–23, Aug 21–27 and Sept 8–14).

## Appendix D: Total PAHs concentration in Chiang Mai and other cities in Southeast Asia

**Table D.** Comparison of total PAHs concentration between Chiang Mai and other cities in Southeast Asia.

City/Country	Location	Total concentration (ng/m <sup>3</sup> )	Reference
Chiang Mai, Thailand	Suburban area	0.60 – 4.14	This study
Bangkok, Thailand	Roadside	10.1 – 28.2	Boonyatumanond <i>et al.</i> (2007)
Ho Chi Minh City, Vietnam	Urban area	7.6 – 8.7	Hein <i>et al.</i> (2007)
	Roadside	19.0	
Hanoi, Vietnam	Roadside (site I)	1.9 – 15.8	Pham <i>et al.</i> (2012)
	Roadside (site T)	6.1 – 10.6	

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