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

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ABSTRACT

Chiang Mai and several other provinces in northern Thailand have been annually facing air pollution problems during the dry season. Ten polycyclic aromatic hydrocarbons (PAHs); 19 nitropolycyclic aromatic hydrocarbons (NPAHs); and levoglucosan (LG), a marker for biomass burning, were quantified in total suspended particulates (TSP) collected in Chiang Mai during the dry, transition, and wet seasons in 2010. The concentrations of PAHs and NPAHs in the dry season were significantly higher than 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. 9-Nitroanthracene (9-NA) was the most abundant NPAH which suggests that 9-NA is generated from biomass burning. We proposed the [9-NA] – [1-nitropyrene (1-NP)] ratio as a new indicator for assessing the contribution of biomass burning. Biomass burning was a major source of PAHs and NPAHs in the dry season, whereas vehicle exhaust was the main contribution 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.

Keywords: Polycyclic aromatic hydrocarbons; Nitropolycyclic aromatic hydrocarbons; Biomass burning; Levoglucosan; Southeast Asia.

INTRODUCTION

The increase in fossil fuel consumption, along with the rapid development of industrial and financial activities in Southeast Asia, has caused serious air pollution problems in cities such as Bangkok, Hanoi, Kuala Lumpur, and Singapore (He *et al.*, 2010). In addition, biomass burning (agricultural burning and forest fires) in Southeast Asia produces high levels of haze, especially in the dry season (Reid *et al.*, 2013). Northern Thailand faces haze-related health threats from February to April every year (Chantara, 2012). In addition, the highest incidence of lung cancer has been recognized in this region of Thailand (Wiwatanadate, 2011). 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 km². During, massive biomass burning, the geographical and meteorological conditions contribute to the high levels of airborne particulate matter (PM) in the air of Chiang Mai. In the city, the PM_{10} concentration increases at the beginning of the dry season (December), peaks in March, and decreases by the end of April (Pengchai *et al.*, 2009). The most severe PM_{10} pollution was observed in March 2007, with the highest concentration of 383 µg/m³ on March 14, exceeding the 24 h average standard level in Thailand (120 µg/m³) (Chantara, 2012). 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).

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

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because of their toxicity (carcinogenicity or mutagenicity) to humans (Ames *et al.*, 1975). The International Agency for Research on Cancer (IARC) has classified benzo[*a*]pyrene (BaP) in Group 1 (carcinogenic to humans) and 1-nitropyrene (1-NP) in Group 2A (probably carcinogenic to humans) (IARC, 2013). PAHs and NPAHs are ubiquitous environmental pollutants and form by the incomplete combustion of fossil fuel; wood; and other organic materials including vehicle exhaust, domestic heating, and industrial processes. Furthermore, several NPAHs form in the atmosphere via reactions of their parent PAHs with OH or NO_3 radicals (Arey *et al.*, 1986; Atkinson and Arey, 1994).

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 *et al.*, 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). 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.

Biomass burning is the largest source of primary PM (Yokelson *et al.*, 2011), and forest fires are the major type of biomass burning in Southeast Asia (Chang and Song, 2010). However, the contribution of biomass burning to PAHs and especially NPAHs remains unclear. This study reports atmospheric levels and profiles of PAHs and NPAHs in Chiang Mai, Thailand, and discusses the possible emission sources and health risks. We used levoglucosan (1,6-Anhydro-β-D-glucose, LG), a marker of biomass burning, to support the estimation of the source of PAHs and NPAHs. The results are expected to facilitate air pollution management in northern Thailand.

METHODS

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. S1). 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. 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°C for six months until analyzed.

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_{12} and BaP-d_{12}), 6-nitrochrysene-d_{11} (6-NC-d_{11}), and LG-$^{13}C_6$ 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.

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-$^{13}C_6$) 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 μL 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 μL of ethanol, and the solution was then filtered through a membrane filter (HLC-DISK 3 with pore size of 0.45 μm, Kanto Chemical Co., Inc., Tokyo, Japan). A 20 μL and 100 μL aliquot of the filtered solution was subjected to HPLC for detecting PAHs and NPAHs, respectively. We analyzed three travel

blank filters and the detected analytes were less than their limits of detection.

Analysis

The 19 NPAHs were analyzed using HPLC with chemiluminescence (CL) detection according to the procedure described in a previous study with some modifications (Tang *et al.*, 2005). The 10 PAHs were determined using HPLC with fluorescence detection (HPLC-FL) without modification (Toriba *et al.*, 2003). LG was analyzed by using GC-MS (Hsu *et al.*, 2007). The detailed information about the analytical methods is described in the Supplementary information.

RESULTS AND DISCUSSION

Ambient Concentrations of TSP

Meteorological conditions during the sampling period (7 days/month) and the concentrations of the collected TSP are shown in Table 1. 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_{10} at downtown (r = 0.900, p < 0.01) and suburban (r = 0.888, p < 0.01) sites from the Pollution Control Department (PCD), Ministry of Natural Resources and Environment, Thailand (Fig. S1). The PM_{10} concentrations during the 7-day sampling period at the PCD monitoring sites showed similar transition of the concentrations to their monthly PM_{10} data (Table S1). 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. S1) (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 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). 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.

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. As shown in Fig. 1, 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 S2). 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.

The proportion of each PAH to the total PAH concentrations was calculated monthly to show the seasonal variations in the PAH profiles (Fig. 2(a)). 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(a), the increase

Table 1. Meteorological parameters, and concentrations of collected PM and forest fires.

	Meteorological conditions[a, b]					TSP[a]	Forest fire[c]	
	Temperature (°C)	Pressure (hPa)	Relative humidity (%)	Wind speed (km/h)	Precipitation (mm)	(µg/m³)	Frequency (time)	Burned area (km²)
February	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
August	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[d]	No data
September	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

[a] All meteorological and TSP data represent mean ± SD during the sampling period (7 days/month).
[b] Data from the Northern Meteorological Center; http://www.cmmet.tmd.go.th/index1.php.
[c] Monthly forest fires in Chiang Mai and Lamphun in 2010: Data from the Protected Area Regional Office 16, National Park, Wildlife and Plant Conservation Department, Thailand. http://www.fca16.com/upload/files/forestfire/09022556.pdf.
[d] It means almost 0.

Table 2. Concentrations (mean ± SD) of LG, PAHs, and NPAHs in the dry, transition, and wet seasons.

Compound	Dry season			Transition	Wet season	
	February (*n* = 7)	March (*n* = 7)	April (*n* = 7)	May (*n* = 7)	August (*n* = 7)	September (*n* = 7)
LG (ng/m³)	**370.8 ± 122.4**	**313.9 ± 98.5**	**90.3 ± 29.7**	**23.2 ± 10.1**	**36.2 ± 13.8**	**20.0 ± 7.0**
PAHs (ng/m³)						
Flu	0.24 ± 0.05	0.20 ± 0.11	0.07 ± 0.03	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
Pyr	0.31 ± 0.05	0.27 ± 0.13	0.12 ± 0.06	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
BaA	0.14 ± 0.01	0.12 ± 0.06	0.05 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.00
Chr	0.35 ± 0.06	0.29 ± 0.17	0.10 ± 0.05	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
BbF	0.71 ± 0.12	0.50 ± 0.35	0.15 ± 0.06	0.08 ± 0.04	0.09 ± 0.03	0.08 ± 0.02
BkF	0.37 ± 0.06	0.25 ± 0.16	0.08 ± 0.03	0.04 ± 0.02	0.05 ± 0.02	0.05 ± 0.01
BaP	0.61 ± 0.08	0.45 ± 0.33	0.14 ± 0.05	0.07 ± 0.03	0.08 ± 0.04	0.07 ± 0.02
DBA	0.03 ± 0.01	0.03 ± 0.02	0.01 ± 0.00	< LOQ	< LOQ	< LOQ
BghiPe	0.65 ± 0.12	0.57 ± 0.25	0.25 ± 0.10	0.17 ± 0.08	0.20 ± 0.08	0.23 ± 0.08
IDP	0.71 ± 0.14	0.47 ± 0.29	0.17 ± 0.07	0.10 ± 0.05	0.16 ± 0.07	0.17 ± 0.07
Total PAHs	**4.14 ± 0.57**	**3.13 ± 1.83**	**1.15 ± 0.45**	**0.60 ± 0.25**	**0.70 ± 0.25**	**0.70 ± 0.20**
NPAHs (pg/m³)						
1,3-DNP	0.037 ± 0.011	0.015 ± 0.013	0.008 ± 0.004	0.009 ± 0.006	0.022 ± 0.013	0.015 ± 0.008
1,6-DNP	0.109 ± 0.045	0.067 ± 0.042	0.042 ± 0.026	0.062 ± 0.038	0.047 ± 0.038	0.058 ± 0.023
1,8-DNP	0.121 ± 0.037	0.030 ± 0.028	0.021 ± 0.006	0.046 ± 0.022	0.088 ± 0.037	0.042 ± 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 ± 92.2	92.0 ± 65.0	23.7 ± 15.2	9.4 ± 10.3	6.6 ± 3.3	9.3 ± 9.3
2-NFR	164.1 ± 63.5	59.4 ± 38.5	29.2 ± 19.1	14.1 ± 8.3	7.6 ± 5.6	9.7 ± 7.7
2-NP	62.5 ± 25.7	20.8 ± 12.8	7.1 ± 5.5	6.2 ± 8.1	2.7 ± 1.8	10.6 ± 10.8
4-NP	1.7 ± 0.6	0.9 ± 0.5	0.5 ± 0.4	0.1 ± 0.1	< LOQ	0.2 ± 0.2
3-NFR	1.2 ± 0.7	2.4 ± 0.8	1.6 ± 1.1	0.2 ± 0.2	0.1 ± 0.0	0.6 ± 0.7
1-NP	10.0 ± 2.7	4.2 ± 1.4	3.3 ± 1.7	2.6 ± 1.4	2.4 ± 0.8	4.7 ± 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 ± 1.1	1.8 ± 0.8	1.3 ± 0.3	1.2 ± 0.5	3.1 ± 1.5	1.9 ± 1.2
7-NBaA	28.9 ± 24.3	8.7 ± 5.6	4.4 ± 4.6	2.5 ± 3.4	1.3 ± 0.5	2.6 ± 3.6
3-NPer	1.2 ± 0.7	0.9 ± 0.6	0.3 ± 0.1	0.2 ± 0.2	0.2 ± 0.1	0.3 ± 0.1
6-NBaP	2.0 ± 1.6	0.9 ± 0.7	0.4 ± 0.1	0.4 ± 0.4	0.5 ± 0.2	0.6 ± 0.2
1-NPer	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Total NPAHs	**523.5 ± 197.4**	**192.0 ± 122.9**	**71.6 ± 46.8**	**36.9 ± 30.4**	**24.7 ± 12.3**	**40.6 ± 33.7**

< 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.

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 *et al.*, 2009), Vietnam (Hien *et al.*, 2007; 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. 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, Fig. 1). 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(b). 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;
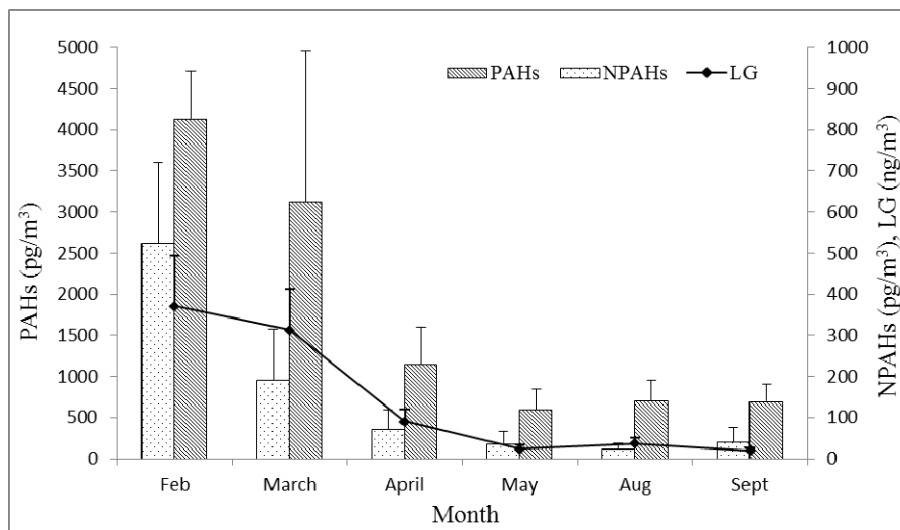
Fig. 1. Monthly concentrations (mean ± SD) of PAHs, NPAHs, and LG. Each bar represents the mean concentrations of the total PAHs or NPAHs; [PAHs] = [Flu] + [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [DBA] + [BghiPe] + [IDP], [NPAHs] = [1,3-DNP] + [1,6-DNP] + [1,8-DNP] + [9-NA] + [2-NFR] + [2-NP] + [4-NP] + [3-NFR] + [1-NP] + [6-NC] + [7-NBaA] + [3-NPer] + [6-NBaP]. The line plot connects the mean concentrations of LG.
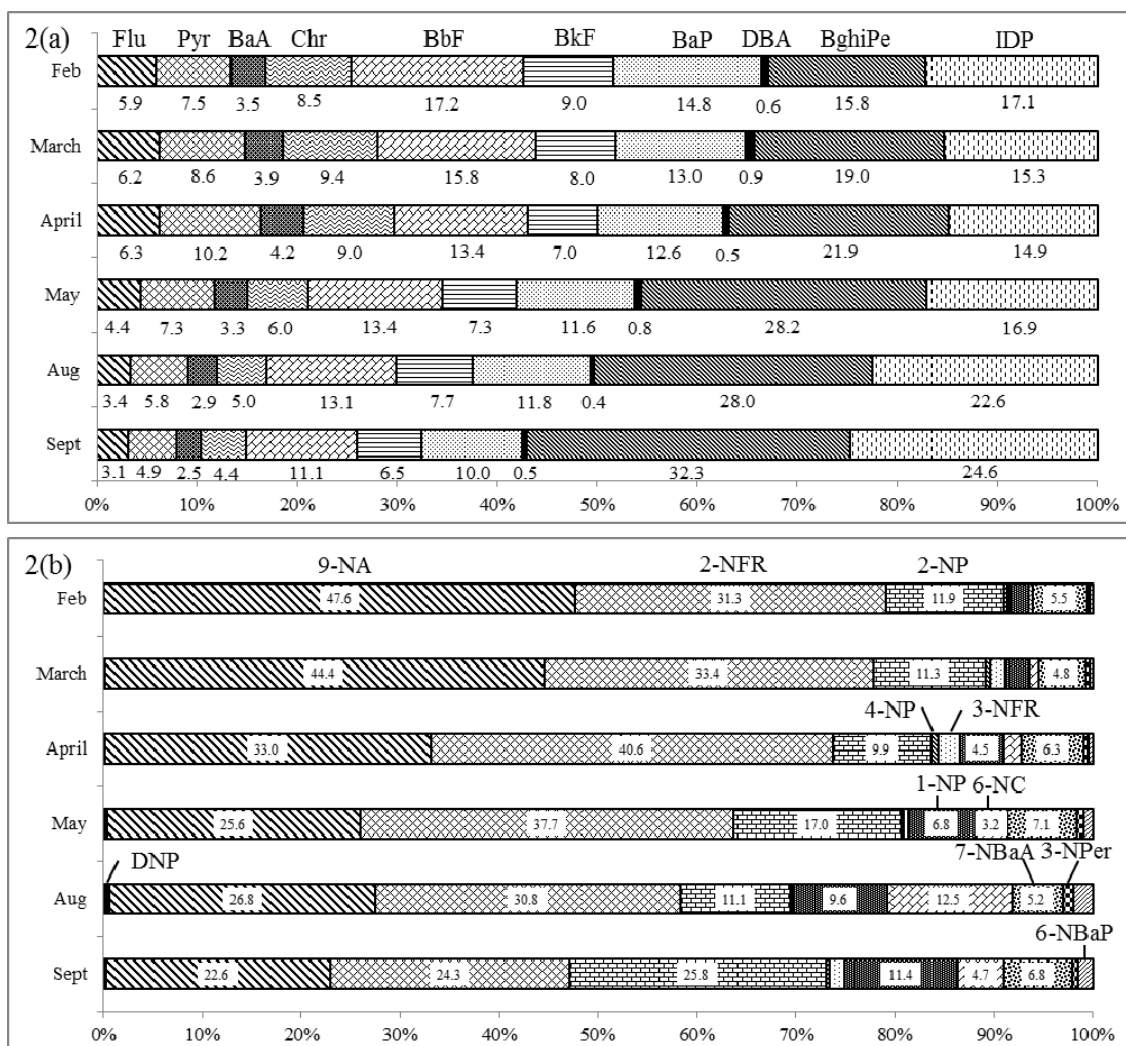
Fig. 2. Monthly composition profiles of 2(a) PAHs and 2(b) NPAHs. The numbers under the bars or in the bars denote the percentage of each compound in the total concentration.
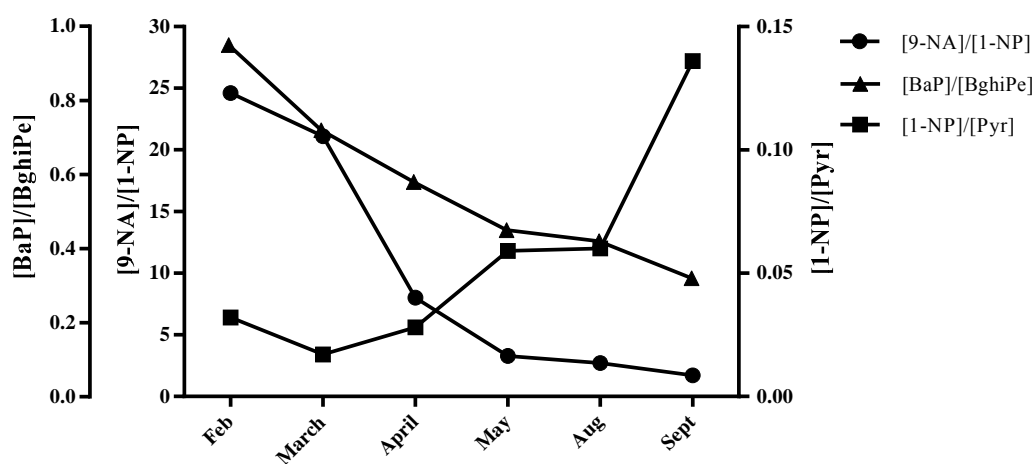
Fig. 3. Monthly diagnostic ratios of [9-NA]/[1-NP], [1-NP]/[Pyr], and [BaP]/[BghiPe].

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 ± 2.8 pg/m^3) is remarkably lower than that in urban Hanoi, which also has high traffic density (43.3–120.7 pg/m^3, 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(b)), suggesting that the contribution of vehicle exhaust increased in the wet season.

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 and Fig. 2(b)). 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). The combustion temperature in wood stoves (500–600°C) is much lower than in diesel engines (2700–3000°C). Anthracene (Ant) 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). 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.

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). LG is the major pyrolysis product of cellulose and hemicelluloses; is emitted in large quantities; is stable in the atmosphere; and is specific to the thermal breakdown of cellulose. To discuss the major sources of PAHs and NPAHs, the correlation coefficients of PAHs and NPAHs with LG in the dry and wet seasons were calculated, and are shown in Table 3. The strong correlation of PAHs and NPAHs with LG in the dry season and the poor correlation in the wet season suggest that biomass burning is the major contributor of PAHs and

Table 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
ΣPAHs	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
ΣNPAHs	0.829**	0.084

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

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 (data not shown). 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.

***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. 3, 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. 3). 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_{10} samples collected during the haze episode ranged from 200–600 ng/m^3 (Fraser and Lakshmanan, 2000). In this study, the LG levels in Feb and March exceeded 200 ng/m^3 (Fig. 1 and Table 2). Although forest fires were still observed in April (Table 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.

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_2 during daytime. OH radicals form via the photolysis of O_3 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_3 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), and were abundant in all seasons, accounting for ca. 50% of the total NPAH concentrations each month (Fig. 2(b)). 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). The 2-NFR–2-NP ratio has been used to evaluate the formation of NPAHs by daytime OH- or nighttime NO_3-initiated reactions (Zielinska *et al.*, 1989). A ratio less than 10 indicates the dominance of daytime OH radical reactions.
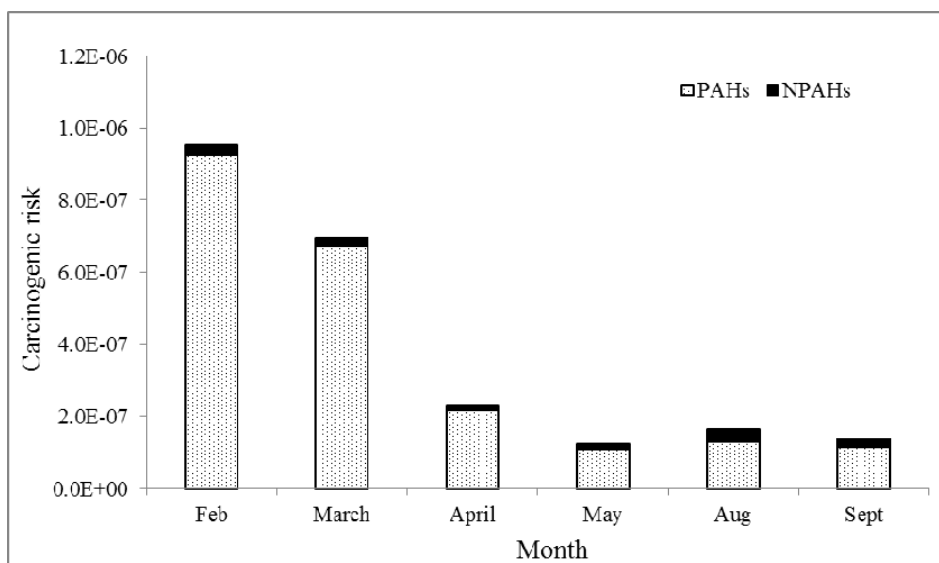
Fig. 4. Total carcinogenic risk calculated from the atmospheric concentrations of eight PAHs and five NPAHs.

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.

Carcinogenic Risk

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

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

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. The TEFs of PAHs and NPAHs were normalized to BaP, which was used as reference compound. UR_{BaP} is the inhalation cancer unit risk factor of BaP ($1.1 \times 10^{-6}\ (\text{ng/m}^3)^{-1}$). The carcinogenic risk calculated using eight PAHs and five NPAHs is shown in Fig. 4. 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.*, 2008), 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. Therefore, the determination of NPAHs levels in ambient air is important for assessing health risks. 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.

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 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.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Supplementary Materials

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

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There are 7 pages, with 2 tables and 1 figure.

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 πNAP, 50 mm × 4.6 mm i.d. 5μm, Nacalai Tesque, Kyoto, Japan) with its guard column (10 mm × 4.6 mm i.d.), and were then reduced to their amino derivatives by using a reduction column (NPpak-RS, 10 mm × 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 × 4.6 mm i.d. 5 μm, Perkin Elmer, MA, USA) by using a switching valve. The concentrated fraction was applied to two separation columns (Cosmosil $5C_{18}$-MS-II, 150 mm × 3.0 mm i.d. 5 μm and Cosmosil $5C_{18}$-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.

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 naphtylethyl 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_{18}-MS-II) and a polymeric ODS column (Cosmosil 5C_{18}-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.

PAH 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). PAHs were separated by using a guard column (Inertsil ODS-P, 10 × 4.0 mm i.d., 5 μm, GL Sciences, Tokyo, Japan) and an analytical column (Inertsil ODS-P, 250 × 4.6 mm i.d., 5 μm, GL Sciences) with acetonitrile/water gradient and fluorescence detection.

LG Analysis

LG analysis was carried out according to a reported method with minor modifications (Hsu *et al.*, 2007). An adequate volume (10 µL) of the ethanol extract was evaporated to dryness, and then the residue was derivatized by adding 10 µL of pyridine, 10 µL of 1,4-dithioerythritol (5 mM), 20 µL of silylating agents and 50 µL of toluene. The reaction mixture was heated at $80^{\circ}C$ for 60 min. After cooling, 10 µL of 1-phenyldodecane (0.1 mM) as a syringe spike was added to the derivatized solution. 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.

PM$_{10}$ Monitoring at the Air Quality Monitoring (AQM) Stations

Ambient PM$_{10}$ 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_{10} 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. S1. Monthly average PM_{10} and average PM_{10} during the 7-day sampling period were shown in Table S1.
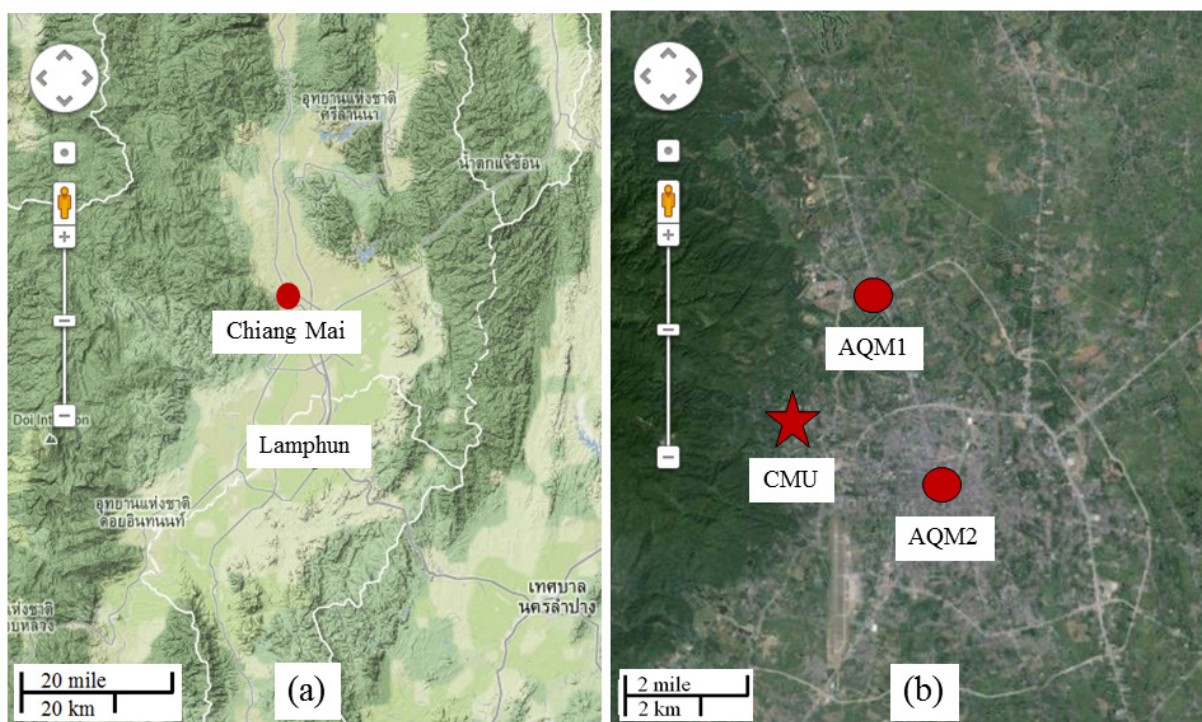
Fig. S1. Locations of (a) Chiang Mai-Lamphun basin and (b) the sampling site at Chiang Mai University (CMU) and the Air Quality Monitoring (AQM) sites (AQM1: suburban; AQM2: downtown) by PCD.

Table S1. Comparison between monthly PM_{10} and average PM_{10} during the 7-day sampling period in 2010 by PCD.

| Month | Average PM_{10} concentration (µg/m^3) | | | |
| | Provincial Hall | | Yupparaj Wittayalai School | |
	Monthly[a]	The 7-day period[b]	Monthly[a]	The 7-day period[b]
February	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
August	17.7	16.6	23.1	23.6
September	18.7	18.6	23.6	22.5

[a] Monthly PM_{10} indicates average PM_{10} concentration in each month.

[b] The 7-day sampling period indicates average PM_{10} concentrations during the period corresponding to our sampling days (Feb 24–March 2, March 24–30, April 24–30, May 17–23, Aug 21–27 and Sept 8–14).

Table S2. Comparison of total PAHs concentration between Chiang Mai and other cities in Southeast Asia.

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