

RESEARCH ARTICLE

Diurnal Variation, Vertical Distribution and Source Apportionment of Carcinogenic Polycyclic Aromatic Hydrocarbons (PAHs) in Chiang-Mai, Thailand

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Abstract

Diurnal variation of particulate polycyclic aromatic hydrocarbons (PAHs) was investigated by collecting PM₁₀ at three different sampling altitudes using high buildings in the city center of Chiang-Mai, Thailand, during the relatively cold period in late February 2008. At site-1 (12 m above ground level), B[a]P concentrations ranged from 30.3 -1,673 pg m⁻³ with an average of 506±477 pg m⁻³, contributing on average, 8.09±8.69% to ΣPAHs. Ind and B[b]F concentrations varied from 54.6 to 4,579 pg m⁻³ and from 80.7 to 2,292 pg m⁻³ with the highest average of 1,187±1,058 pg m⁻³ and 963±656 pg m⁻³, contributing on average, 19.0±19.3% and 15.4±12.0% to ΣPAHs, respectively. Morning maxima were predominantly detected in all observatory sites, which can be described by typical diurnal variations of traffic flow in Chiang-Mai City, showing a morning peak between 6 AM. and 9 AM. Despite the fact that most monitoring sites might be subjected to specific-site impacts, it could be seen that PAH profiles in Site-1 and Site-2 were astonishingly homogeneous. The lack of differences suggests that the source signatures of several PAHs become less distinct possibly due to the impacts of traffic and cooking emissions from ground level.

Keywords: Diurnal variation - vertical distribution - PAHs - agricultural-waste burning - Chiang-Mai

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Introduction

Several attempts have been made to obtain information related to the fate of particulate polycyclic aromatic hydrocarbons (PAHs) in atmospheric environment from different countries (Tsapakis et al., 2005; Hong et al., 2007; Tasdemir and Esen, 2007; Tham et al., 2008; Zhang and Tao, 2008; Lee et al., 2011; Hanedar et al., 2011; Tan et al., 2011; Choi et al., 2012; Hu et al., 2012). PAHs are classified as a group of persistent organic pollutants (POPs), typically contain two to eight aromatic rings, generated by imperfect combustions or high-pressure processes when organic materials are exposed to high temperatures or pressures. PAHs can be released by both anthropogenic (e.g. traffic emissions, domestic heating, industrial activities) and natural emission sources (e.g. agricultural waste and biomass burnings, forest fires) (Li et al., 1999; Okuda et al., 2002; Yang et al., 2002; Rajput et al., 2011; Riva et al., 2011; Slezakova et al., 2011; Lu et al., 2012). Numerous interests have been focusing over its negative impacts on human health associated with cancer, endocrine disruption, reproductive and developmental effects in the past decades (Hoyer, 2001; Matsui, 2008; Liao et al., 2011; Wickramasinghe et al., 2012). It is also

well known that PAHs play a major role in causing lung cancers (Okona-Mensah et al., 2005; Liao et al., 2011; Xia et al., 2013).

Currently, there are some trends in that more studies are highlighting the behaviour of particulate PAHs in tropical countries (Mayol-Bracero et al., 2001; Bourotte et al., 2005; Boonyatumanond et al., 2007; He and Balasubramanian, 2009; Vasconcellos et al., 2010). In spite of copious studies related to the determination of PAH compositions in coarse and fine particles around the world, there is inadequate information considering the characterization of particulate PAHs in tropical atmosphere. Most examinations have been focused on empirical estimations of source apportionment of PAHs using factor analysis' technique with data from ground-based measurement (Wan et al., 2006; Gupta et al., 2011; Dvorská et al., 2012; Hu et al., 2012). Unfortunately, there are only limited studies observing the fate of particulate PAHs in Thailand (Chetwittayachan et al., 2002; Ruchirawat et al., 2002; 2005; 2007; Boonyatumanond et al., 2007; Pongpiachan et al., 2009). Above all, there are no international publications associated with both diurnal and vertical distribution of PAHs in the atmospheric environment of Thailand.

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Many studies have mentioned the deterioration of air quality level triggered by agricultural-waste and biomass burnings in the northern part of Thailand over the past few years (Oanh et al., 2011; Wiwatanadate and Liwsrisakun, 2011; Li et al., 2012). For example, the significant enhancement in the number of patients continually feeling distressed with respiratory disease was detected to increase 20% in 2007 as compared to the identical period in 2006 (Pengchai et al., 2009). Unintentional biomass burnings, agricultural-waste burnings and forest fires, including trans boundary haze pollution from neighboring countries appears to responsible for the heightening of PM₁₀ level and thus the increasing number of patients admitted to hospital during the haze episode. Apart from smoking, the environmental and occupational factors might have played a significant role on lung cancer in Chiang-Mai province (Wiwatanadate, 2011). For instance, in the year 2007, the age-standardized incidence rate in males was 31.3 and that in female was 22.9 per 100,000 population (Wiwatanadate, 2011). These findings are consistent with the results of relatively high monohydroxy polycyclic aromatic hydrocarbons (OHPAHs) found in urine samples from non-smoking taxi drivers, traffic policemen and rural villagers of Chiang Mai, Thailand (Chetianukornkul et al., 2006).

Although meteorological factors can dramatically influence the fate of particulate PAHs, there has been no study examining both diurnal variations and vertical distributions of particulate PAH contents in different altitudes of urban atmosphere in a northern city of Thailand. Overall, the major objectives of this study are to i) examine the diurnal variation of PAH contents in PM₁₀ at three different heights and ii) conduct the source apportionment of PAHs at different atmospheric layers by using principal component analysis (PCA). PM₁₀ samples were collected every three hours for three days at three different levels (i.e. site-1: 12 m; site-2: 52 m; site-3: 152 m above the ground level) at the Imperial Mae Ping Hotel (site-2) and Centara Duangtawan Hotel (site-1 and site-3) from February 25th-28th, 2008.

Materials and Methods

Description of observatory stations

Two observatory stations, namely Centara Duangtawan Hotel (18°47'03.46"N 98°59'56.72"E) and Imperial Mae Ping Hotel (18°46'59.03"N 98°59'53.29"E), are situated in the most densely populated area in Chiang-Mai City, which is highly reputed among foreign visitors as tourism hotspots called "Night Bazaar". Three different sampling stations were cautiously chosen due to their heights. Site-1 and site-3 were located at Centara Duangtawan Hotel at 12 m and 152 m above ground level respectively, whilst site-2 was situated at Imperial Mae Ping Hotel at 52 m above the building basement. Figure 1 shows the map of sampling sites area. The street map of Night Bazaar is shown in the left panel of Figure 1 with the Ping river and Khlong Mae Sa canal shown as blue. The monitoring stations are situated ~640 m away from the Ping River in the west and ~3.65 km from the Chiang-Mai International Airport in the east.

Chiang-Mai is the largest and most culturally significant city in northern Thailand. The city of Chiang-Mai consists of a total population of approximately 160,000. The observatory site is roughly 2.85 km away from a heavy traffic highway No.11 in the west and ~1 km away from the city center in the southeast. Apart from the traffic, there are no major industrial and agricultural-waste burning activities for several kilometers around the observatory site and thus the PAH contents are more representative of the urban background. An intensive sampling campaign was conducted at all observatory sites instantaneously from February 25th (Monday) to 28th (Thursday) 2008 in the relatively cold period. PM₁₀ samples were collected every three hours consecutively from 2100 h February 25th to 2100 h February 28th by using Andersen High Volume Air Sampler PM₁₀ TE6001 with the flow rate of 1.132 m³ min⁻¹. Further detailed information of the PM₁₀ sampling method was given in "Compendium Method IO-2.2. Sampling of Ambient Air for PM₁₀ Using an Andersen Dichotomous Sampler".

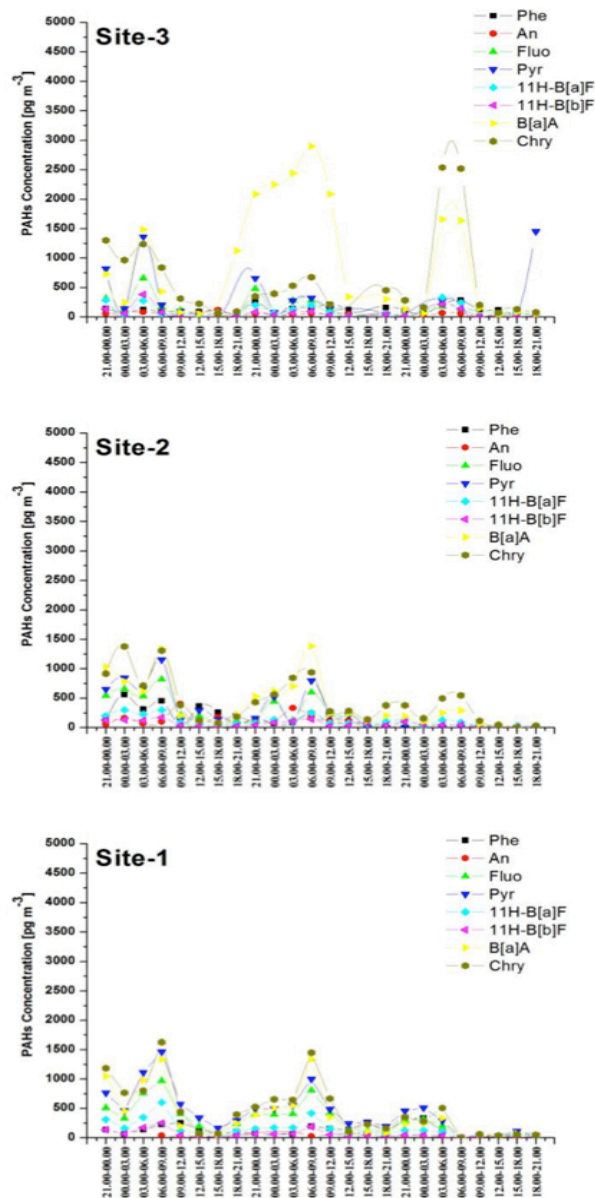


Figure 1. Diurnal Variation of Three-to-Four Ring PAHs in Chiang-Mai from 25/02/08-28/02/08

Filter sample collection and meteorological data

Local meteorological parameters such as barometric pressure, temperature, humidity, rainfall, wind speed and direction, UV/solar radiation were measured at 1 min intervals using instruments and cabled weather station with a versatile sensor suite, Davis Vantage Pro2. The wind and other meteorological parameter sensors were installed at ~1.5 m from the ground level from each observatory site. PM₁₀ samples were collected on 47 mm Whatman quartz microfibre filters (QM/A) for the analysis of PAHs and water-soluble ionic species. The QM/A were pre-heated to 800°C for 3 h prior to use to avoid any potential contamination. The weight of PM₁₀ samples was obtained by subtracting the initial weight of QM/A by using electronic microbalance Mettler Toledo AB204-S (Columbus (Ohio), USA). The vertical atmospheric temperature, pressure, relative humidity and wind speed profiles were monitored every six hours by using weather balloon coupled with radiosonde and carefully analyzed by research staff from the Meteorological Department of Thailand.

Polycyclic aromatic hydrocarbons (PAHs)

All organic solvents (i.e. DCM and Hexane) are HPLC grade, purchased from Fisher Scientific. A cocktail of 15 PAHs Norwegian Standard (NS 9815: S-4008-100-T) (phenanthrene (Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), 11h-benzo[a]fluorene (11H-B[a]F), 11h-benzo[b]fluorene (11H-B[b]F), benz[a]anthracene (B[a]A), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (D[a,h]A), benzo[g,h,i]perylene (B[g,h,i]P); each 100 µg mL⁻¹ in toluene: unit: 1×1 mL) and a mix of recovery Internal Standard PAHs (d₁₂-perylene (d₁₂-Per), d₁₀-fluorene (d₁₀-Fl); each 100 µg mL⁻¹ in xylene: unit: 1×1 mL) were supplied by Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). Standard stock solutions of 4 µg mL⁻¹ of deuterated PAHs (used as internal standard) and 100 µg mL⁻¹ of native PAHs were prepared in nonane. Working solutions were obtained by appropriate dilution in n-cyclohexane. All solutions were stored in amber colored vials at -20°C. Silica gel (0.040-0.063 mm), purchased from Merck. All materials used (silica gel, glass and cotton wool etc.) were Soxhlet extracted with DCM for 24 h, and kept dry (in desiccator) until use. All glassware was cleaned by washing with decanted water before drying at 55°C, and rinsed with DCM just before use. The fractionation/cleanup and blow-down process followed the method reported by Gogou et al. (1996). After the extraction, the DCM solvent was concentrated to dryness by a combination of rotary evaporation and blowing under a gentle nitrogen stream. The concentrated extract was then diluted in 10 ml of n-hexane before application to the top of a disposable silica gel column. The extract was then fractionated into individual compound classes by flash chromatography on silica gel as follows: The concentrate was applied to the top of a 30×0.7 cm diameter column, containing 1.5 g of silica gel (activated at 150°C for 3 h). Nitrogen pressure was used to in order to obtain a flow of 1.4 ml min⁻¹ at

the bottom of the column. The following solvents were used to elute the different compound classes: (1) 15 ml n-hexane (fraction 1, light molecular weight PAHs); (2) 15 ml toluene-n-hexane (5.6:9.4) (fraction 2, middle and heavy molecular weight PAHs). The sample was further reduced to incipient prior to being made up to volume with cyclohexane (exactly 100 µl in a GC/MS vial insert for both GFF/QMF and PUF samples) prior to GC/MS analysis (i.e. Varian Saturn Ion Trap 2000 GC/MS System with CP-3800 GC). More detailed GC/MS method was provided in a previous reference and will not be discussed here (Pongpiachan et al., 2009). Accuracy was evaluated using the standard SRM 1941b. Mean recovery (based on extraction of matrix-matched certified reference materials) of Phe, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[e]P, Ind, B[g,h,i]P were 119±16%, 112±12%, 95±11%, 82±13%, 77±28%, 87±29%, 87±38%, 125±53%, 128±26%, 124±27% respectively. The precision of the procedure, calculated as relative standard deviation on the duplicate samples, was less than 15%. All sample concentrations were calculated using standardized relative response factors run with each batch (Pongpiachan et al., 2009).

Trace gaseous and water soluble ionic species

The determination of atmospheric trace gas concentrations constitutes (i.e. NO_x, CO and O₃) was performed by using a chemiluminescence technique. NO/NO₂/NO_x Analyzer (Model 200E, Teledyne Technologies Incorporated, USA), which gives an average of sampling data in the range of 50 ppb to 20 ppm with the instrumental detection limit of 0.4 ppb, was carefully selected for the NO_x measurement. CO was detected by a gas filter correlation CO Analyzer: Model 300E, Teledyne Technologies Incorporated, USA with the function of continuous self-checking with alarms and bi-directional RS-232 for remote operation. The instrumental sensitivity for CO determination ranges from 0-1 ppm to 0-1,000 ppm with the instrumental detection limit of 0.04 ppm. In this study, O₃ was monitored by UV Adsorption O₃ Analyzer Model 400 E, Teledyne Technologies Incorporated, USA with the analytical range of 0-100 ppb to 0-10 ppm with the instrumental detection limit of 0.6 ppb. NO_x, CO and O₃ were continuously monitored and then automatically averaged over 15 minutes. Seven water-soluble ionic species (WSIS), namely Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺ and Ca²⁺, in PM₁₀ were also measured during the monitoring campaign. The Metrohm IC system which comprise 819 Advance IC Pump, 819 Advance IC Detector, 820 Advance IC Separation Center, 833 Advance IC Liquid Handling Suppressor Unit and 830 Advance IC Interface, was employed for the analysis of seven WSIS. The setup, quality control and quality assurance of instrument and analytical method have been previously explained (Lai et al., 2007; Tao et al., 2007). For more details the reader is referred to the aforementioned publications.

OC/EC analysis

Procedures for OC/EC analysis including calibrations and QA/QC were conducted at the laboratory of the Department of Civil and Structural Engineering, Research Centre for Urban Environmental Technology and

Management The Hong Kong Polytechnic University, China. These procedures are essentially the same as described earlier by Cao et al. (2003). Generally, OC and EC were defined as sum of OC fractions and EC fractions (OC1+OC2+OC3+OC4) and EC fractions (EC1+EC2+EC3+OP) individually, based on the IMPROVE TOC (Interagency Monitoring to Protect Visual Environments Total Organic Carbon) protocol (Chow et al., 1993; 2001; Fung et al., 2002). For more details, the quality control and quality assurance (QA/QC) have been discussed in Cao et al. (2003).

Data analysis

In *agglomerative hierarchical clustering* every case is initially considered as a cluster then the two cases with the lowest distance (i.e. highest similarity) are combined into a cluster. The case with the lowest distance to either of the first two is considered next. If that third case is closer to a fourth case than it is to either of the first two, the third and fourth cases become the second two-case cluster; if not, the third case is added to the first cluster. The process is repeated, adding cases to existing clusters, creating new clusters, or combining clusters to get to the desired final number of clusters. In contrast, the *divisive clustering* works in the opposite direction, starting with all cases in one large cluster. As one might have an interest in investigating the diurnal variation patten of PAHs, the *agglomerative hierarchical cluster analysis* is probably the most suitable for this objective, with relatively small sample numbers.

The fundamental principles of various chemical methods for receptor modeling, including chemical mass balance (CMB) and multivariate method, have been review in details (Blifford, 1967; Gordon, 1988; Watson, 1994). Factor analysis offers the advantages of not requiring prior knowledge of the chemical composition and size distribution of emissions from specific sources (source profiles) but has the drawback of being mathematically indeterminate, allowing a wide range of possible solutions even when it is applied to relatively simple simulated data sets. In urban atmosphere, which is composed by many potential and diverse sources, principal component analysis (PCA) has been chosen by many researchers for source apportionment. This technique has been widely applied to source apportionment of particulate pollutants, especially trace metals, and more recently, PAHs.

In order to identify sources, multivariate receptor modeling can be applied to the observed target compound data. Multivariate approaches are based on the idea that the time dependence of a chemical species at the receptor site will be the same for species from the same source. Chemical species are measured in a large number of samples gathered at a single receptor site over time. Species of similar variability are grouped together in a minimum number of factors that explain the variability of data set. It is assumed that each factor is associated with a source or source type. However, the method has some limitations in that it can recognize at most only about eight individual source categories in any study, and poor discrimination of closely related source categories is commonly found. A further disadvantage of multivariate factor analysis is that large numbers of ambient air samples

must be collected and analyzed (usually at least 50) and the statistically independent source tracers are required for each major source type.

In contrast to CMB model, multivariate techniques such as PCA are preferable since they require no qualitative insight of the sources of certain chemical species, and thus overcome the limitations of CMB, (Rachdawong et al., 1998; Park et al., 2005). The aim of PCA is to identify the major sources of air pollutant emissions and to select statistically independent source tracers, (Bruno et al., 2000; Miller et al., 2002; Guo et al., 2003). All variables are expressed in standardized form with a mean of 0 and a standard deviation of 1. The total variance therefore equals the total number of variables, and the variance of each factor expressed as a fraction of the total variance (referred to as the eigenvalue). If a factor has a low eigenvalue, then it is contributing little to the explanation of variances in the variables and may be ignored. PCA is generally used when the research purpose is data reduction (i.e. to reduce the information in many measured variables into a smaller set of components). PCA seeks a linear combination of variables such that the maximum variance is extracted from the variables. It then removes this variance and seeks a second linear combination that explains the maximum proportion of the remaining variance, and so on. This is called the principal axis method and results in orthogonal (uncorrelated) factors. Thus, the largest combination, accounting for most of the variance, becomes principal component 1 (PC1), the second largest accounts for the next largest amount of variances and becomes principal component 2 (PC2), and so on. In general, the first component (P_1) for observed variables X_1, X_2, \dots, X_p can be expressed as:

$$P_1 = a_{(1)1}X_1 + a_{(1)2}X_2 + \dots + a_{(1)p}X_p \quad \text{Equation 1}$$

Where the $a_{(1)1}, a_{(1)2}, \dots, a_{(1)p}$ are the weights chosen to maximize the ratio of the variance of P_1 to the total variation, subject to the constraint that

$$\sum_{i=1}^p a_{(1)i}^2 = 1 \quad \text{Equation 2}$$

The second principal component (P_2) is the combination of the observed variables, which is uncorrelated with the first linear combination and which accounts for the maximum amount of the remaining total variance not already accounted for by P_1 . Assume that the data set has n samples for p variables. The basic ($n \times p$) data matrix can be written as:

$$X_{(n \times p)} = \begin{matrix} X_{11} & X_{12} & \dots & \dots & X_{1p} \\ X_{21} & X_{22} & \dots & \dots & X_{2p} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ X_{n1} & X_{n2} & \dots & \dots & X_{np} \end{matrix} \quad \text{Equation 3}$$

Where X_{ij} is the value of variable j obtained for sample i . When the matrix X is used, P can be rewritten as:

$$P = (X - M)A \quad \text{Equation 4}$$

Where M is the mean matrix given by:

$$\begin{matrix} \bar{X}_1 & \bar{X}_2 & \dots & \dots & \bar{X}_p \\ \bar{X}_1 & \bar{X}_2 & \dots & \dots & \bar{X}_p \end{matrix}$$

$$M = \begin{matrix} \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \bar{X}_1 & \bar{X}_2 & \dots & \dots & \bar{X}_p \end{matrix}$$

Equation 5

Where Equation (5) is the mean for variable *j*.

$$\bar{X}_j = (1/n) \sum_{i=1}^n X_{ij}$$

Equation 6

The matrix of *standardised loadings*, *A*, is a (*p* × *p*) matrix such that *A*^T*A* = *I*. The *scores matrix*, *P*, is a (*n* × *p*) matrix such that *P*^T*P* is a diagonal matrix. Equation (3) becomes

$$X = M + PA^T$$

Equation 7

Factor analysis of PCA has been accomplished in this study on the three-hour average PM₁₀ data sets including 15 PAHs, seven water-soluble ionic species, three trace gaseous species, six meteorological parameters, organic carbon and elemental carbon. The minimum number of samples (*n*) for conducting factor analysis can be calculated by using the following equation;

$$n > 30 + (V + 3) / 2$$

Equation 8

where *V* represents the number of variables (Henry et al., 1984). Since outliers (i.e. as defined by three times of standard deviation from the mean) of raw data can dramatically cause unusual errors or events in the analytical results, it is important to remove these outliers prior to data analysis to avoid propagation of errors (Kumar et al., 2001). In the present investigation, 33 variables and 70 samples (after removing outliers) were taken into accounts for conducting PCA. Varimax rotated factor analysis was selected for performing PCA on meteorological parameters of the ambient air, chemical compositions of PM₁₀ and trace gaseous species of the observatory sites. It is worth mentioning that only those factors having eigenvalue of more than one were selected to have normalized variables that carry out unit of variance (Kumar et al., 2001). It is therefore not necessary to perform factor analysis of those initial variables, which possess an eigenvalue less than one (Maenhaut and Cafmeyer, 1987). The number of principal components (PC) will be carefully chosen based on the sum of cumulative percentage variance higher than 80%. In addition, PCA has been widely used in performing source apportionment of PAHs in aerosol particle samples from the atmospheric environment of New Dehli, India (Gupta et al., 2011), Harbin, China (Ma et al., 2010), Porto Alegre, RS, Brazil (Teixeira et al., 2012) and Flanders, Belgium (Ravindra et al., 2006). In addition, SPSS 13.0 was also used for the Analysis of Variance (ANOVA) technique of Multiple Linear Regression Analysis (MLRA) for the speculation of influence of meteorological parameters and carbonaceous fractions on variation of particulate PAHs as previously described by Dachs et al. (2002). In addition, all statistical analysis was carried out using the software “SPSS version 13”.

Results

Statistical descriptions of PAHs collected during the observatory period at Centara Duangtawan Hotel and Imperial Mae Ping Hotel are illustrated in Table 1. At all monitoring elevations, the mean contents for PM₁₀ ranged from 49.4 to 203.1 µg m⁻³ and for ΣPAHs (i.e. sum of 15 PAHs Norwegian Standard (NS 9815: S-4008-100-T)) and B[a]P from 304 to 18,672 pg m⁻³ and from 13.7 to 4,673 pg m⁻³, respectively. At site-1 (12 m above ground level), B[a]P concentrations ranged from 30.3 to 1,673 pg m⁻³ with an average of 506 ± 477 pg m⁻³, contributing on average, 8.09 ± 8.69% to ΣPAHs. Ind and B[b]F concentrations varied from 54.6 to 4,579 pg m⁻³ and from 80.7 to 2,292 pg m⁻³ with the highest average of 1,187 ± 1,058 pg m⁻³ and 963 ± 656 pg m⁻³, contributing on average, 19.0 ± 19.3% and 15.4 ± 12.0% to ΣPAHs, respectively. This implies that five-to-six ring PAHs (PAHs (5,6)) are crucial contributors to ΣPAHs mass concentrations. It is also interesting to note that the majority of PAHs (5,6) shows the maximum values at Site-3. Since vehicular exhausts and cooking emissions are two main sources of PAHs at ground level, it appears reasonable to assume the highest contents of B[a]A, Chry, B[k]F, B[e]P, B[a]P and B[g,h,i]P at Site-3 are as a consequence of long range transportation of biomass burnings from forests and agricultural

Table 1. Statistic Description of PAH Concentrations (pg n⁻³) in PM₁₀ and its Percentage Contributions

	Phen	An	Fluo	Pyr	1H-B[a]F	1H-B[b]F	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P
PAH concentrations (pg n ⁻³) in PM ₁₀															
Site-3	125±65.6	49.8±26.5	160±171	365±449	108±106	73.1±91.3	924±958	619±717	834±739	287±356	685±659	899±1,144	726±605	ND.	880±653
Site-2	186±160	151.0±98.3	246±247	381±345	110±83.2	61.9±47.9	405±404	465±389	1134±975	157±147	688±475	511±494	1175±1085	ND.	N.D.
Site-1	136±92.4	27.8±14.5	314±259	451±358	153±142	63.4±63.1	382±408	484±451	963±656	169±137	535±417	506±477	1,187±1,057	120±95.6	769±859
Percentage Contribution to ΣPAHs															
Site-3	1.86±0.974	0.793±0.393	2.37±2.53	5.42±6.66	1.60±1.57	1.01±1.36	13.7±14.2	9.20±10.6	12.4±11.0	4.26±5.28	10.2±9.78	13.3±17.0	10.8±8.97	ND.	13.1±9.69
Site-2	2.83±2.820	2.29±1.720	3.75±4.32	5.79±6.03	1.67±1.46	0.94±0.84	6.16±7.07	7.08±6.80	17.3±17.1	2.40±2.57	10.5±8.31	7.78±8.65	17.9±8.65	ND.	13.7±13.4
Site-1	2.17±1.680	0.44±0.264	5.02±4.71	7.20±6.52	2.44±2.58	1.01±1.15	6.10±7.44	7.73±8.22	15.4±12.0	2.70±2.50	8.55±7.61	8.09±8.69	19.0±19.3	1.91±1.74	12.3±15.7

Table 2. Atmospheric Concentrations of PAH (pg n⁻³) in PM₁₀ Collected at Different Cities Around the World

Year	Month	City/Town	Country	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	
2011	8	Bogotá	Colombia ^a	1.4	31.1	0.8	9.8	223	14.9	243	153	ND.	2,130	409	503	31.9	
2012	1	Ohio	USA ^b	44,500±6,600	25,400±3,600	28,800±3,900	25,800±6,300	58200±10600	49,800±8,600	ND.	53,900±21,200	ND.	15,700±7,900	ND.	ND.	ND.	ND.
2012	3	Tianjin	China ^c	11,150±3,960	2,500±740	9,970±1,430	9,270±2,230	73,100±2,120	5,590±2,080	7,620±3,810	3,640±6,990	5,750±2,230	4,240±710	4,160±1,080	3,120±920	6,140±3,480	
2008	NA.	São Paulo	Brazil ^d	100	110	1,310	1,190	1450	920	2,820	970	ND.	1,900	2,010	850	2,320	
2009	12	Algiers	Algeria ^e	950	170	270	290	550	390	880	ND.	480	270	450	20	760	
2009	2	Konya	Turkey ^f	7,800	2,700	11,200	9,500	7,000	11,700	6,400	7,700	ND.	5,300	ND.	2,400	ND.	
2009	China	Baoji	China ^g	38,000	3,000	82,300	56,800	39,500	52,300	107,000	25,700	31,300	24,600	34,600	6,800	33,100	
2009	4	Beijing	China ^h	5,900	1,450	6,450	8,760	3,570	7,330	2,600	1,560	4,180	1,460	2,070	60	1,810	
2011	11	Istanbul	Turkey ⁱ	100	160	60	80	10	50	10	10	ND.	20	10	10	20	
2012	11	Mt. Hua	China ^j	900±300	200±100	1,100±400	600±300	300±200	600±300	900±500	900±500	800±500	400±200	700±400	100±100	300±200	
2012	8	Damascus	Syria ^k	640	1,780	630	1200	490	320	1,780	560	ND.	1,100	740	320	790	
2012	9	Korba	India ^l	60	20	60	80	70	40	40	110	190	170	580	170	550	
2010	7	Gdan'sk	Poland ^m	86,000	7,900	49,000	3700	3,400	13,400	ND.	ND.	ND.	ND.	ND.	ND.	ND.	
2012	3	Araraquara, SP,	Brazil ⁿ	91	8.8	230	78	60	60	2.5	13	160	26	150	750	1,200	
2006	6	Athens	Greece ^o	120	20	170	170	230	460	710	ND.	350	210	320	70	340	
2008	12	Taichung	Taiwan ^p	179,000±112,000	164,000±86,000	55,000±19,000	67000±47000	76000±29000	67,000±30,000	106,000±69,000	85,000±57,000	160,000±103,000	82,000±59,000	ND.	ND.	ND.	
2008	1	Beijing	China ^q	4,360±5,700	700±920	96,910±125,360	13070±13590	5650±5300	5,580±6,220	20,380±26,700	37,990±73,670	8,390±8,990	17,780±18,860	4,080±4,240	19,180±21,020		
2009	7	Athens	Greece ^r	100	20	150	40	20	10	60	30	ND.	ND.	ND.	ND.	ND.	
2007	12	Guangzhou	China ^s	560	70	410	470	290	1,160	1,820	1,820	2,340	1,170	2,770	830	3,640	

^aRojas et al., 2011. ^bTimothy et al., 2012. ^cKong et al., 2012. ^dAllen et al., 2008. ^eLadji et al., 2009. ^fOzcan and Aydin, 2009. ^gXie et al., 2009. ^hZhou et al., 2009. ⁱHamedar et al., 2011. ^jLi et al., 2012. ^kAlkurd et al., 2012. ^lGiri et al., 2012. ^mTsakovski et al., 2010. ⁿCristale et al., 2012. ^oVasilakos et al., 2007. ^pLin et al., 2008. ^qWang et al., 2008. ^rAndreou and Rapsomanikis, 2009. ^sDuan et al., 2007

areas surrounded the City.

As illustrated in Table 2, the highest B[a]P concentrations were in Taichung, Taiwan (82,000±59,000 pg m⁻³), followed by Baoji, China (24,600 pg m⁻³) and Ohio, USA (15,700±7,900 μg m⁻³), while average D[a,h]A and B[g,h,i]P concentrations were also the highest in Baoji, China (6,800 pg m⁻³ and 33,100 pg m⁻³), followed by Beijing, China (4,080±4,240 pg m⁻³ and 19,180±21,020 pg m⁻³) and Tianjin, China (3,120±920 pg m⁻³ and 6,140±3,480 pg m⁻³), respectively. The average B[a]P at Site-1 (506±477 pg m⁻³) were in the range between those of Algiers, Algeria (270 pg m⁻³) and Damascus, Syria (1,100 pg m⁻³). While the vertical distribution of ΣPAH contents observed at various altitudes were to some extent comparable to each other, some significant differences (p<0.001) in atmospheric concentration were observed in An and B[a]A compositions. As illustrated in Table 1, the average concentrations of An were 27.8±14.5 pg m⁻³, 151±98.3 pg m⁻³ and 49.8±26.5 pg m⁻³ for site-1, site-2 and site-3 respectively. In spite of the fact that all observatory positions were close to each other, the average contents of An measured at site-2 were significantly (p<0.001) 5.4 times and 3.0 times higher than those observed at site-1 and site-3, respectively. These dissimilarities appear to reflect the differences in building configurations and wind directions' distribution patterns. It is worth mentioning that Site-1 was mainly influenced by the group of East and East-Northeast wind direction (40%), whilst the mixtures of South-Southeast and North-Northwest were the main contributors at Site-2 (44%).

Discussion

Three-hour average particulate PAH contents were used to examine diurnal and vertical variability of PAHs in PM₁₀. Figure 1 displays diurnal variation of PAH concentrations in PM₁₀ at various altitudes from February 25th to 28th, 2008. For all observatory sites, PAH concentrations show similar diurnal variation. The morning maxima were mostly observed in all sampling altitudes. This can be explained by typical diurnal variations of traffic flow in Chiang-Mai City showing a morning peak between 6 AM. and 9 AM. and an evening peak between 3 PM. and 6 PM. PAHs (3,4) displayed the highest peak during morning rush hour (i.e. 0600-0900) observed at Site-1 and Site-2, whilst Site-3 had slightly different trend exhibiting the maximum peak at 0300-0600. Since South-Southwesterly wind directions play a major role in Site-3 whilst East-Northeasterly and South-Southeasterly dominate the air parcel in site-1 and site-2 respectively, it seems reasonable to interpret this phenomenon as a consequence of wind direction effect. This trend is also in accordance with those of PAHs (5,6) as can be seen in Figure 2, indicating that vehicular exhausts play an important role in diurnal variation patterns

of HMW PAHs. Several papers highlight the importance of a sharp increase in particulate PAH concentrations, especially in early morning detected between 700-800 and followed by a relatively prompt decline during the afternoon and progressively enhanced once again after sunset (Chetwittayachan et al., 2002). Similar phenomena had also been observed in Shanghai, China (Gu et al., 2010) and Los Angeles, USA (Fine et al., 2004). Gu et al (2010) interpret the gradually increase of particulate PAH concentrations from early morning (00:00-06:20) to morning (06:30-10:00) in all observatory days as a consequence of traffic contributions. On the contrary, Fine et al. (2004) highlight the importance of stagnant atmospheric condition, particularly during the relatively cold period, as one of the main factors lowering mixing height that are responsible for thermal inversion and thus high PAHs. It is also worth mentioning that cooking emissions from barbecue stalls and noodle peddlers at night markets adjacent to observatory sites could to some extent enhance the atmospheric contents of PAHs from 6 PM to midnight.

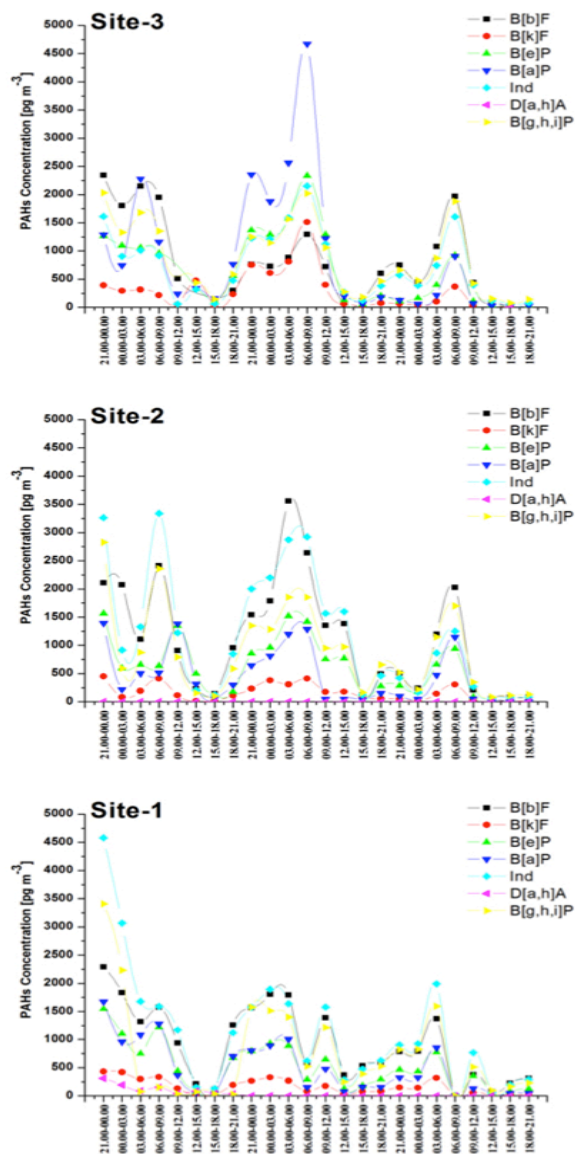
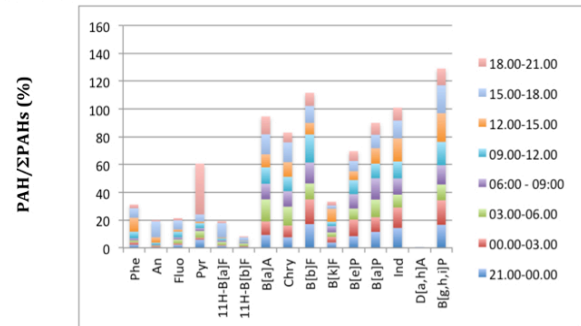


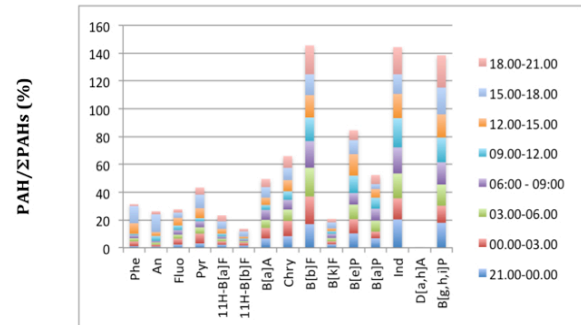
Figure 2. Diurnal Variation of Five-to-Six Ring PAHs in PM_{10} in Chiang-Mai from 25/02/08-28/02/08

Fingerprinting reflects the chemical characteristics of various source emissions of the ambient air sample collected at any receptor, because a simple ratio of two or three PAHs is sensitive to both photolysis and chemical/biological degradation and may be insufficient to identify PAH emission sources at fixed monitoring sites. Hence, the best strategy to investigate the atmospheric fate of particulate PAHs is the use of the entire PAH profiles. As illustrated in Figure 3, the averaged percentage contribution of $PAH/\Sigma PAHs$ (%) source profiles (n=3) of eight different observatory periods were compared in which the visual comparison process can be applied to investigate the impact of emission sources from ground level at Site-1 on higher altitudes at Site-2 and Site-3. Since the removal rate of PAHs depends on their exposure time to UV light (i.e. photodecomposition) and other trace gaseous species (i.e. heterogeneous reaction), the monitoring period applied in this study should be as short as possible. Therefore, the sampling time is strictly limited to three hours. The assumption was that site-specific factors such as building configurations and wind directions

Site-3



Site-2



Site-1

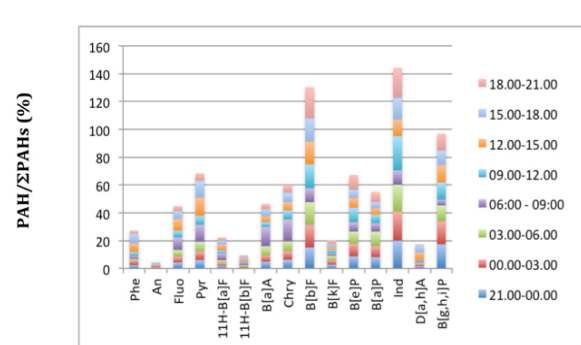


Figure 3. Fingerprinting Characteristics of Average Percentage Contribution ($PAH/\Sigma PAHs$ (%)) at Eight Different Sampling Periods Observed in All Sites from 25/02/08-28/02/08

that influenced the variability of the individual compound concentrations and the fingerprint patterns are of minor importance. The presentation of PAH/ Σ PAHs (%) in Figure 3 permits a rapid visual categorization of group-1: Site-1 and Site-2, and group-2: Site-3. Figure 3 shows the distributional characteristics of group-1, corresponding to the three major features. Firstly, the most abundant quantified PAHs in decreasing order are: Ind>B[b]F>B[g,h,i]P in HMW PAHs, secondly: B[e]P>Chry>B[a]P in MMW PAHs, and thirdly: B[a]A>Fluo>Phe in LMW PAHs. Regardless of the site-specific, monitoring period and the difference of PAHs concentration level determined in Site-1 and Site-2, the fingerprints of all PAHs are almost equivalent to each other. This suggests potential influences of traffic and cooking emissions from ground level on Site-2. There are some remarkable differences between group-1 and group-2. Firstly, the decreasing order of PAHs(5,6) in group-2 was B[g,h,i]P>B[b]F>Ind>B[a]P>B[e]P>B[k]F in that order. Secondly, there are the reverse descending order of PAHs(3,4) from Chry>B[a]A observed in group-1 to B[a]A>Chry detected in group-2. Thirdly, group-2 has the highest percentage contribution of observatory period of 1800-2100 detected in Pyr, indicating that Site-3 might have been influenced by other PAH emission sources apart from vehicular exhausts and cooking emissions.

Dachs et al. (2002) had investigated the processes driving short-term variability of PAHs at Baltimore and northern Chesapeake Bay atmosphere using the Analysis of Variance (AVOVA) technique of Multiple Linear Regression Analysis (MLRA). Air samples collected from Chesapeake Bay represent clean air from coastal and rural area while those of Baltimore represent contaminated air from urban/industrial area. PAH concentrations in Chesapeake Bay increased when air masses passed the Baltimore area. By contrast, the volatilization of PAHs out of the Bay could be an alternative emission source of PAHs to adjacent bay and rural atmosphere, at least when air masses are not influenced by the Baltimore urban and industrial area. The variation of gaseous PAH depends mainly on meteorological variables such as ambient temperature, wind speed and wind direction (Dachs et al., 2002). For particulate PAH, the chemical compositions, namely, the content of OC and EC could be responsible for the variations. In order to investigate the influence of carbonaceous fractions and meteorological variables, PAH aerosol concentrations have been fitted by multiple linear regressions to

$$C_{Aerosol} = a + bT + cU_{10} + d\sin(WD) + eC_{os}(WD) + fC_{OC} + gC_{EC}$$

Equation 9

where $C_{Aerosol}$, T , U_{10} , WD , C_{OC} and C_{EC} represent for PAH contents in PM_{10} , temperature, wind speed, wind direction, OC and EC fractions respectively. MLRA can establish the relative predictive importance of these parameters on the dependent variables (i.e. PAH concentrations). Calculations were made with the 'stepwise' MLRA method. Table 3 summarized the standardized coefficients (β), R^2 and its significance of MLRA obtained from Eq. (9). It is usually inappropriate to interpret the regression coefficients as indicators of relative importance of variables, as the actual magnitude

of the coefficients depends upon the unit in which the variables are measured. β -values allow the statistician to directly compare the weight of effect each independent variable has upon the dependent variable by standardizing the regression coefficients for each independent variable.

During the observatory period, particulate PAH contents display a strong correlation with OC fractions, while only An shows a significant correlation with EC contents over the Chiang-Mai City's atmosphere (Table 3). The findings of the current study are inconsistent with those of Dachs et al. (2002), who found a strong correlation between aerosol-phase PAH concentrations and EC fractions over the Chesapeake Bay. Dachs et al. (2002) interpret this phenomenon as a consequence of relatively high soot-air partition coefficients, which are two to three orders of magnitude higher than those of octanol-air partition coefficients. However, this interpretation could be problematic in a couple of ways. Firstly, on the recent speculations of Arp et al. (2008a) that EC in airborne particles may be inaccessible to PAH partitioning. Arp et al. (2008a) strongly suggested that EC is contributing little to the overall gas-particle partitioning mechanisms because of two major reasons: "EC has small contribution to over all urban aerosol" and "EC is coated with salts and organics". Secondly, Arp et al. (2008a) reported that the surface area of urban aerosols (e.g., 0.2–2.2 $m^2 g^{-1}$, (Roth et al., 2005); 0.82–2.4 $m^2 g^{-1}$, (Sheffield and Pankow, 1994) and even road tunnel aerosols (e.g., 7.4 $m^2 g^{-1}$, (Roth et al., 2005)) are one to two orders of magnitude smaller than values for diesel soot (e.g., 91 $m^2 g^{-1}$, (Roth et al., 2005)), indicating that EC is contributing little to the overall surface area. Thirdly, the OC/EC ratios observed in this study ranged from 4.9-8.4 with an average of 5.8 ± 3.9 , highlighting the importance of OC on carbonaceous fractions and thus minimizing the impact of EC on gas-particle partitioning of PAHs.

Temperature negatively influences the aerosol-phase

Table 3. Results Obtained from Applying Eq. (9) to Aerosol Phase Concentrations for site-1, site-2 and site-3

	T	U_{10}	Sin (WD)	Cos (WD)	OC	EC
Phe	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
An	n.s.	n.s.	n.s.	n.s.	n.s.	0.93
Fluo	-0.26	-0.27	-0.28	n.s.	n.s.	n.s.
Pyr	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
11H-B[a]F	-0.39	-0.23	n.s.	n.s.	n.s.	n.s.
11H-B[b]F	-0.46	n.s.	n.s.	n.s.	n.s.	n.s.
B[a]A	-0.25	n.s.	n.s.	0.24	n.s.	n.s.
Chry	-0.50	n.s.	n.s.	n.s.	n.s.	n.s.
B[b]F	n.s.	n.s.	n.s.	2.54	n.s.	n.s.
B[k]F	n.s.	n.s.	n.s.	0.39	n.s.	n.s.
B[e]P	n.s.	n.s.	n.s.	0.37	0.45	n.s.
B[a]P	n.s.	0.22	n.s.	0.43	0.47	n.s.
Ind	-0.28	-0.32	n.s.	n.s.	n.s.	n.s.
D[a,h]A	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
B[g,h,i]P	n.s.	n.s.	0.19	0.41	0.41	n.s.

*Values shown are significant with a p-value lower than 0.05. n.s. means not significant

***** HIERARCHICAL CLUSTER ANALYSIS *****

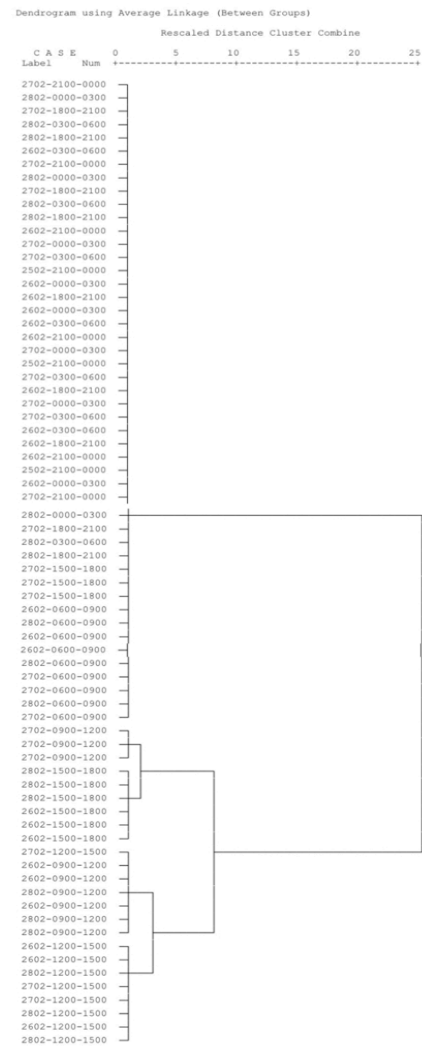


Figure 4. Hierarchical Cluster Analysis of 33 Variables Observed in All Sites from 25/02/08 to 28/02/08

concentrations of PAHs, suggesting that the atmospheric inversion layer significantly elevated the concentrations of Fluo, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry and Ind during nighttime. On the other hand, wind speed displays negative correlations with only three particulate contents, namely Fluo, 11H-B[a]F and Ind, implying that wind speed does not induce a dilution of the atmospheric signal due to a greater mixing height. In other words, an incidental and concealed impact of elevated aerosol-phase concentrations may be covered by the influence of wind direction as can be seen in relatively high positive values of parameter e (i.e. the standardized coefficients (β) of $\text{Cos}(\text{WD})$) displayed in Table 3. The PAHs (5,6) show higher concentrations for air masses from the northwesterly sector, thus from the Doi Suthep area, a mountain located 15 km away from the northwest of observatory sites (positive values of the parameter e in Equation (9), see Table 3). This is in agreement with the fact that the vast majority of hotspots occurred in Doi Suthep area, and thus emphasizing the significance of biomass burnings on air quality level of Chiang-Mai City. In addition, the agricultural waste burning from rice fields located in Northern and Northeastern region can also be considered as potential sources of PAHs during the sampling period.

HCA can be a suitable statistical tool for investigating the diurnal variation patterns of PAHs. To obtain more information on the diurnal variation patterns of PAHs collected at all sampling sites, HCA had been conducted on the 33 variables (i.e. 15 PAHs, seven water-soluble ionic species, three trace gaseous species, six meteorological parameters, organic carbon and elemental carbon) and 70 samples (after removing outliers). The cluster analysis revealed the presence of two different groups at all observatory sites. The dendrogram in Figure 4 represents the two major groups. The first cluster ($n=48$) consists of sampling periods of 1800-2100, 2100-0000, 0000-0300, 0300-0600, 0600-0900 and 1500-1800. The second cluster ($n=24$) can be divided into four subgroups; the first consists of sampling period of 0900-1200, the second is composed of 1500-1800, the third contains 0900-1200 and the fourth composes of 1200-1500.

The strong unification of 33 variables were observed in subgroup-4 of the second cluster during the observatory period of 1200-1500, followed by subgroup-2 and subgroup-3 of the second cluster, which possess cluster members of 1500-1800 and 0900-1200 respectively. These results suggest that the behaviour of PAHs during daytime is quite consistent, especially the periods from 0900-1500. It is also worth mentioning that noodle stalls and barbecue peddlers were for the most part closed from 0900-1500 and thus might allow vehicular exhausts to be dominant sources of pollutants during that period. Furthermore, both forest fires and agricultural waste burnings can be considered as continuous emission sources. Therefore, it seems rational to assume that hotspots have little effects on diurnal variation of PAHs during the sampling period. On the contrary, the irregular distributions of observatory periods are quite distinct for the first cluster. This can be explained by more complicated emission sources, which can be attributed to cooking emissions from night markets, vehicular exhausts, and short and long range transportation

of biomass burnings during nighttime.

The principal component analysis (PCA) was employed to categorize the emission sources of PAH compositions. In the present study, two principal components (PC1 and PC2) were identified based on PAH loadings and accounted for 71.7% and 28.2% respectively, which cooperatively explained for 99.9% of the total variance. The resulting data set of variables in atmospheric environment was also interpreted by PCA, which facilitates identification of the different groups of correlated components. The levels of Phe, Fluo, Pyr, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry, B[b]F, B[k]F, B[a]P, B[e]P, D[a,h]A and B[g,h,i]P showed a significant positive correlation ($R>0.70$) with each other, suggesting a similar origin of their emission sources and identical behavior during transport in the atmospheric system. Since K^+ and Ca^{2+} can be used as indicators of biomass burning contribution (Allen et al., 2004; Duan et al., 2004), the considerably strong positive correlation between these two ionic species and PAHs reveal the main influence of agricultural waste burning on the atmospheric levels of carcinogenic components in PC1. It is also crucial to emphasize that PC1 was predominantly connected with PAHs and negatively correlated with temperature

and solar radiation, which could be due to the fact that higher intensity of UV light in daytime decreased the concentrations of pyrogenic PAHs by photochemical decomposition process. The weather balloon coupled with radiosonde detected a consistent relationship amongst the trend profiles such that very steep shallow temperature inversions occur during nighttime in the near-surface layer at the altitude of approximately 500 m above ground level. During the relatively cold period when the angle of the sun is extremely low, particularly in the mountainous region like Chiang-Mai City, an inversion can be occurred and hence could some way be responsible for the enhancement of PAH (5,6) after midnight.

It is worth mentioning that PC2 was dominated by Phe, CO, NO₂, NO₃⁻, OC and EC (Table 4). Several papers report that the most abundant PAH compounds from diesel engine exhausts was Phe (Nelsen, 1989; Lim et al., 2005; He et al., 2010), indicating that PC2 can be attributed to traffic emissions. This interpretation is further supported by the strong positive loadings of

CO and NO₂, which are well known as trace gaseous species from vehicle emissions in urban atmospheric environment (Schnitzhofer et al., 2008; Chen et al., 2009; Gokhale, 2012). OC and EC are also two major chemical compounds that are generally considered as traffic exhaust pollutants in urban atmospheric environment (Grieshop et al., 2006; Ancelet et al., 2011; Tian et al., 2012). Hence it appears reasonable to assume PC2 as a representative of traffic emission. Overall, the PCA results emphasize the importance of both agricultural waste and biomass burnings during the haze episode in the relatively cold period.

In conclusions, cancer is defined as one of the major health problems in Thailand and has been the most common cause of death since 1999. There is a higher incidence rate of lung cancer in northern Thailand than other areas. Irrespective of sampling altitudes, MLRA reflects the high contribution of forest fires and agricultural waste burnings over atmospheric contents of particulate PAHs during the observatory period. The morning peaks are remarkably noticeable as consequences of traffic emissions, whilst the afternoon diminution in mass concentrations can be described by the dilution effect triggered by the daytime expansion of air mass. PCA highlights the significance of biomass burnings and traffic emissions as two dominant sources accounted for 71.7% and 28.2% during the monitoring period, respectively. In addition, wind direction can play a major role in altering particulate PAH fingerprints, particularly at high altitude.

Table 4. Principal Component Analysis (PCA) of Physicochemical Parameters

	Rotated Component Matrix ^a	
	PC1	PC2
Temperature	-0.790	-0.613
Relative Humidity	0.797	0.604
Atmospheric Pressure	-0.011	1.000
Solar Radiation	-0.925	-0.380
Wind Speed	-0.273	-0.962
Cl ⁻	0.954	-0.300
NO ₃ ⁻	0.489	0.872
SO ₄ ⁻²	-0.879	0.477
Na ⁺	-0.377	-0.926
NH ₄ ⁺	-0.895	-0.447
K ⁺	0.961	0.277
Ca ⁺²	0.991	-0.137
OC	0.129	0.992
EC	0.550	0.835
NO ₂	-0.137	0.991
CO	-0.321	0.947
O ₃	0.929	0.371
Phe	0.113	0.994
An	0.926	-0.377
Fluo	0.919	0.393
Pyr	0.944	0.330
1H-B[a]F	0.979	0.203
1H-B[b]F	0.974	0.227
B[a]A	0.973	0.231
Chry	0.934	0.357
B[b]F	0.766	0.643
B[k]F	0.888	0.461
B[e]P	0.896	0.444
B[a]P	0.926	0.377
Ind	0.624	0.781
D[a,h]A	0.962	-0.274
B[g,h,i]P	0.983	-0.183
PM ₁₀	0.258	0.966
Eigen Value	23.69	9.32
%Variance	71.77	28.20
%Cumulative Variance	71.77	99.97
Possible Emission Sources	Agricultural Waste /Biomass Burnings	Traffic Emissions

^aRotation method: Varimax with Kaiser Normalization

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