

# PM10 and Its Chemical Composition: A Case Study in Chiang Mai, Thailand

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## 1. Introduction

This chapter describes the chemical composition and spatial and temporal variations of airborne particulate matter that have a diameter of less than 10  $\mu\text{m}$  (PM10), as well as its possible health effects. A case study of air pollution in the city of Chiang Mai, Thailand was conducted due to its geographical features and meteorological conditions; i.e. temperature inversion, wind velocity and precipitation levels. Chiang Mai, with an altitude of approximately 310 m above sea level, is situated approximately 700 km north of Bangkok. The city covers an area of approximately 20,107 km<sup>2</sup> and is the country's second largest province. The city is situated in the Chiang Mai-Lamphun Basin and is surrounded by mountains. In the dry season, there is a low level of precipitation, and there are calm winds and a vertical temperature inversion, while air pollutants are generated from various sources of mostly anthropogenic activities and accumulate in the lower atmosphere and definitely have an effect on human health and the environment. PM10 is considered the most significant air pollutant that contributes to serious air pollution in the dry season of Northern Thailand. Its major sources are open burning and internal combustion exhaust from traffic. However, traffic density seems to be constant for the whole year, while open burning is mostly performed in the dry season, which coincides with the peak of the annual haze episode in the upper region of Northern Thailand. Large scale open burning in this region consists of forest fires and the burning of agricultural waste. These activities definitely emit a variety of air pollutants in the forms of both particulates and gases.

Air pollution is quite common in most countries with big cities. Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted from sources, such as biomass burning, incomplete combustion of fossil fuels and traffic-related suspension of road, soil, dust, sea salt and biological materials. Secondary particles are formed by gas-to-particle conversion in the atmosphere (Pöschl, 2005). Concentration, composition and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. The predominant particle components of air particulate matter (PM) are sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds and black or elemental carbon (Pöschl, 2005). The effects of aerosols to the atmosphere, climate and public health are among the central topics in the current environmental research. An airborne particulate matter consists of several of inorganic and organic species, many of which can adversely affect human health (Pöschl, 2005; Mauderly

& Chow, 2008). Of these constituents, the classes of polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which are formed during the incomplete combustion process of organic material emitted from a large variety of industrial processes, motor vehicles, domestic waste burning and regenerated burning in agriculture (Lee, et al., 1995). PAHs have been measured in many media (air, water, food, and soil samples) because some of them are known to be carcinogenic. Specifically prepared foods, such as charcoal broiled or smoked meat, contain higher concentrations of PAHs than city air. Nevertheless, the daily air intake of humans (10–25 m<sup>3</sup>) is of comparable mass to the daily intake of food and water (2–4 kg) (Furton & Pentzke, 1998). Therefore, the air polluted by airborne PAHs is of significant concern.

Numerous particulates and gaseous compounds (e.g. CO and volatile organic compounds) that come from biomass burning are known to be hazardous to human health (Torigoe et al., 2000). Mass concentrations of CO, NO<sub>2</sub>, PM<sub>2.5</sub>, organic carbon (OC) and elemental carbon (EC) in PM<sub>2.5</sub> were significantly associated with emergency department visits at hospitals due to cardiovascular diseases (Metzger et al., 2004). The most important gases which have affected the acidic dry deposition are HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub>. Those gases can be transformed into aerosols by neutralization reactions (Seinfeld & Pandis, 1998). Semi-volatile NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl are formed via reversible phase equilibrium with NH<sub>3</sub>, HNO<sub>3</sub> and HCl (Pio & Harrison, 1987). Understanding the formation of secondary particulate species SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> formation, requires investigation of the atmospheric concentration levels for HNO<sub>3</sub>, HCl and SO<sub>2</sub> and related aerosol ions. The inorganic component is made up of some insoluble dust and ash material, and soluble salts, in which potassium, ammonium, sulfate and nitrate are the most important species (Fuzzi et al., 2007).

Toxic metals in air are considered a global problem and a growing threat to the environment. Heavy metals are part of a large group of air pollutants called air toxins, which upon inhalation or ingestion can be responsible for a range of health effects such as cancer, neurotoxicity, immunotoxicity, cardiotoxicity, reproductive toxicity, teratogenesis and genotoxicity. For most metals, the bound or complex species are less toxic than the elemental forms, hence there is a loss in specificity when they are broadly classified as metals and their compounds. When inhaled, very small particles containing metals or their compounds deposit beyond the bronchial regions of the lungs into the alveoli region. Epidemiological studies have established relationships between inhaled PM and morbidity or mortality in populations. Studies in occupational or community settings have established the health effects of exposure to heavy metals, such as lead and their compounds. The localised release of some heavy metals from inhaled PM have been hypothesised to be responsible for lung tissue damage (U.S. EPA, 1999c). Metals occur in air in different phases as solids, gases or adsorbed to particles having aerodynamic sizes ranging from below 0.01 to 100 μm and larger. Two major categories of PM are fine particles (PM<sub>2.5</sub>) and coarse particles (PM<sub>10</sub>). Heavy metals such as As, Ga, Eu, W, Au, Cd, Ga, Mo, Pb, Sb, W, Zn, Fe, V, Cr, Co, Ni, Mn, Cu and Se exist in both coarse and fine fractions in ambient air. Ca, Al, Ti, Mg, Sc, La, Hf and Th exist predominantly in the coarse fraction. Metals such as Ba, Cs and Se enrich the fine fraction of PM. The degree to which the metals are absorbed depends on the properties of the metals concerned, i.e. valence, radius, degree of hydration and coordination with oxygen, physicochemical environment, nature of the adsorbent, other

metals present and their concentrations and the presence of soluble ligands in the surrounding fluids (Valerie et al., 2003). The metals that are of high environmental priority, due to their toxicity from char and ash samples of biomass, could be released to the atmosphere when biomass is burnt. The elemental compositions of biomass are complex. They involve 6 major elements (C, Cl, H, N, O and S) in the organic phase and at least 10 other elements (Al, Ca, Fe, K, Mg, Na, P, Si, Sr and Ti) in the inorganic phase called ash elements, which is important to ash characterization. Heavy metals (As, Cd, Co, Cr, Hg, Ni, Pb, Sb and Se) in both phases of biomass are trace levels (Demirbas et al., 2008).

In attempt to identify the major emission sources responsible for adverse health effects, several comprehensive surveys of atmospheric contaminants from a variety of sources have been performed worldwide (Furton & Pentzke, 1998; Pengchai, et al., 2009). In Thailand, only a few studies have been conducted to determine atmospheric PAHs in big cities, such as Bangkok and Chiang Mai. In particular, the northern part of Thailand has been facing air pollution in the dry season almost every year. It is important to know the levels of air pollutants, including PAHs and their variations, throughout the year. Moreover, sources of air pollutants are also needed to be identified.

## 2. PM10 situation in the city of Chiang Mai

Ambient PM10 concentrations have been automatically measured at the Air Quality Monitoring (AQM) station set up by the Pollution Control Department (PCD) of Thailand. They were measured with the tapered element oscillating microbalance (TEOM) Series 1400a (Rupprecht & Patashnick, USA). TEOM mass detectors or microbalances utilize an inertial mass weighing principle. A TEOM detector consists of a substrate (usually a filter cartridge) placed on the end of a hollow tapered tube. The tube with the filter on the free end was oscillated in a clamped-free mode at its resonant frequency. This frequency depends on the physical characteristics of the tube and the mass on its free end. A particle laden air stream was drawn through the filter where the particles were deposited and then through the hollow tube. The frequency of oscillation was measured and recorded by the microprocessor; the change in frequency was used to calculate the mass of particulate matter deposited on the filter (Teflon coated with glass fiber filter surface). The air-flow rate at  $16.67 \text{ L min}^{-1}$  was sampled through the sampling head and divided between the filter flow ( $3 \text{ L min}^{-1}$ ) and an auxiliary flow ( $13.67 \text{ L min}^{-1}$ ). The filter flow was sent to the instrument's mass transducer, which contained the analyte fraction of the particulate. The inlet was heated to  $50^\circ\text{C}$  prior to the particles being deposited onto the filter in order to eliminate the effect of condensation or evaporation of particle water (Washington State Department of Ecology, 2004; Patashnick et al., 2002).

Twenty-four hour PM10 concentrations from 2005-2009 monitored at Chiang Mai AQM station located at the city center were plotted and are illustrated in Fig.1. The trend of PM10 concentrations are almost the same every year. They were high in the dry season especially in February and March. The level decreased in the middle of April due to rain precipitation. During the first 2 weeks of March 2007, air pollution levels in Chiang Mai and the surrounding provinces rose steadily above the safety limit and produced haze that significantly cut visibility down to less than 1 km. PM10 reached their peak concentration on

March 14th 2007 at  $383 \mu\text{g}/\text{m}^3$  three times higher than 24 hrs PM<sub>10</sub> standard of Thailand ( $120 \mu\text{g}/\text{m}^3$ ). About 500,000 people were reported by the Public Health Ministry to be affected by the heavy air pollution. Hospitals and clinics across the affected area reported a surge in the number of patients with respiratory problems in March 2007, approximately a 20% increase compared to the same period in 2006 (Pengchai, et al., 2009).

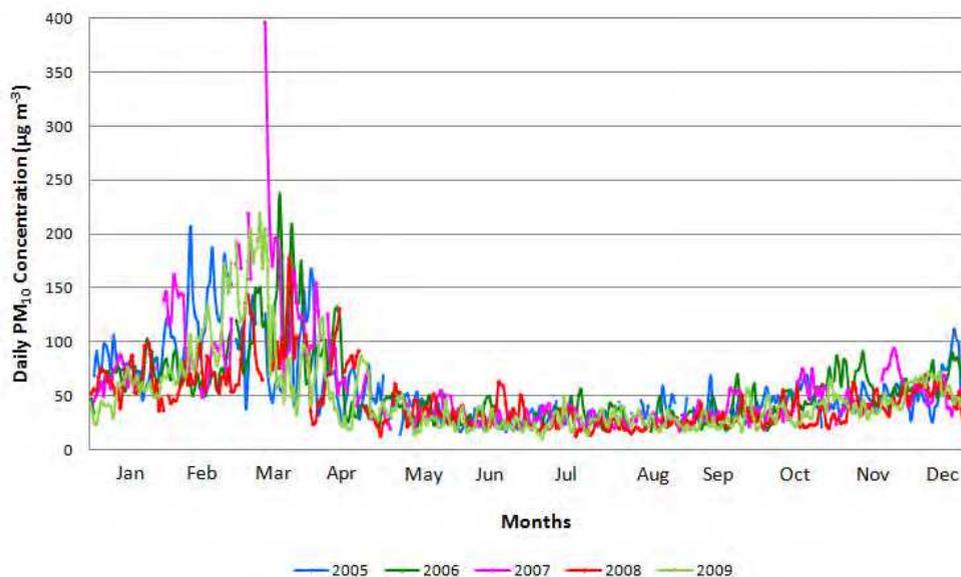


Fig. 1. PM<sub>10</sub> concentrations in Chiang Mai's ambient air from 2005-2009.

PM<sub>10</sub> concentrations and rain precipitation from late February 2010 to the beginning of March 2011 are illustrated in Fig. 2. PM<sub>10</sub> samples were collected by mini volume air samplers (Airmetric, USA) at the rooftop of a 9-storey building (ScB1), Faculty of Science, Chiang Mai University (CMU). This station was set up to monitor ambient PM<sub>10</sub> variation by avoiding the direct effects of traffic emissions. Another two PM<sub>10</sub> data series were obtained from the AQM Station belonging to PCD located at Provincial Hall (PH) and Yupparaj Wittayalai School (YP). Regional area air quality data was downloaded from the PCD website (Pollution Control Department, 2011). All mentioned sampling sites are shown in Fig. 3. Data of rain precipitation was obtained from website of Chiang Mai meteorological station (<http://www.cmmet.tmd.go.th/index1.php>).

In the dry season of the year 2010, PM<sub>10</sub> concentrations obtained from those 3 stations were much closer to each other. This is probably due to the effect from the large scale of open burning, which is mostly performed in the dry season. In the rainy season of the year 2010 and at the beginning of the dry season in the year 2011, PM<sub>10</sub> in the air was generated from

other anthropogenic sources, such as traffic, etc. Due to the fact that the station at CMU was on the rooftop of high building, it had a minimized influence from traffic emissions. Therefore, during the non-burning season PM10 concentrations at this sampling site were lower than the other two sites, where increased human activities existed.

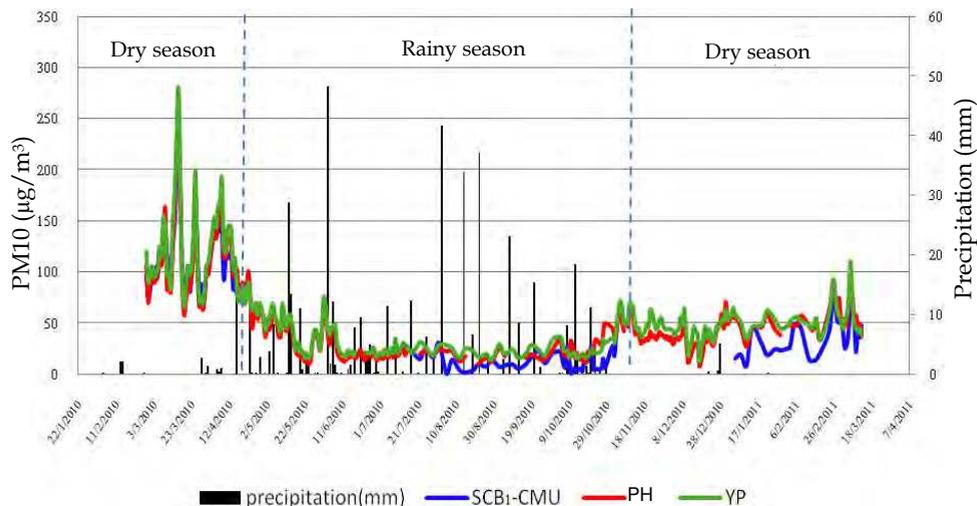


Fig. 2. PM10 concentrations ( $\mu\text{g}/\text{m}^3$ ) at Chiang Mai University (CMU), Provincial Hall (PH) and Yupparaj Wittayalai School (YP) and precipitation (mm) from 2010-2011

### 3. Sampling site selection for the study of PM10 and its chemical composition

This study aims to investigate PM10 concentrations and PM10 chemical composition in the ambient air of the cities located in the Chiang Mai-Lamphun Basin in order to assess the air quality and predict possible health effects. Three study sites were located in Chiang Mai Province: Yuparaj Witayalai School (YP), Municipality Hospital (HP), Sarapee District (SP) and one site was located in Muang District, Lamphun Province (LP). A map of the sampling sites is illustrated in Fig. 3. YP site is located at the centre of Chiang Mai City. It is a residential area surrounded by government buildings, schools and temples with quite high traffic density. HP site is a densely populated commercial area. It has been reported to possess particulate concentrations exceeding the standard throughout the year (Pengchai, et al., 2009 as cited in Vinitketkumnuen et al., 2002). SP site is surrounded by government buildings and is considered an area experiencing dense traffic within the countryside. There have been significant reports of people suffering from respiratory disease (Pengchai, et al., 2009 as cited in Vinitketkumnuen et al., 2002). LP site is located in a residential area at the centre of Lamphun with light traffic density.

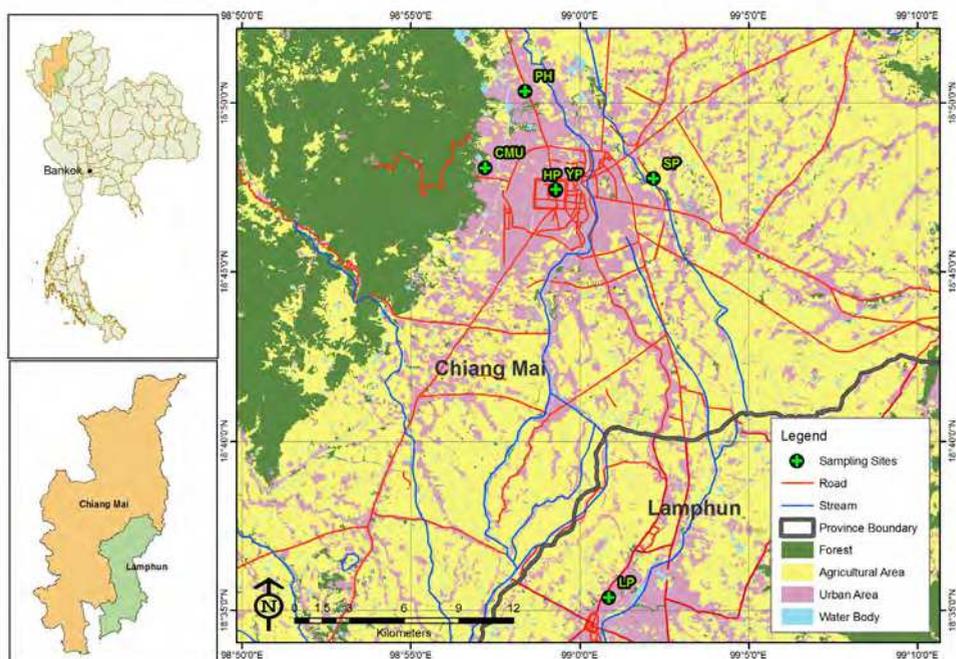


Fig. 3. Map of sampling sites

### 3.1 Ambient PM<sub>10</sub> concentrations

Twenty-four hour PM<sub>10</sub> samples were collected on quartz fiber filters every 3 days at each sampling site using a High Volume PM<sub>10</sub> Air Sampler (Wedding & Associates Inc., USA) at the flow rate of 1,130 L/min. Sampling had been done for 1 year from June 2005 to June 2006 to cover 3 seasonal periods, which were the wet season (June - September), the dry season (December - March) and the transition periods (October - November and April - May). PM<sub>10</sub> samples were weighed using the five digit-scale balance (Mettler Toledo AG285, USA) covered by the temperature and humidity controlling cabinet (DE-300).

PM<sub>10</sub> concentrations of all sampling stations from June 2005 - June 2006 are illustrated in Fig. 4. Their concentrations for all seasons were almost the same. They were lower than 80  $\mu\text{g}/\text{m}^3$  in the rainy season and getting higher in the dry season. The highest concentration was found in March ( $\sim 150 \mu\text{g}/\text{m}^3$ ) at all three sampling sites except at the LP site, which was uncommonly high in April. This was probably due to local activities, such as open burning of community garbage.

Seasonal and spatial variations of mean PM<sub>10</sub> concentrations and their standard deviation (SD) are illustrated in Table 1. It was found that concentrations of PM<sub>10</sub> collected in the dry season (Dec - Mar) were significantly higher than those of the other seasons, while the lowest concentration was found in the rainy season (Jun - Sep). Average PM<sub>10</sub> concentrations in each sampling site were found to be very much similar. However, the

mean concentration of the Sarapee (SP) site was higher than those of the other sites (Chantara et al., 2009).

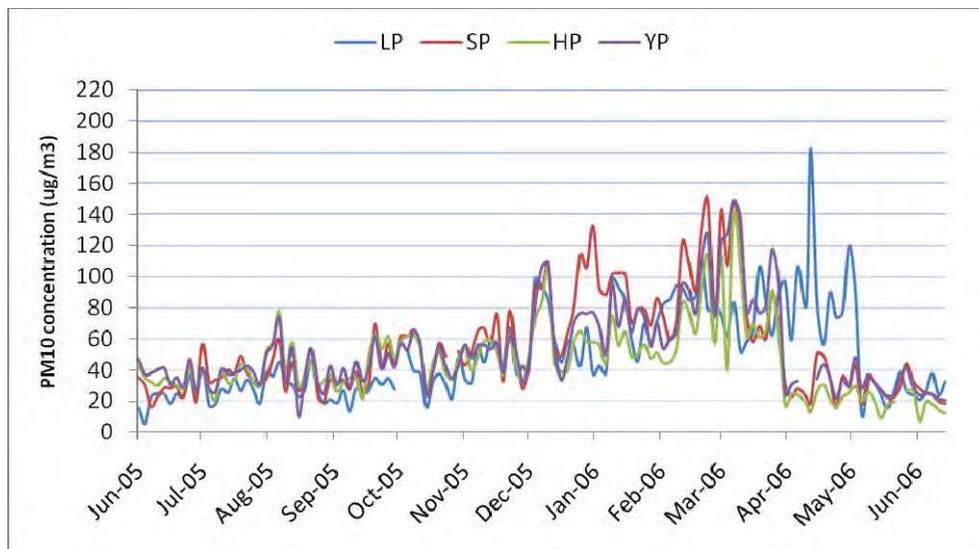


Fig. 4. PM<sub>10</sub> concentrations of all sampling stations from June 2005 – June 2006

Season <sup>a,b</sup>	PM10 concentration	Sampling site <sup>a,b</sup>	PM10 concentration
Dry: Dec – Mar (n = 160)	73.64 ± 25.34 <sup>/7</sup>	LP (n=127)	46.53 ± 29.30 <sup>/1</sup>
Trans I: Apr – May (n = 84)	40.44 ± 25.33 <sup>/2</sup>	SP (n=127)	<b>55.94 ± 36.64</b> <sup>/2</sup>
Rainy: Jun – Sep (n = 184)	33.17 ± 21.39 <sup>/1</sup>	HP (n=127)	44.08 ± 20.60 <sup>/3</sup>
Trans II: Oct – Nov (n = 80)	<b>47.19 ± 12.36</b> <sup>/2</sup>	YP (n=127)	<b>50.30 ± 23.26</b> <sup>/6</sup>

<sup>a/n</sup> number of non detected or incomplete data

<sup>b</sup> Groups of number in *italic* and/or **bold** are not significant different ( $p > 0.05$ )

Table 1. Mean PM<sub>10</sub> concentrations (µg/m<sup>3</sup>) ± SD for 4 periods and 4 sampling sites

#### 4. Analysis of PM10 chemical composition

The post-weighed quartz fiber paper (8 x 10 inches) of the PM<sub>10</sub> sample was equally divided into eight pieces (2.5 x 4 inches) by a stainless steel roller blade cutter. Two of the eight pieces were grouped for the analysis of carbon, PAHs, soluble ions and elements. All fiber samples, except the samples for carbon analysis, were cut into small pieces by stainless steel scissors prior to analysis.

## 4.1 Analysis of total carbon in PM10 samples

### 4.1.1 Analysis method of PM10 carbon content by CHN-S/O analyzer

A tin capsule (1 x 1 cm) as a sample container was weighed by MX5 Automated-S Microbalance (Mettler Toledo). The quartz filter contains PM10 was punched by a puncher with a diameter of 0.55 cm. The punched filter was put into a prepared capsule, wrapped and weighed. The sample was then analysed for total carbon (TC) by Elemental Analyzer (PE 2400 series II CHN-S/O analyzer, Perkin Elmer Cooperation) (Perkin Elmer, 1991) using L-cystine and BS Slag 2 as standards and an unused quartz filter paper as a blank.

### 4.1.2 Carbon content of PM10 samples

Spatial and temporal variations of mean carbon concentrations are shown in Fig. 5. It was found that the distribution pattern of carbon contents in all stations were almost the same. However, the PM10 samples collected at the SP station had higher carbon content than the others. A high concentration of carbon was found in the dry season, especially in March, while in the rainy season the carbon content was low. A correlation of carbon content with PM10 weight (Table 2) revealed that they were strongly correlated in the dry season and the transition period (Apr-May) for all sampling sites. It can be concluded that carbon content was positively correlated to PM<sub>10</sub> weight. However, this consumption relationship can not be applied to the rainy season, in which the correlation was low. It can be explained that low concentrations of PM10 and carbon in the rainy season gave a relatively high variation of values. Moreover, ratios of carbon and PM10 ( $\mu\text{g}/\text{mg PM}_{10}$ ) at all sites were higher in the rainy season than the other seasons. Therefore a correlation was not obviously observed.

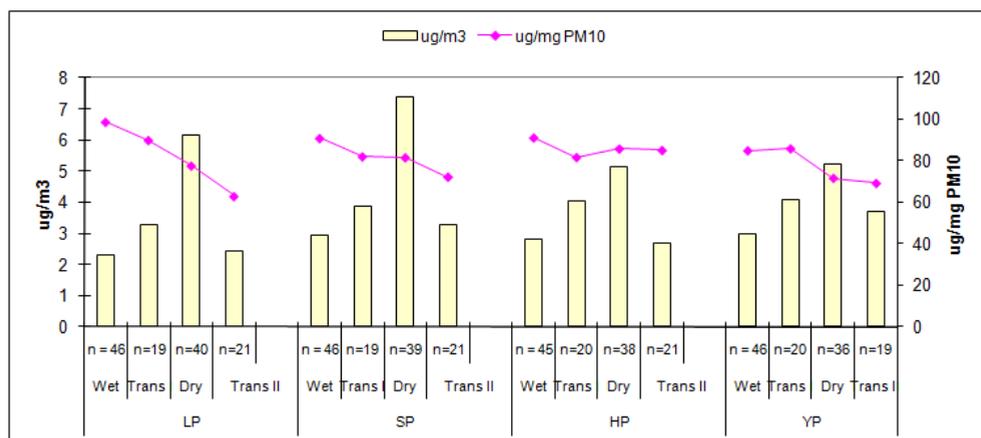


Fig. 5. Spatial and temporal variations of mean carbon concentrations

Carbon concentrations found in this study were compared with the study in Bangkok (Chuersuwan et. al., 2008), in which carbon content in PM<sub>2.5</sub> was determined. The carbon concentrations were  $38.5 \pm 19.3$ ,  $21.7 \pm 12.7$ ,  $21.9 \pm 13.3$  and  $17.6 \pm 11.0 \mu\text{g}/\text{m}^3$  in Din Daeng, Chankasaem, Ban Somdej and Bangna, respectively. The contents were 4-8 times higher

than those found in the PM10 samples in this study. This is probably due to a much higher number of carbon sources, especially in terms of the traffic in Bangkok.

Sampling site	r	Season	r
LP	0.861	Dry (Dec-Mar)	0.849
SP	0.682	Transition (Apr-May)	0.836
HP	0.784	Rainy (Jun-Sep)	0.208
YP	0.798	Transition (Oct-Nov)	0.445

Table 2. Correlation of carbon ( $\mu\text{g}/\text{m}^3$ ) and PM<sub>10</sub> weight (mg)

## 4.2 PM10-bound PAHs

### 4.2.1 Validation of analysis method for PM10 bound PAHs using GC-MS

Gas Chromatography - Mass Spectrometry (GC-MS) (Hewlett Packard, USA) was used for investigation of PAHs in this study. One micro liter of a mixed solution of 16-PAH standards (2,000  $\mu\text{g}/\text{ml}$  in methylenechloride, Restek, USA) and internal standards (D10-ACE, D10-PHE and D12-PYR from Supelco, USA) was injected in splitless mode onto an HP-5MS GC capillary column of 30 m length, 0.25 mm diameter and 0.25  $\mu\text{m}$  thickness internally coated with 5% phenyl methyl polysiloxane stationary phase. Standard solutions of the 16 PAHs with concentrations ranging from 0.005 to 0.500  $\mu\text{g}/\text{ml}$  were combined with 0.10  $\mu\text{g}/\text{ml}$  internal standards and were injected onto the same GC capillary column of the GC-MS employed under an optimum condition in order to obtain a suitable calibration curve in which peak area ratios were plotted against concentrations. The GC condition was as follows. The injector temperature was 275°C. The GC oven was programmed with an initial temperature of 70°C, held for 2 min, then increased to 290°C at 8°C/min. The MS was operated in SIM mode. Characteristic ions of selected PAHs were used for quantification, which was based on the peak area of the PAH standard relative to the deuterated internal standard closest in molecular weight to the analyte. Detection limits of GC-MS for PAHs and recoveries of PAHs from extraction are illustrated in Table 3. Detection limit of GC-MS for an individual PAH was calculated as three times of the standard deviation of blank concentration (Miller & Miller, 1993). Detection limits for 16-PAHs obtained were ranged from 0.003-0.007  $\text{ng}/\text{m}^3$ . Recoveries of PAHs from the extraction of spiked filters ranged from 58-120%. Of all the 16 PAHs investigated, 12 PAHs were found to yield the recovery higher than 70%.

Optimization for the extraction procedure of PAHs in PM 10 samples was conducted using ultrasonication to obtain an appropriate extraction volume of acetonitrile (HPLC grade, Lab-Scan Analytical Science) and evaporation conditions. The quartz filter was cut into small pieces using a pair of stainless steel scissors and the cut filter was put into a 60-ml amber-bottle wrapped with aluminium foil and mounted by paraffin film. The 0.3  $\mu\text{g}/\text{ml}$  of mixed 16-PAH standards was spiked onto the paper, covered and left for 10 min. The spiked samples were extracted in 35 ml acetonitrile by ultrasonicator (T710DH, Elma, Germany) at 100% ultrasound power for 30 min under controlled temperature (approximately 20°C). The

solution was filtered through a 0.45  $\mu\text{m}$  nylon filter and evaporated by low-pressure evaporator at 30°C until it became nearly dry. The pellet was re-extracted in 30 ml acetonitrile by repeating the previous step. The solution was transferred into a 1 ml volumetric flask and a mixed solution of internal standards was added, with the final volume adjusted to 1 ml with acetonitrile. The solution was then analyzed for 16 PAHs by GC-MS. Percent recoveries of individual PAHs were obtained.

Compound	Number of ring	DL (ng/m <sup>3</sup> )	Recovery $\pm$ SD (%)
Naphthalene (NAP)	2	0.006	64 $\pm$ 5
Acenaphthylene (ACY)	3	0.005	76 $\pm$ 6
Acenaphthene (ACE)	3	0.006	66 $\pm$ 6
Fluorene (FLU)	3	0.004	80 $\pm$ 7
Phenanthrene (PHE)	3	0.006	60 $\pm$ 1
Anthracene (ANT)	3	0.004	77 $\pm$ 2
Fluoranthene (FLA)	4	0.003	76 $\pm$ 2
Pyrene (PYR)	4	0.003	72 $\pm$ 1
Benzo(a)anthracene* (BaA)	4	0.007	120 $\pm$ 4
Chrysene* (CHR)	4	0.005	78 $\pm$ 2
Benzo(b)fluoranthene* (BbF)	5	0.006	112 $\pm$ 7
Benzo(k)fluoranthene* (BkF)	5	0.007	84 $\pm$ 4
Benzo(a)pyrene* (BaP)	5	0.005	81 $\pm$ 12
Indeno(1,2,3-cd)pyrene* (IND)	5	0.004	73 $\pm$ 14
Dibenzo(a,h)anthracene* (DBA)	6	0.005	77 $\pm$ 16
Benzo(g,h,i)perylene (BPER)	6	0.007	58 $\pm$ 15

\* carcinogen suspects

Table 3. Detection limits (DL) of GC-MS for PAHs and recoveries of PAHs from extraction

#### 4.2.2 Analysis of 16 PAHs in PM10 samples by GC-MS

After sampling, the weighed quartz filter was cut into small pieces by a pair of stainless steel scissors and put into a 60-ml amber-bottle wrapped with aluminium foil and mounted with paraffin film. The samples were extracted using the same conditions as the standards described above. Each of the sample solutions was then analyzed for 16 PAHs by GC-MS.

Fig. 6 illustrates spatial and temporal variations of PAHs concentrations (Chantara et al., 2010). The highest concentrations of an individual and total PAHs, as well as carcinogenic PAHs, were found in the dry season and were higher than those found in other seasons.

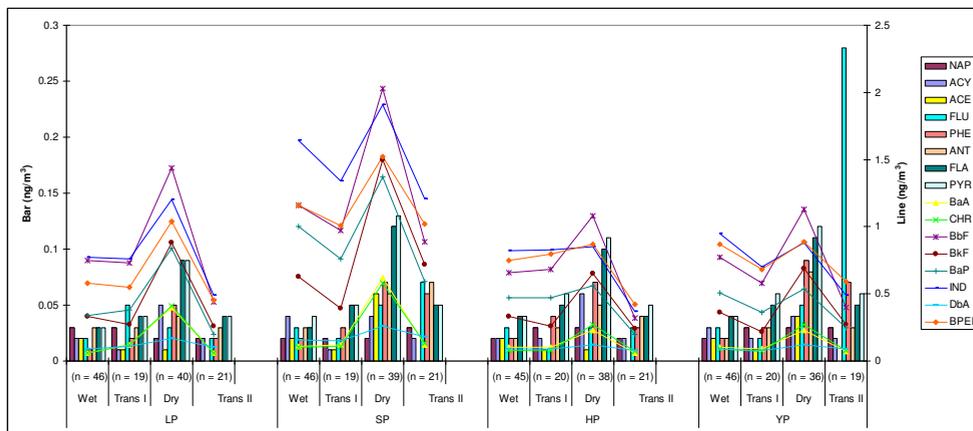


Fig. 6. Spatial and temporal variations of PAHs concentrations

Seasonal variation of PM<sub>10</sub>-bound PAHs can be observed in Table 4 . Mean concentrations of various groups of PAHs including those with 2-3 rings, 4-6 rings, carcinogenic and non-carcinogenic PAHs and sums of 16 PAHs were statistically tested based on the season basis. The results revealed that all PAH groups presented a similar pattern. The highest concentration was found in the dry season (Dec-Mar) and were significantly higher ( $p < 0.05$ ) than the other seasons, in which PAHs concentrations were not significantly different. In terms of the sampling site (Table 5), high molecular weight (4-6 rings) and carcinogenic PAHs were significantly higher at the SP site than the other sites (Chantara et al., 2010).

PAHs <sup>†</sup>	Dec - Mar (n = 160)	Apr - May (n = 84)	Jun - Sep (n = 184)	Oct - Nov (n = 80)
2-3 rings	<b>0.15 ± 0.13</b> / <sup>1</sup>	0.10 ± 0.16 / <sup>2</sup>	0.07 ± 0.04 / <sup>5</sup>	0.08 ± 0.06 / <sup>4</sup>
4-6 rings	<b>6.58 ± 3.20</b> / <sup>1</sup>	<u>2.76 ± 2.05</u> / <sup>2</sup>	4.06 ± 2.96 / <sup>1</sup>	<u>3.59 ± 1.69</u> / <sup>2</sup>
Carcinogenic <sup>‡</sup>	<b>5.29 ± 2.72</b> / <sup>1</sup>	<u>2.05 ± 1.65</u> / <sup>2</sup>	3.15 ± 2.42 / <sup>1</sup>	<u>2.73 ± 1.41</u> / <sup>2</sup>
Non carcinogenic	<b>0.36 ± 0.20</b> / <sup>1</sup>	0.20 ± 0.18 / <sup>2</sup>	0.13 ± 0.06 / <sup>1</sup>	0.18 ± 0.09 / <sup>2</sup>
Total 16 PAHs	<b>6.72 ± 3.20</b> / <sup>1</sup>	<u>2.87 ± 2.08</u> / <sup>2</sup>	4.13 ± 2.97 / <sup>1</sup>	<u>3.67 ± 1.71</u> / <sup>2</sup>

<sup>\*</sup> /<sup>n</sup> number of non detected or incomplete data

<sup>†</sup> Groups of number in *italic*, underline and/or **bold** are not significant different ( $p > 0.05$ )

<sup>‡</sup> Carcinogenic PAHs are BaA, CHR, BbF, BkF, BaP, DBA and IND

Table 4. Mean concentrations (ng/m<sup>3</sup>) ± SD of PM<sub>10</sub>-bound PAHs in the four seasons

PAHs <sup>†</sup>	LP (n=127)	SP (n=127)	HP (n=127)	YP (n=127)
2-3 rings	0.07 ± 0.06 / <sup>5</sup>	0.10 ± 0.09 / <sup>3</sup>	0.10 ± 0.08 / <sup>2</sup>	<b>0.14 ± 0.17</b> / <sup>2</sup>
4-6 rings	3.97 ± 2.53 / <sup>1</sup>	<b>6.93 ± 4.16</b> / <sup>2</sup>	3.58 ± 2.03 / <sup>1</sup>	3.82 ± 1.81 / <sup>2</sup>
Carcinogenic <sup>‡</sup>	3.18 ± 2.12 / <sup>1</sup>	<b>5.57 ± 3.51</b> / <sup>2</sup>	2.71 ± 1.61 / <sup>1</sup>	2.88 ± 1.46 / <sup>2</sup>
Non carcinogenic	0.17 ± 0.11 / <sup>1</sup>	0.23 ± 0.16 / <sup>2</sup>	<b>0.22 ± 0.15</b> / <sup>1</sup>	0.28 ± 0.22 / <sup>2</sup>
Total 16 PAHs	4.04 ± 2.55 / <sup>1</sup>	<b>7.03 ± 4.18</b> / <sup>2</sup>	3.68 ± 2.06 / <sup>1</sup>	3.96 ± 1.84 / <sup>2</sup>

\* /<sup>n</sup> number of non detected or incomplete data

† Groups of number in *italic* and/or **bold** are not significant different ( $p > 0.05$ )

‡ Carcinogenic PAHs are BaA, CHR, BbF, BkF, BaP, DBA and IND

Table 5. Mean concentrations (ng/m<sup>3</sup>) ± SD of PM<sub>10</sub>-bound PAHs from four sampling sites

Table 6 illustrates the ratios of non-carcinogenic and carcinogenic PAHs found in PM<sub>10</sub> samples from each sampling site, which were 1.0:3.7 (LP), 1.0:3.8 (SP), 1.0:2.7 (YP) and 1.0:2.8 (HP). SP and LP ratios revealed that carcinogenic PAHs were obviously higher than non-carcinogenic ones. The highest carcinogenic PAHs content was found at the SP site and was significantly higher than other sites (Table 5). The carcinogenic ratios of all sites found in this study were higher than those found along the roadsides of the inner part of Bangkok (1.0:2.5) from November 02 to April 03 (Norrarnit et al., 2005). This reveals that our study sites presented higher concentrations of carcinogenic PAHs but lower PM<sub>10</sub> content in comparison to the Bangkok area. This fact should be noted and brought into the attention of relevant authorities for subsequent air quality management.

Sampling site	% Non-carcinogenic PAHs	% Carcinogenic PAHs	non-carcinogenic : carcinogenic PAHs
LP	21.3	78.7	1.0 : 3.7
SP	20.8	79.2	1.0 : 3.8
HP	26.4	73.6	1.0 : 2.8
YP	27.3	72.7	1.0 : 2.7
Bangkok (Norrarnit et al., 2005)	28.6	71.4	1.0 : 2.5

Table 6. Ratios of non-carcinogenic to carcinogenic PM<sub>10</sub>-bound PAHs

Mean total PAHs concentrations detected in this study were almost the same as values found in the community area of the previous study (Chantara & Sangchan, 2009) carried out in 2004 (Table 6). However, the concentrations found in this study were obviously lower than those found in Bangkok and Pathumthanee, even under the same category (roadside area) (Boonyatumanond et al., 2007; Norramit et al., 2005; Chetwittayachan et al., 2002; Kim Oanh et al., 2000), but the values were similar to the rural area (Boonyatumanond et al., 2007) and the general area (Chetwittayachan et al., 2002) as is shown in Table 7. This is attributed to the transport pattern and the traffic volume that exist near the sampling site.

Based on the ratios of non-carcinogenic and carcinogenic PAHs found in PM<sub>10</sub> samples from each sampling site (Table 6), the highest carcinogenic PAHs content was found at the SP site.

The carcinogenic ratios of all sites found in this study were higher than those found in roadsides of the inner part of Bangkok from November 02 to April 03 (Norramit et al., 2005) (Table 7). This reveals that our study sites presented higher concentrations of carcinogenic PAHs but lower PM<sub>10</sub> contents in comparison to the Bangkok area. This should be noted and of significant concern for air quality management.

City	Study period	Location	Mean (ng/m <sup>3</sup> )	Reference
Chiang Mai	Jun 05 - Jun 06	Roadside area	1.3-12.2	This study
Lamphun	Jun 05 - Jun 06	Roadside area	1.7-7.4	This study
Chiang Mai	Jun - Nov 04	Traffic area Community area Rural area	7.6-16.6 3.9-9.1 2.7-8.4	Chantara & Sangchan, 2009
Bangkok <sup>a</sup>	Nov 03 - Jan 04	Rural area Roadside area	7.2-10.0 10.1-28.1	Boonyatumanond et al., 2007
Bangkok	Nov 02 - Apr 03	Roadsides	12.59±0.94	Norramit et al., 2005
Bangkok <sup>b</sup>	Mar 01	Roadside area General area	50-53 11-12	Chetwittayachan et al., 2002
Pathumthani (40 km north of Bangkok)	Jun 1996 - Apr 1997	Road site	17.4	Kim Oanh et al., 2000

<sup>a</sup> Sum of concentrations of 18 PAHs: PHE, ANT, 1-methyl PHE, 2-methyl PHE, 3-methyl PHE, 9-methyl PHE, FLA, PYR, BaA, CHR, BbF, BfF, BkF, BeP, BaP, IND, BPER and coronene.

<sup>b</sup> Sum of concentrations of 11 PAHs: ANT, PHE, PYR, BaA, CHR, BbF, BkF, BaP, IND, DBA and BPER

Table 7. Comparison of mean PAH concentrations in Chiang Mai, Lamphun and Bangkok, Thailand

#### 4.2.3 Correlation of PM<sub>10</sub> and PAHs

Correlations between PM<sub>10</sub> content and total PAH concentrations for each sampling site in each season are shown in Table 8. Correlations between PM<sub>10</sub> content and PAH concentrations for all seasons were found to be in the range 0.618 - 0.731. The highest correlation was found in the LP site, while the lowest one was in the YP site. The correlations for all sites were relatively high in the dry season and low in the wet season, respectively. The correlations for the SP and HP sites were high throughout the year; they were also high in the transition periods and were obviously higher than those for the LP and YP sites. This is probably due to local sources, which distributed PM<sub>10</sub>-bound PAHs into the atmosphere during the sampling time period. In terms of PAH source, both SP and HP sampling sites are surrounded by markets with high traffic volume and human activities. The difference between these two places is that the SP site is a place where small scale factories are situated. The fuels used in such factories could have contributed to the level of pollutants emitted to the air.

Season	LP	SP	HP	YP
Wet (Jun-Sep)	0.530	0.549	0.703	0.595
Dry (Dec- Mar)	0.704	0.572	0.601	0.590
Transition period (Apr-May, Oct-Nov)	0.257	0.650	0.690	0.365
All Season	0.731	0.686	0.659	0.618

Table 8. Pearson correlation of PM<sub>10</sub> and PAHs

In comparison to previous studies, the correlation found in this study is almost the same as that reported by Chantara & Sangchan (2009) in which the mass of PM<sub>10</sub> collected by a Minivol air sampler in traffic areas was found to be slightly correlated ( $R^2 = 0.45$ ) with the total PAH concentration of the solution obtained from extraction of the collected particulate. The afore-mentioned correlation was higher than the value in the study by Koyano et al. (1998) in which airborne particulate samples were collected from commercial and residential sites of Chiang Mai from July to December 1989 and their results revealed that there was not a large difference in PAHs concentrations between different sampling sites. However, the airborne particulates and large amounts of rough particulates encountered in their study prompted them to conclude that there was wide spread air pollution throughout the city.

#### 4.2.4 BaP and BaP-equivalent carcinogenic power (BaPE)

The limit value of BaP recommended by WHO is 1 ng/m<sup>3</sup> due to its high carcinogenic property. Other PAHs such as BaA, BbF, BkF and DBA also have carcinogenic potential. To combine these potential carcinogenic compounds, the benzo(a)pyrene-equivalent carcinogenic power (BaPE) is calculated. The BaPE is an index that has been introduced for better denoting aerosol carcinogenicity related to the whole PAH fraction instead of the BaP (Liu et al., 2007). The BaPE was calculated in this study using the following equation:

$$\text{BaPE} = (\text{BaA} \times 0.06) + ((\text{BbF} + \text{BkF}) \times 0.07) + \text{BaP} + (\text{DBA} \times 0.6) + (\text{IND} \times 0.08) \quad (1)$$

Values of monthly mean BaPE and PM<sub>10</sub> concentrations for each sampling site are illustrated in Fig. 7. It can be obviously seen that the BaPE values of the SP site are the highest, while those of the other sites are approximately two times lower. It can therefore be concluded that the air quality of the SP site was worse than the other sampling sites.

Patterns of the BaPE values from June 05 to June 06 were found to be similar for all sites. Fig. 7 shows two peaks of BaPE values. The first peak was obtained in the rainy season (Aug 05) while the second one was obtained in the dry season (Jan-Mar 06). Based on the fact that traffic is the main PAHs source in the urban area, it presents almost the same level of pollutants to the air throughout the year. Therefore, the BaPE values contributed from the traffic should be a background value for all sites. It is quite clear that in the dry season, open burning, i.e. burning of agricultural waste and community garbage, as well as forest fires, mainly contributed pollutants to the atmosphere. In the rainy season, the high BaPE values might have come from other sources. The air pollutants in this season could be from various local activities apart from open burning. One of the possibilities is from small scale factories in the area, whereby seasonal agricultural products are processed.

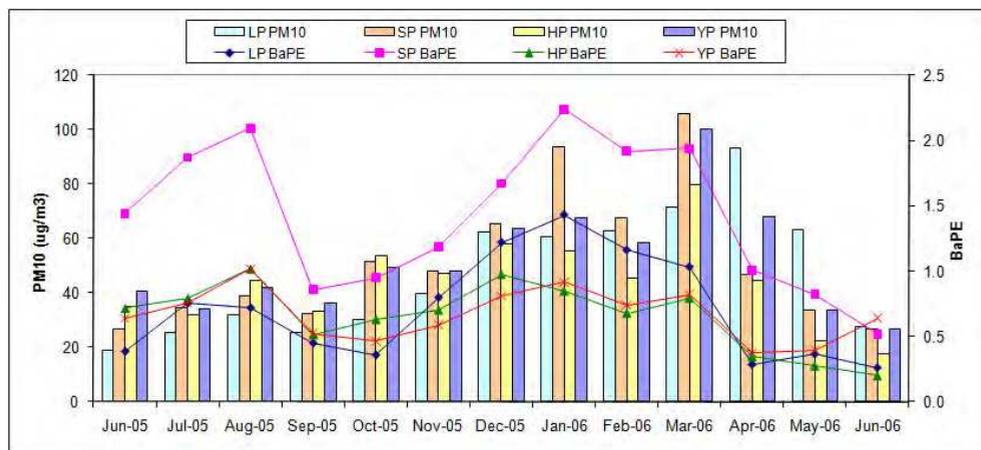


Fig. 7. Monthly mean BaPE and PM10 concentrations from all sampling sites

#### 4.2.5 Diagnostic ratios

Dianostic ratio can be used for the identification of possible emission sources. The diagnostic ratios of this study were calculated by separating sampling sites and months as shown in Table 9 (Chantara et al., 2010). The  $IND/(IND+BPER)$  ratio can be used to identify traffic sources. The value in a range from 0.35-0.70 indicates that the PAHs were emitted from diesel engines (Lui et. al, 2007 and Kavouras et. al, 2001). In this study, the average ratios of all sites were 0.50-0.56. Therefore, the PAHs found in this study could have originated from diesel engine emissions. The  $BaP/BPER$  ratio was also used for characterization of the PAHs sources. The low  $BaP/BPER$  ratio ( $<0.60$ ) is an evidence of greater emission of BPER from traffic sources (Pandey et. al., 1999). The mean ratios of the 4 sampling sites were 0.56-0.80. The mean ratios of HP and YP sites were fitted with the low ratio value, therefore traffic might be the main source for these two sites. However, the ratio values in some months, especially in the dry season were greater than 0.60, which indicated some other PAH sources. The SP and LP sites had a higher mean ratio value (0.80 and 0.64, respectively) as well as monthly values, depicted as *italic* values in Table 9. This could indicate that the PAHs in these two sites were not only from the traffic but were also from some other sources on a similar basis described for the BaPE above. Apart from these two ratios, the  $BaP/(BaP + CHR)$  ratio was also considered. The ratio values of 0.57 and 0.89 could be related to diesel and gasoline exhaust, respectively (Khalili et al., 1995). The  $BaP/(BaP + CHR)$  ratio values obtained in this work were 0.68-0.77, which could be reckoned as somewhere between 0.57 and 0.89. Based on this ratio alone, it could not be concluded what the major source of PAHs was in the areas studied in this work. However, the  $IND/(IND+BPER)$  ratio of 0.50-0.56 obtained in this study fits within the range of 0.35-0.70 which suggests that the diesel engine source plays a more important role than the gasoline source.

	IND/(IND+BPER)				BaP/BPER				BaP/(BaP+CHR)			
	LP	SP	HP	YP	LP	SP	HP	YP	LP	SP	HP	YP
Jun-05	0.54	0.57	0.50	0.48	0.61	0.87	0.63	0.50	0.66	0.57	0.58	0.60
Jul-05	0.53	0.55	0.49	0.48	0.70	1.06	0.66	0.61	0.86	0.79	0.83	0.83
Aug-05	0.61	0.62	0.56	0.55	0.61	0.95	0.70	0.67	0.90	0.83	0.86	0.86
Sep-05	0.57	0.60	0.52	0.52	0.46	0.59	0.48	0.46	0.77	0.71	0.71	0.72
Oct-05	0.60	0.58	0.52	0.52	0.48	0.62	0.51	0.45	0.83	0.78	0.79	0.80
Nov-05	0.56	0.55	0.50	0.50	0.81	0.94	0.69	0.61	0.75	0.77	0.83	0.86
Dec-05	0.52	0.54	0.47	0.48	0.83	1.03	0.64	0.63	0.68	0.66	0.73	0.76
Jan-06	0.52	0.56	0.45	0.46	0.86	0.86	0.66	0.64	0.67	0.56	0.81	0.78
Feb-06	0.57	0.58	0.53	0.52	0.89	1.01	0.71	0.63	0.65	0.62	0.81	0.78
Mar-06	0.55	0.55	0.54	0.54	0.65	0.79	0.59	0.54	0.68	0.55	0.67	0.67
Apr-06	0.52	0.55	0.48	0.48	0.53	0.66	0.50	0.48	0.72	0.49	0.65	0.64
May-06	0.52	0.53	0.45	0.43	0.40	0.50	0.45	0.38	0.79	0.73	0.81	0.77
Jun-06	0.52	0.52	0.47	0.54	0.44	0.56	0.47	0.61	0.88	0.80	0.88	0.80
<b>Avg</b>	<b>0.55</b>	<b>0.56</b>	<b>0.50</b>	<b>0.50</b>	<b>0.64</b>	<b>0.80</b>	<b>0.59</b>	<b>0.56</b>	<b>0.76</b>	<b>0.68</b>	<b>0.77</b>	<b>0.76</b>
SD	0.03	0.03	0.03	0.03	0.17	0.20	0.10	0.09	0.09	0.11	0.09	0.08

Table 9. Diagnostic ratios of PAHs for four sampling sites in different months

## 5. Analysis of dissolved ions in PM10 samples by Ion Chromatography

### 5.1 Ion analysis method by Ion Chromatography

Dissolved ions including  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were analyzed following a method developed from the Technical Document for Filter Pack Method (Acid Deposition Monitoring Network in East Asia, 2003) using Ion Chromatograph (IC). Samples were put into 100 ml beakers followed by 50 ml of deionized water. The beakers were then covered by paraffin film and ultrasonicated at 100% ultrasound power (T490DH, Elma, Germany) for 30 min. The solution was filtered through a cellulose acetate filter (pore size 45  $\mu\text{m}$ , diameter 13 mm) into a plastic bottle for further analysis by IC (Metrohm, Switzerland). Analytical columns were Metrosep A Supp4 (4 x 250 mm) and Metrosep C2 (4 x 100 mm) for anions and cations, respectively.

### 5.2 pH and ion contents of PM10

The extracted samples were divided into 2 parts for pH measurement and ion analysis. The pH distribution for all sampling stations was plotted as shown in Fig. 8. More than 50% of the samples from all sampling sites except the YP station (45%) had pH value less than 5.6. Specifically, half of all the samples from the SP station was in the lower pH range value (<5.0). The seasonal variation of the pH values illustrated that low pH values were inspected in the dry season, particularly in March and April.

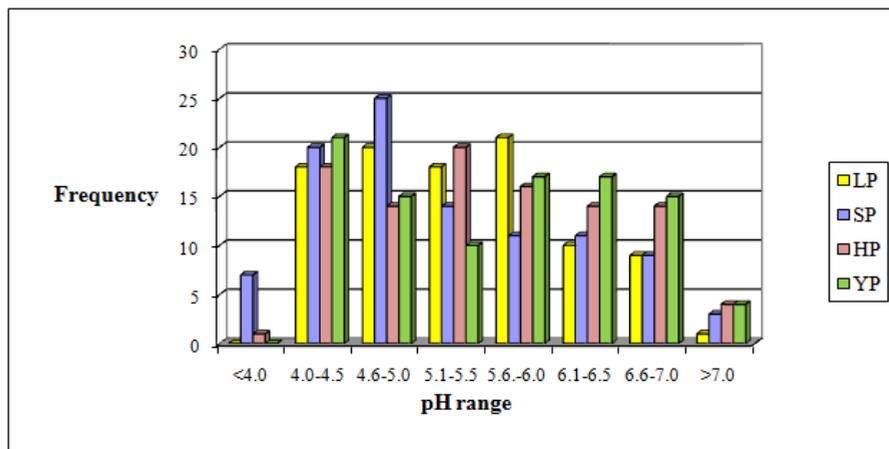


Fig. 8. pH distribution of PM<sub>10</sub> extractions from four sampling stations

Average (SD) concentrations (ng/m<sup>3</sup>) of PM<sub>10</sub>-bound ions in each season and sampling site are shown in Tables 10-11 and Fig. 9. Both anions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>) and cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were significantly higher in the dry period (Dec-Mar) and the transition period I (Oct-Nov) than those found in other seasons (Table 10). The dominant anion and cation were SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, respectively. There was a strong correlation between NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ( $r = 0.953$ ), followed by Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ( $r = 0.651$ ) and K<sup>+</sup> and Cl<sup>-</sup> ( $r = 0.606$ ). This suggested that the main acidity of dry deposition in this region was due to H<sub>2</sub>SO<sub>4</sub>, which was neutralized by NH<sub>4</sub><sup>+</sup> (Chantara & Chunsuk, 2009). Noticeably, K<sup>+</sup> (biomarker of vegetative burning) was significantly 2-3 times higher in the dry season. Therefore, it can be

Ion <sup>†</sup>	Dec - Mar (n = 160)	Apr - May (n = 84)	Jun - Sep (n = 184)	Oct - Nov (n = 80)
SO <sub>4</sub> <sup>2-</sup>	<b>4.02 ± 2.39</b>	2.56 ± 1.92 <sup>/2</sup>	1.20 ± 0.97 <sup>/2</sup>	<b>6.04 ± 5.35<sup>/2</sup></b>
NO <sub>3</sub> <sup>-</sup>	<b>1.84 ± 1.31</b>	0.68 ± 0.61 <sup>/2</sup>	0.46 ± 0.24 <sup>/7</sup>	0.71 ± 0.34 <sup>/2</sup>
Cl <sup>-</sup>	<b>0.33 ± 0.33</b>	0.11 ± 0.10 <sup>/2</sup>	0.15 ± 0.11 <sup>/1</sup>	0.20 ± 0.15 <sup>/2</sup>
<b>Total anions</b>	<b>6.21 ± 3.09</b>	3.35 ± 2.44 <sup>/2</sup>	1.79 ± 1.10 <sup>/1</sup>	<b>6.95 ± 5.35<sup>/2</sup></b>
NH <sub>4</sub> <sup>+</sup>	<b>1.45 ± 1.22</b>	0.96 ± 0.78 <sup>/17</sup>	0.15 ± 0.16 <sup>/7</sup>	<b>1.17 ± 1.06<sup>/4</sup></b>
Na <sup>+</sup>	<b>0.17 ± 0.09<sup>/3</sup></b>	0.11 ± 0.09 <sup>/2</sup>	<b>0.15 ± 0.11<sup>/4</sup></b>	<b>0.16 ± 0.11<sup>/2</sup></b>
K <sup>+</sup>	<b>1.38 ± 0.65</b>	0.56 ± 0.50 <sup>/2</sup>	0.24 ± 0.13 <sup>/1</sup>	0.55 ± 0.46 <sup>/2</sup>
Mg <sup>2+</sup>	<b>0.09 ± 0.17<sup>/3</sup></b>	0.03 ± 0.02 <sup>/2</sup>	0.04 ± 0.04 <sup>/2</sup>	<b>0.09 ± 0.04<sup>/2</sup></b>
Ca <sup>2+</sup>	<b>1.29 ± 0.52</b>	0.92 ± 0.39 <sup>/2</sup>	0.79 ± 0.29 <sup>/1</sup>	<b>1.17 ± 0.43<sup>/2</sup></b>
<b>Total cations</b>	<b>4.38 ± 1.89</b>	2.41 ± 1.55 <sup>/2</sup>	1.36 ± 0.48 <sup>/1</sup>	<b>3.11 ± 1.31<sup>/2</sup></b>
<b>Total ions</b>	<b>10.59 ± 4.62</b>	5.76 ± 3.87 <sup>/2</sup>	3.14 ± 1.49 <sup>/1</sup>	<b>10.07 ± 6.56<sup>/2</sup></b>

\* /<sup>n</sup> number of non detected or incomplete data

† Groups of number in *italic* and/or **bold** are not significant different ( $p > 0.05$ )

Table 10. Mean concentrations (ng/m<sup>3</sup>) ± SD of PM<sub>10</sub>-bound ions in each season

concluded that biomass burning took place in the area during the dry season. Total ion concentrations including total anions and cations were not significantly different among all sites (Table 11). Standing out was the SP site with significantly higher concentrations of some major ions such as  $\text{NO}_3^-$  and  $\text{K}^+$ . This is probably due to a higher frequency or larger scale of open burning happening in the area.

Ion <sup>†</sup>	LP (n=127)	SP (n=127)	HP (n=127)	YP (n=127)
$\text{SO}_4^{2-}$	$2.67 \pm 2.62$ / <sup>2</sup>	$3.39 \pm 3.40$ / <sup>1</sup>	$2.86 \pm 3.16$ / <sup>1</sup>	$3.37 \pm 3.45$ / <sup>2</sup>
$\text{NO}_3^-$	$1.07 \pm 1.21$ / <sup>4</sup>	<b><math>1.16 \pm 1.09</math></b> / <sup>3</sup>	$0.78 \pm 0.78$ / <sup>2</sup>	$0.91 \pm 0.87$ / <sup>2</sup>
$\text{Cl}^-$	<b><math>0.27 \pm 0.28</math></b> / <sup>1</sup>	<b><math>0.31 \pm 0.30</math></b> / <sup>1</sup>	$0.13 \pm 0.11$ / <sup>1</sup>	$0.13 \pm 0.10$ / <sup>2</sup>
<b>Total anions</b>	$3.98 \pm 3.42$ / <sup>1</sup>	$4.84 \pm 3.98$ / <sup>1</sup>	$3.76 \pm 3.44$ / <sup>1</sup>	$4.42 \pm 3.79$ / <sup>2</sup>
$\text{NH}_4^+$	$0.76 \pm 0.92$ / <sup>6</sup>	$1.00 \pm 1.09$ / <sup>8</sup>	$0.79 \pm 1.00$ / <sup>7</sup>	$0.89 \pm 1.13$ / <sup>7</sup>
$\text{Na}^+$	<b><math>0.17 \pm 0.12</math></b> / <sup>1</sup>	<b><math>0.16 \pm 0.10</math></b> / <sup>3</sup>	$0.12 \pm 0.08$ / <sup>3</sup>	$0.14 \pm 0.09$ / <sup>4</sup>
$\text{K}^+$	$0.69 \pm 0.62$ / <sup>1</sup>	<b><math>0.84 \pm 0.73</math></b> / <sup>1</sup>	$0.59 \pm 0.62$ / <sup>1</sup>	$0.68 \pm 0.67$ / <sup>2</sup>
$\text{Mg}^{2+}$	$0.07 \pm 0.11$ / <sup>2</sup>	$0.07 \pm 0.08$ / <sup>2</sup>	$0.06 \pm 0.08$ / <sup>3</sup>	$0.07 \pm 0.14$ / <sup>2</sup>
$\text{Ca}^{2+}$	$0.91 \pm 0.48$ / <sup>1</sup>	$1.00 \pm 0.43$ / <sup>1</sup>	$1.02 \pm 0.39$ / <sup>1</sup>	$1.19 \pm 0.52$ / <sup>2</sup>
<b>Total cations</b>	$2.56 \pm 1.77$ / <sup>1</sup>	$3.02 \pm 1.91$ / <sup>1</sup>	$2.55 \pm 1.69$ / <sup>1</sup>	$2.93 \pm 2.03$ / <sup>2</sup>
<b>Total ions</b>	$6.54 \pm 4.99$ / <sup>1</sup>	$7.85 \pm 5.64$ / <sup>1</sup>	$6.31 \pm 4.83$ / <sup>1</sup>	$7.35 \pm 5.51$ / <sup>2</sup>

\* /n number of non detected or incomplete data

† Groups of number in *italic* and/or **bold** are not significant different ( $p > 0.05$ )

Table 11. Mean concentrations ( $\text{ng}/\text{m}^3$ )  $\pm$  SD of  $\text{PM}_{10}$ -bound ions in each sampling site

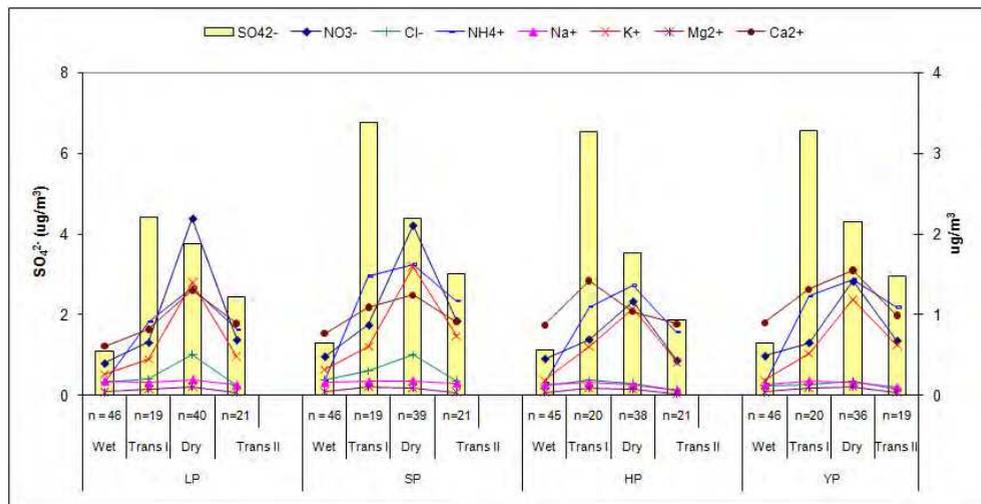


Fig. 9. Spatial and temporal variations of ion concentrations ( $\mu\text{g}/\text{m}^3$ )

Correlations of ion concentrations ( $\mu\text{g}/\text{m}^3$ ) and PM10 weight (mg) were analysed among all sampling stations (Fig. 10a) and among all seasons (Fig. 10b). It was found that almost all ions, except  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , were well correlated with PM10 ( $p < 0.001$ ).  $\text{K}^+$  concentrations and had a very strong correlation with PM10 in every sampling site in the dry season (December – May) and the transition period (April – March). As mentioned above,  $\text{K}^+$  is often used as a tracer for biomass burning. This figure obviously showed the possibility of a high frequency and huge area of open burning, including forest fires and agricultural burning in Northern Thailand and neighboring countries.

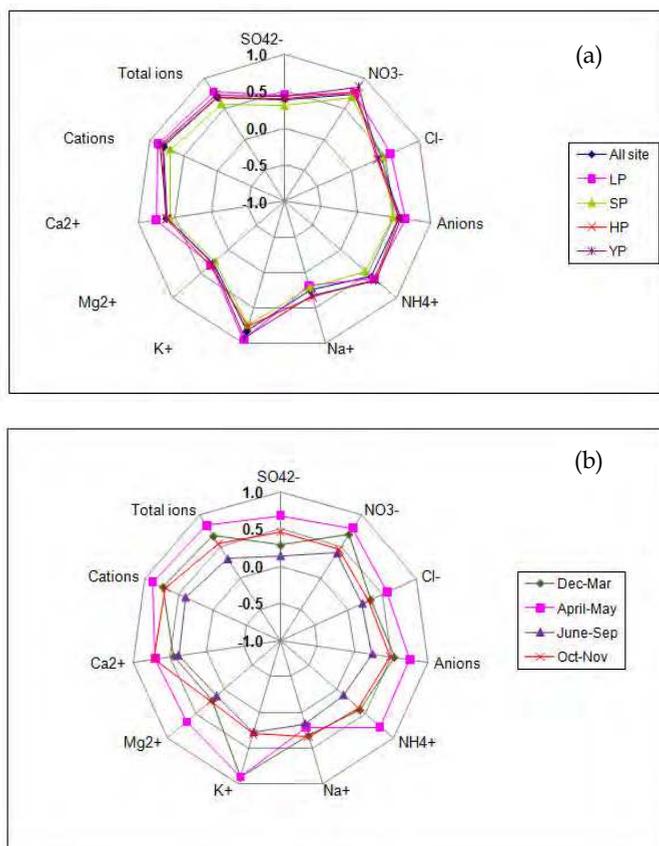


Fig. 10. Correlations between ion and PM10 concentrations; (a) sampling sites and (b) seasons

Table 12 illustrates the major ion composition of PM<sub>10</sub> samples in this study in comparison with other studies, which were 1) ion composition of dry deposition collected by 4-stages filter pack sampler of the Mae Hia sampling site (approximately 7 km southwest from the city center of Chiang Mai) from Oct 05 – Sep 06 and 2) PM<sub>10</sub>-bound ions in the Bangkok area from Feb 02 – Jan 03. It was found that concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  detected in this study were approximately 2 times higher than those in Mae Hia. This is

because Mae Hia is located in a sub-urban area with lower human activities than the stations of this study. When comparing the results of this study with Bangkok, it reveals that  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations were almost the same, while  $\text{SO}_4^{2-}$  of this study was slightly higher. Unsurprisingly,  $\text{Cl}^-$  content in the Bangkok area was 7-10 times higher than that which was found in this study. This must be related with the distance from sea.

Ion	This research (Jun 05 – Jun 06)		Mae Hia, Chiang Mai (Oct 05 – Sep 06)*	Bangkok (Feb 02 – Jan 03) (Chuersuwan, et al., 2008)	
	Min±SD	Max±SD		Min±SD	Max±SD
$\text{SO}_4^{2-}$	2.67±2.62	3.37±3.42	1.55±1.52	1.79±0.59	2.37±0.72
$\text{NO}_3^-$	0.73±0.65	1.13±1.04	0.69±1.04	1.16±0.55	1.45±0.66
$\text{Cl}^-$	0.13±0.11	0.31±0.30	0.29±0.76	1.10±0.56	2.00±0.91
$\text{NH}_4^+$	0.76±0.92	1.00±1.09	0.45±0.50	0.62±0.31	0.94±0.62
$\text{Na}^+$	0.12±0.08	0.17±0.12	0.19±0.30	-	-
$\text{K}^+$	0.56±0.57	0.83±0.71	0.86±2.07	-	-
$\text{Mg}^{2+}$	0.06±0.08	0.07±0.14	0.16±0.34	-	-
$\text{Ca}^{2+}$	0.91±0.48	1.18±0.53	0.69±1.06	-	-

\* Mean values from filter pack samples; dry deposition

Table 12. Mean concentrations ( $\mu\text{g}/\text{m}^3$ )  $\pm$  SD of  $\text{PM}_{10}$ -bound ions in Chiang Mai and Bangkok, Thailand

## 6. Analysis of PM10 bound elements by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

### 6.1 Method efficiency for analysis of PM10 bound elements by ICP-OES

Filter samples were extracted based on Compendium Method IO-3.1 (US. EPA, 1999a) for 20 elements including Ca, Al, Si, Fe, Mg, K, Zn, Ti, P, Pb, Ba, Sr, Mn, Ni, Cu, V, Cr, Cd, Hg and As. They were analysed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Optima 3000 operated with WinLab32TM software) based on Compendium Method IO-3.4 (US. EPA, 1999b). Samples were put into Erlenmeyer flasks followed by the addition of 40 ml of mixed acid solution (5.55%  $\text{HNO}_3$ /16.75%  $\text{HCl}$ ) and refluxed on hot plates for 3 hours. They were left until cool and transferred into 50 ml volumetric flasks. Prior to analysis by ICP, they were filtered through a 0.45  $\mu\text{m}$  syringe nylon filter into plastic bottles.

Percent recoveries of elements were tested by the spiking of 2.50  $\mu\text{g}/\text{ml}$  of mixed standards onto the quartz filter paper and followed the analysis method described above. The recoveries ranged between 76.0% (Mg) to 97.2% (Cr), except for Fe which was quite high

(157%). The instrument detection limit (IDL) ranged from between 0.01 ng/m<sup>3</sup> (Sr) to 5.47 ng/m<sup>3</sup> (K).

### 6.2 PM10 bound elements

Fig. 11 shows the spatial and temporal variation of elements in all sampling sites. Mean concentrations of elements and metals were high in the dry season, except for zinc, for which its concentrations were quite high in the rainy season in every sampling site. Calcium concentration was high all year round in all sampling sites. It was generated from soil re-suspension, which was related to high amounts of particulates being suspended in the air during the dry season. Potassium and silicon concentrations were high in the dry season in every sampling site, especially at the SP site. Both of them were ash elements that were emitted from biomass burning (Demirbas et al., 2008). The result was very well in agreement with the dissolved ion content mentioned earlier.

Toxic metals including lead (Pb), mercury (Hg), cadmium (Cd) and arsenic (As), were detected only in some samples in tracer levels in the dry season as well as in the transition period (Oct-Nov). There was no significant difference of element concentrations in terms of the sampling site.

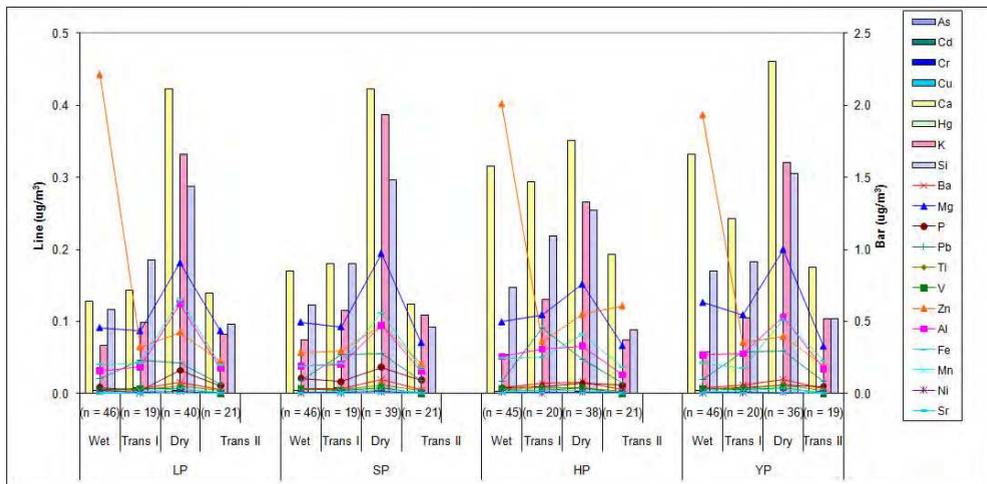


Fig. 11. Spatial and temporal variations of PM10 bound elements

Element concentrations found in this study were compared with the study in the Bangkok area, in which 14 elements were determined from 4 areas including Din Daeng, Chankasaem, Ban Somdej and Bangna, from Feb 02 – Jan 03 (Chuersuwan et al., 2008) (Table 13). It was found that the mean concentration of almost all elements found in the Bangkok area was higher than those in this study. This is probably because sources of elements and heavy metals, especially traffic emissions in Bangkok, were higher both in terms of variations and number.

Element	This research (Jun 05 – Jun 06)		Bangkok (Feb 02 – Jan 03) (Chuersuwan, et al., 2008)	
	Min ± SD	Max ± SD	Min ± SD	Max ± SD
PM10	33.2±21.4	73.6±25.3	57.6±23.9	108.1±35.5
Al	0.27±0.19	0.31±0.43	1.32±0.78	3.02±2.73
As	0.01±0.00	0.02±0.01	0.18±0.13	0.32±0.14
Ca	1.13±1.18	1.67±1.21	1.89±1.50	4.79±2.38
Cr	0.01±0.02	0.02±0.02	0.10±0.05	0.14±0.09
Cu	0.01±0.01	0.02±0.03	0.05±0.02	0.09±0.04
Fe	0.29±0.24	0.37±0.38	1.36±0.69	2.13±0.92
Hg	0.02±0.02	0.03±0.02	-	-
K	0.67±0.75	0.92±0.98	0.55±0.33	1.21±0.72
Mg	0.11±0.09	0.14±0.10	0.49±0.27	0.83±0.32
Mn	0.02±0.01	0.02±0.01	0.07±0.04	0.09±0.09
Ni	0.01±0.01	0.01±0.02	0.03±0.20	0.24±0.31
P	0.01±0.01	0.03±0.03	-	-
Pb	0.04±0.03	0.05±0.08	0.13±0.12	0.22±0.15
Si	0.90±0.68	1.03±0.75	-	-
Sr	0.003±0.003	0.003±0.003	-	-
Ti	0.01±0.01	0.01±0.01	-	-
V	0.01±0.01	0.01±0.01	0.80±0.38	1.13±0.51
Zn	0.07±0.07	0.201±1.023	0.65±0.35	0.84±0.47

Table 13. Min and max concentrations ( $\mu\text{g}/\text{m}^3$ )  $\pm$  SD of mean PM10 and its elemental composition found in this study and in Bangkok, Thailand

## 7. Conclusion

Sampling and analysis of PM10 and its chemical composition in the Chiang Mai – Lamphun Basin, Thailand revealed interesting patterns of ambient PM10 concentrations in the urban areas. The background level of PM10 was mainly generated from traffic volume, which was quite constant throughout the year. Seasonal variation of PM10 levels was quite distinct between the dry and wet seasons. Rain precipitation was a main factor that reduced concentrations of air pollutants, as both particulate and gas phases. In the wet season, a high amount of precipitation scavenges contaminated atmosphere, and the sky becomes clear. In the dry season, there is a low amount of rain and high air pressure leading to air pollutant accumulation. The geographical characteristics of the basin are that it surrounded by a wall of high mountains. Temperature inversion occurs in the dry season, especially in February and March, acting as a lid covering the basin. Heavy haze occurs almost every year in the basin, especially in the past ten years. It was proof that the main sources are open burning,

especially in the way of forest fires and agricultural burning in Northern Thailand and neighbouring countries.

The PM10 chemical composition, including both organic parts (carbon and PAHs) and inorganic parts (dissolved ions and elements & heavy metals) revealed that their concentrations were obviously high in the dry season in all sampling stations. They were well correlated with PM10 concentrations, especially in the dry season. The dominant organic compounds found in the PM10 samples were 4-6 rings PAHs. The ratios of carcinogenic PAHs over non-carcinogenic ones were approximately 3:1-4:1, which was about 1.0-1.5 times higher than those that were reported from the Bangkok area. The BaPE values representing carcinogenic power were highest in the samples taken from the SP site, which is located in the eastern part of the city, and this was due to the higher number of sources, i.e. open burning, street food cooking and small-scale factories. The dominant water-soluble inorganic substances were  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , which showed high amounts of fossil fuel combustion. PM10 major elemental composition was Ca, K and Si, which were reported to be emitted from biomass burning. To reduce air pollution in this area, their sources must be reduced. Open burning from both forest fires and agricultural burning need to be managed. Biomass residues have to be removed or reused for other purposes, such as organic fertilizer, green or bio-fuels for cooking in households, etc., to avoid the practice of large-scale burning. Better management of forest areas in the dry season with plenty of leaf litter is also needed. Apart from that, potential sources of air pollution in the urban area also need to be considered. Mobile sources; traffic volume, number and types of vehicles and fuel used, as well as the point source, such as small scale factories, should also be considered. Air pollution management campaigns are only going to be successful and sustained when the issue is brought, as a priority, into the area of public concern. Moreover, increasing the number of air quality monitoring stations is necessary to cover and represent a wider area. This will, in turn, lead to higher precision and accuracy in recording and interpreting the data for solid air quality management.

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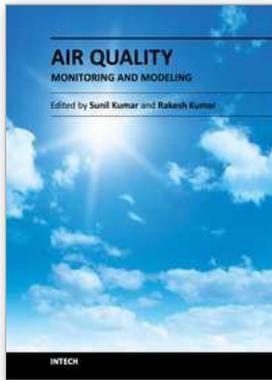
## 9. References

- Acid Deposition Monitoring Network in East Asia (EANET). (2003). *Technical Document for Filter Pack Method in East Asia*, The Third Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.
- Boonyatumanond, R., Murakami, M., Wattayakorn, G., Togo, A., & Takada, H. (2007). Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Science of the Total Environment*, 384, pp. 420-432. ISSN 0048-9697.

- Chantara, S., & Chunsuk, N. (2008). Comparison of wet-only and bulk deposition at Chiang Mai (Thailand) based on rainwater chemical composition. *Atmospheric Environment*, 42, pp. 5511-5518. ISSN 1352-2310.
- Chantara, S., & Sangchan, W. (2009). Sensitive analytical method for particle-bound polycyclic aromatic hydrocarbons; A case study in Chiang Mai, Thailand. *ScienceAsia*, 35, pp. 42-48. ISSN 0303-8122.
- Chantara S., Wangkarn S., Sangchan W. & Rayanakorn M. (2010). Spatial and Temporal Variations of Ambient PM<sub>10</sub>-bound Polycyclic Aromatic Hydrocarbons in Chiang Mai and Lamphun Provinces, Thailand. *Desalination and Water Treatment*, 19, pp. 17-25. ISSN 1944-3994.
- Chantara, S., Wangkarn, S., Tengcharoenkul, U., Sangchan, W. & Rayanakorn, M. (2009). Chemical Analysis of Airborne Particulates for Air Pollutants in Chiang Mai and Lamphun Provinces, Thailand. *Chiang Mai Journal of Science*, 36(2), pp. 001-013. ISSN 0125-2526.
- Chetwittayachan, T., Shimazaki, D., & Yamamoto, K. (2002) A comparison of temporal variation of particle-bound polycyclic aromatic hydrocarbons (pPAHs) concentration in different urban environments: Tokyo, Japan, and Bangkok, Thailand. *Atmospheric Environment*, 36, pp. 2027-2037. ISSN 1352-2310.
- Chiang Mai Meteorological Station. Statistic of Chiang Mai climate. 2 August 2011. Available from <<http://www.cmmet.tmd.go.th/index1.php>>
- Chuersuwan, N., Nimrat, S., Lekphet, S., & Kerdkumrai, T. (2008). Levels and major sources of PM<sub>2.5</sub> and PM<sub>10</sub> in Bangkok Metropolitan Region. *Environmental International*, 34, pp. 671-677. ISSN 0160-4120.
- Demirbas, A. (2008). Hazardous Emissions from Combustion of Biomass. *Energy Sources, Part A*, 30, pp. 170-178. ISSN 1556-7036.
- Furton, K.G., & Pentzke, G. (1998). Polycyclic Aromatic Hydrocarbon, In: *Chromatographic Analysis of Environmental Food Toxicants*, Shibamoto, T. pp. 1-30. Marcel Dekker Inc., ISBN 0824701453, New York.
- Fuzzi, S., Decesari, S., Facchini, M.C., Cavalli, F., Emblico, L., Mircea, M., Andreae, M.O., Trebs, I., Hoffer, A., Guyon, P., Artaxo, P., Rizzo, L., Lara, L., Pauliquevis, T., Maenhaut, W., Raes Chi, N.X., Mayol-Bracero, O., Soto-García, L.L., Claeys, M., Kourtchev, I., Rissler, J., Swietlicki, E., Tagliavini, E., Schkolnik, G., Falkovich, A., Rudich, Y., Fisch, G., & Gatti L. (2007). Overview of the inorganic and organic composition of size-segregated aerosol in Rondonia, Brazil, from the biomass burning period to the onset of the wet season. *Journal of Geophysical Research*, 112(D1), D01201, doi:10.1029/2005JD006741. ISSN 0148-0227.
- Kavouras, I.G., Koutrakis, P., Tzapakis, M., Lagoudaki, E., Stephanou, E., Von Baer, D. & Oyola, P. (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods, *Environmental Science and Technology*, 25, pp. 2288-2294, ISSN 1735 1472.
- Khalili, N.R., Scheff, P.A., & Holsen, T.M. (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions, *Atmospheric Environment*, 29, pp. 533-542, ISSN 1352-2310.
- Kim Oanh, N.T., Bætz Reutergårdh, L., Dung, N.T., Yu, M.H., Yao, W.X. & Co, H.X. (2000). Polycyclic aromatic hydrocarbons in the airborne particulate matter at a location 40

- km north of Bangkok, Thailand. *Atmospheric Environment*, 34, pp. 4557-4563, ISSN 1352-2310.
- Koyano, M., Endo, O., Goto, S., Tanabe, K., Koottatep, S. & Matsushita, H., (1998). Carcinogenic polynuclear aromatic hydrocarbons in the atmosphere in Chiang Mai, Thailand, *Japanese Journal of Toxicology and Environmental Health*, 44(3), pp. 214-225, ISSN 0013-273X.
- Liu, L.B., Hashi, Y., Liu, M., Wei, Y. & Lin, J.M. (2007). Determination of particle-associated polycyclic aromatic hydrocarbons in urban air of Beijing by GC/MS. *Analytical Science*, 23, pp. 667-671, ISSN 0910-6340.
- Mauderly, J.L. & Chow, J.C. (2008). Health effects of organic aerosols. *Inhalation Toxicology*, 20, pp. 257-288, ISSN 0895-8378.
- Metzger, K.B., Tolbert, P.E., Klein, M., Peel, J.L., Flanders, W.D., Todd, K., Mulholland, J.A., Ryan, P.B., & Frumkin, H. (2004). Ambient air pollution and cardiovascular emergency department visits. *Epidemiology* 15, pp. 46-56, ISSN 1044-3983.
- Miller J.C. & Miller J.N. (1993). *Statistics for Analytical Chemistry*, 3<sup>rd</sup> edition, Ellis Horwood, ISBN 0130309907/0-13-030990-7, New York.
- Norramit, P., Cheevaporn, V., Itoh, N. & Tanaka, K. (2005). Characterization and carcinogenic risk assessment of polycyclic aromatic hydrocarbons in the respirable fraction of airborne particles in the Bangkok metropolitan area. *Journal of Health Science*, 51, pp. 437-446. ISSN 1347-5207.
- Pandey, P.K., Patel, K.S. & Lenicek, J. (1999). Polycyclic aromatic hydrocarbons: Need for assessment of health risks in India? *Environmental Monitoring and Assessment*, 59, pp. 287-319. ISSN 1573-2959.
- Patashnick, H., Meyer, M. & Rogers, B. (2002). Tapered element oscillating microbalance technology, *Proceedings of the North American/Ninth U.S. Mine Ventilation Symposium*, Kingston, Ontario, Canada, 8-12 June 2002.
- Pengchai, P., Chantara, S., Sopajaree, K., Wangkarn, S., Tengcharoenkul, U. & Rayanakorn, M. (2009). Seasonal variation, risk assessment and source estimation of PM10 and PM10-Bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand. *Environmental Monitoring and Assessment*, 154, pp. 197-218. ISSN 1573-2959.
- Perkin Elmer Cooperation. (1991). *Users Manual PE 2400 Series II CHNS/O Analyser*, Perkin Elmer, Connecticut.
- Pio, C.A. & Harrison, R.M. (1987). Vapor-pressure of ammonium-chloride aerosol - effect of temperature and humidity. *Atmospheric Environment* 21, pp. 2711-2715. ISSN 1352-2310.
- Pollution Control Department (2011). Regional area air quality data, 2 August 2011, Available from:  
<<http://www.pcd.go.th/AirQuality/Regional/QueryAirThai.cfm?task=default>>
- Pöschl, U. (2005). Atmospheric aerosols: composition, transformation, climate and health effects. *Angewandte Chemie International Edition*, 44, pp. 7520-7540, ISSN 1521-3773.
- Seinfeld, J.H. & Pandis, S.N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley and Sons Inc., ISBN 0-471-17815-2, New York.
- Torigoe, K., Hasegawa, S., Numata, O., Yazaki, S., Matsunaga, M., Boku, N., Hiura, M. & Ino, H. (2000). Influence of emission from rice straw burning on bronchial asthma in children. *Pediatrics International*, 42, pp. 143-150, ISSN 1328-8067.

- U.S. EPA (Environmental Protection Agency): Center for Environmental Research Information, Office of Research and Development. (1999a). *Compendium of methods for the determination of inorganic compounds in ambient air*. Compendium Method IO-3.1., Selection, preparation, and extraction of filter material, Retrieved from <[www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-1.pdf](http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-1.pdf)>
- U.S. EPA (Environmental Protection Agency):Center for Environmental Research Information, Office of Research and Development. (1999b). *Compendium of methods for the Determination of inorganic compounds in ambient air*. Compendium Method IO-3.4., Determination of metals in ambient particulate matter using inductively coupled plasma (ICP) spectrometry, Retrieved from <[www.epa.gov/nrmrl/pubs/625r96010/iocompen.pdf](http://www.epa.gov/nrmrl/pubs/625r96010/iocompen.pdf)>
- U.S. EPA (Environmental Protection Agency). (1999c). *National Air Toxics Program: The Integrated Urban Strategy*, United States Environmental Protection Agency's Federal Register Vol. 64, No. 137,1999, Retrieved from <[www.epa.gov/ttnatw01/urban/fr19jy99.pdf](http://www.epa.gov/ttnatw01/urban/fr19jy99.pdf)>
- Valerie, S., Clare, S. & Aoife, D. (2003). Microwave digestion of sediment, soils and urban particulate matter for trace metal analysis. *Talanta*. 60, pp. 715-723, ISSN 0039-9140.
- Washington State Department of Ecology, (2004). PM<sub>10</sub> Tapered Element Oscillating Microbalance Operating Procedure, In: *Air Quality Program*, 1 September 2011, Available from: <[www.ecy.wa.gov](http://www.ecy.wa.gov) › Ecology home › Publications & Forms>



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