RESEARCH ARTICLE

Vertical Distribution and Potential Risk of Particulate Polycyclic Aromatic Hydrocarbons in High Buildings of Bangkok, Thailand

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Abstract

Vertical variations of polycyclic aromatic hydrocarbon (PAH) concentrations in PM_{10} were investigated in order to assess the factors controlling their behavior in the urban atmosphere of Bangkok City, Thailand. Air samples were collected every three hours for three days at three different levels at Bai-Yok Suit Hotel (site-1 and site-2) and Bai-Yok Sky Hotel (site-3) in February 18th-21st, 2008. The B[a]P concentration showed a value 0.54 fold, lower than the United Kingdom Expert Panel on Air Quality Standard (UK-EPAQS; i.e. 250 pg m^{-3}) at the top level. In contrast, the B[a]P concentrations exhibited, at the ground and middle level, values 1.50 and 1.43 times higher than the UK-EPAQS standard respectively. PAHs displayed a diurnal variation with maximums at night time because of the traffic rush hour coupled with lower nocturnal mixing layer, and the decreased wind speed, which consequently stabilized nocturnal boundary layer and thus enhanced the PAH contents around midnight. By applying Nielsen's technique, the estimated traffic contributions at Site-3 were higher than those of Site-1: about 10% and 22% for Method 1 and Method 2 respectively. These results reflect the more complicated emission sources of PAHs at ground level in comparison with those of higher altitudes. The average values of incremental individual lifetime cancer risk (*ILCR*) for all sampling sites fell within the range of 10^{-7}-10^{-6}, being close to the acceptable risk level (10^{-6}) but much lower than the priority risk level (10^{-4}).

Keywords: Polycyclic aromatic hydrocarbons - vertical distribution - diurnal variation - traffic emissions - Bangkok

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Introduction

Polycyclic aromatic hydrocarbons, particularly benzo[a]pyrene (B[a]P), have been widely acknowledged as a group of persistent organic pollutants (POPs) to be responsible for cancer, endocrine disruption, reproductive and developmental effects (Hoyer, 2001; Matsui, 2008; Liao et al., 2011; Wickramasinghe et al., 2012). In addition to several experimental studies in rat lungs on the carcinogenicity and dose-response of PAHs (Rosenkranz, 1996; Müller et al., 2004; Borm et al., 2005), the role of meteorological parameters on the fate of PAHs has been comprehensively investigated in various places during the past few years (Hong et al., 2007; Tasdemir and Esen, 2007; Tham et al., 2008; Zhang and Tao, 2008; Akyüz and Çabuk, 2009; Amodio et al., 2009; Hanedar et al., 2011; Lee et al., 2011; Choi et al., 2012; Hu et al., 2012; Massei et al., 2003; Tan et al., 2011). Since PAHs are commonly considered as carcinogenic and mutagenic compounds, it is therefore important to comprehend the factors influencing the spatial distribution and temporal variation of PAH contents in the Atmospheric Environment. It is worth stressing that PAHs have complicated emission sources and thus numerous studies focused on characterization of source profiles and source apportionment by using field measurement of particulate PAHs collected from network monitoring stations around the world (Okuda et al., 2002; Yang et al., 2002; Tsapakis and Stephanou, 2005; Pongpiachan, 2006; Wan et al., 2006; Vasconcellos et al., 2010; Oanh et al., 2011; Rajput et al., 2011; Riva et al., 2011). In spite of innumerable publications in the field regarding the diurnal and seasonal variation of PAHs, its vertical distribution in tropical aerosols are still unclear, in particular in Southeast Asian countries where air pollution is a daily concern.

Bangkok city captures an administrative area of 1,569 square kilometers in the Chao Phraya River delta in Central Thailand, and possesses 50 districts under the authority of Bangkok Metropolitan, making it the 73rd largest city in the world. A rapid increase in the number

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of vehicles in Bangkok appears to be responsible for the deterioration of air quality, causing adverse respiratory health effect (Muttamara and Leong, 2002). While the atmospheric concentration of trace gaseous species in residential zones of Bangkok are basically at a satisfactory level, the roadside detection of NO_x and CO frequently exceeds the national air quality standard as issued by the Pollution Control Department (PCD), Ministry of Natural Resources and Environment. For this reason, numerous research studies attempted to clarify the fate of other traffic-originated organic compounds like PAHs in airborne particles in Bangkok's atmosphere (Chetwittayachan et al., 2002; Ruchirawat et al., 2002; 2005; 2007; Boonyatumanond et al., 2007). Since the literature is sparse concerning the atmospheric contents of particulate PAHs in the capital and/or other cities in Thailand (Chetwittayachan et al., 2002; Boonyatumanond et al., 2007; Pengchai et al., 2009; Pongpiachan et al. 2009), it appears problematic to perform the assessment of adverse respiratory health impact caused by exposure to PAHs, particularly in higher altitudes. To the best of our knowledge, there have not been any studies associated with monitoring of PAH contents in different atmospheric layers. Overall, the major aims of this research are to i) study the diurnal variations and vertical distributions of PAHs in PM_{10}, ii) interpret the influence of meteorological factors on behaviors of PAH compositions in PM_{10} and iii) perform a risk assessment of airborne PAHs at three different atmospheric layers at the heart of Bangkok Metropolitan.

Materials and Methods

Sampling sites

Two monitoring sites, explicitly at Baiyoke Suit Hotel (13°45'10.65'' N 100°32'24.92'' E) and Baiyoke Sky Hotel (13°45'15.69'' N 100°32'29.73'' E), were located in the heart of Bangkok Metropolitan, surrounded by tourism spots and shopping streets. Three sampling sites were prudently selected at specific altitudes. Site-1 and Site-2 were placed at Baiyoke Suit Hotel at 38 m and 158 m above ground level respectively, whilst site-3 was situated at Baiyoke Sky Hotel at 328 m above the building basement. It is noteworthy and should be emphasized that Baiyoke Sky Hotel is the highest building in Southeast Asia, and the fourth-highest all-hotel structure in the world. Intensive monitoring campaigns were performed at all monitoring sites simultaneously from February 18th to 21st 2008 in the winter season. PM_{10} samples were taken every three hours sequentially from 2100 h February 18th to 2100 h February 21st by employing Graseby-Andersen High Volume Air Sampler PM_{10} TE-6001 with the flow rate of 1.132 m^3 min^{-1}. A more comprehensive explanation of the air sampling method was given in "Compendium Method IO-2.2. Sampling of Ambient Air for PM_{10} using an Andersen Dichotomous Sampler".

Filter sample collection and meteorological data

Three Graseby-Anderson high volume air samplers TE-6001 were employed to achieve unmanned three-hour and six-hour samplings for PM_{10}. The high volume air samplers were controlled by time, namely, operated from 2100 to midnight, midnight to 0300 and so on. A total of 72 samples (i.e. 24×3=72) were acquired using high volume yielding sample volumes of approximately 180 m^3 for each 3 h sample. Aerosol particles were collected on 20×25 cm Whatman quartz microfibre filters (QMFs) at a flow rate of about 1.133 m^3 min^{-1} (i.e. 40 cfm): Sample air flow rate was calibrated for standard temperature and pressure conditions. After sampling, each of the QMF samples were wrapped by DCM rinsed aluminum foil, sealed in plastic bags and preserved in refrigerator at 4°C until chemical analysis. To estimate potential contamination over field sampling and analytical process, several filed and method blank samples were collected and treated in the same manner as actual aerosol sampling during the observation. QMF samples were cleaned up using DCM by Soxhlet extraction for 8 h prior to use, to remove any potential contamination of PAHs. A versatile sensor suite, Davis Vantage Pro2, was used to record all meteorological parameters such as barometric pressure, temperature, humidity, rainfall, wind speed, wind direction and UV/solar radiation every hour. In addition, PM_{10} mass loadings were measured gravimetrically operated by electronic microbalance Mettler Toledo AB204-S (Columbus (Ohio), USA).

PAHs analysis

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 (d_{12}-perylene (d_{12}-Per), d_{10}-fluorene (d_{10}-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 100μg 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), which were 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. The fractionation/cleanup and blow-down process followed the method reported by Gogou et al. (1996).

The analysis, calibrations and QA/QC procedures were performed at the laboratory of the Inter-Department of Environmental Science, Faculty of Graduate Studies, Chulalongkorn University, Bangkok, Thailand. The samples were analyzed for PAHs using Varian GC/MS-MS system comprising a CP-3900 gas chromatograph (Walnut Creek, CA, USA) with a 1077 universal injector and a three dimensional quadrupole ion-trap selected ion storage mass

spectrometer (Varian Saturn 2200). The target compounds were separated on a 60 m length×0.25 mm i.d. capillary column coated with a 0.25 µm film thickness (phase composition: cross-linked/surface bonded 5% phenyl, 95% methylpolysiloxane. Specified in EPA methods 207, 508, 515, 515.2, 524.2, 525, 548.1, 680, 1625, 1653, 8081, 8141, 8270 and 8280) stationary phase (Agilent JW Scientific DB-5 GC columns). Helium (99.999%) was employed as carrier gas at a constant column flow of 1.0 mL min^{-1} and a pressure pulse of 25 psi with duration of 0.50 min. The chromatographic conditions coupled with the quantification and identification of PAHs was clearly described in a previous study (Pongpiachan et al., 2009). Quantification of the compounds is based upon the Internal Standard (IS) method. One of the fundamental requirements of using an IS is that it displays similar physiochemical properties or the same type of substitution as the analytes because be similar to each other. A relative response factor (RRF) for each native analyte was first determined. This is used for quantification, as the relative response between the internal standard (IS) and the native analyte should remain constant. It is a convenient method because recovery losses of the compound during extraction and analysis are assumed to match those of the IS. The calculation of relative response factor (RRF) is described as follows;

$$RRF=(A_{nat}/A_{is})\times(C_{is}/C_{nat}) \qquad \textbf{Equation 1}$$

Where A_{nat}=Peak area of the native compound in the standard; C_{nat}=Concentration of the native compound in the standard; A_{is}=Peak area of internal standard; C_{is}=Concentration of the internal standard. The RRF_{STD} used for quantifying samples are the mean of those calculated for the two quantification standards run on the same day. Concentration (C) of analytes in sample extracts is calculated using the following formula:

$$C=(A_{nat}/A_{is})\times(1/RRF_{STD})\times(W_s/W_{is}) \qquad \textbf{Equation 2}$$

Where W_{is}=weight of IS added to the sample, W_s=weight or volume of the sample analyzed. Analytical precisions and accuracies were calculated using the standard SRM 1941b. Mean recovery (based on extraction of matrix-matched certified reference materials, (n=8) was in range of 77-119%. 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). In addition, six field blanks from all sampling sites were analyzed to determine the background contamination from the analytical procedure, filter storage and transportation. Pre-cleaned QMFs were taken to the sampling site, exposed to the ambient air by using DCM cleaned tongs for a few seconds, then placed QMFs on the top of pre-cleaned filter media holder. At this stage, QMFs were left inside PM_{10} head high volume air sampler for 3 h. Most individual compounds had blank levels less than 5% of the mean concentrations before correction for blanks level were made and hence blank values for all PAHs detected were subtracted for all samples.

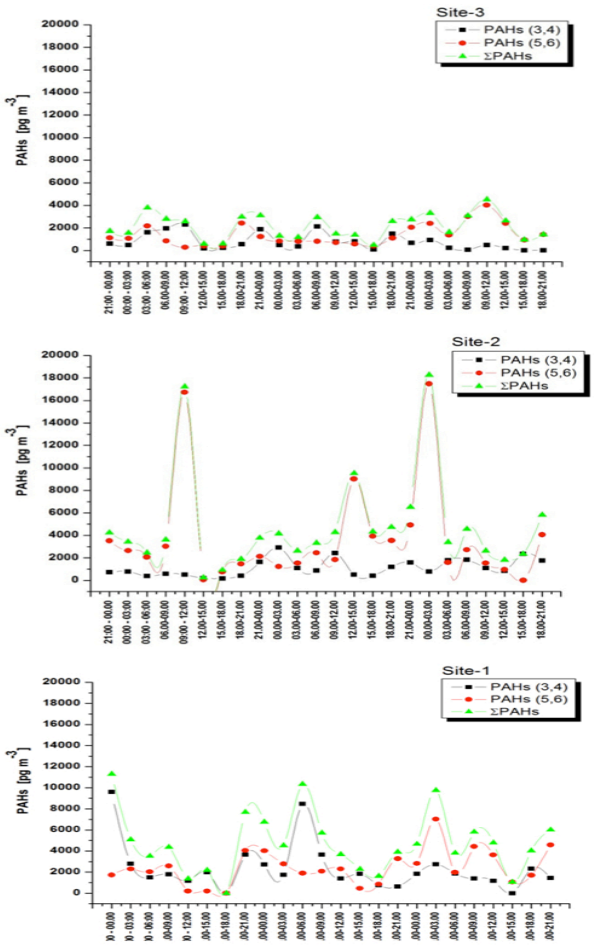

Figure 1. Diurnal Variation of Three-to-Four Ring PAHs (PAHs (3,4)), Five-to-Six Ring PAHs (PAHs (5,6)) and Σ PAHs at Three Sampling Sites from February 18th-21st 2008

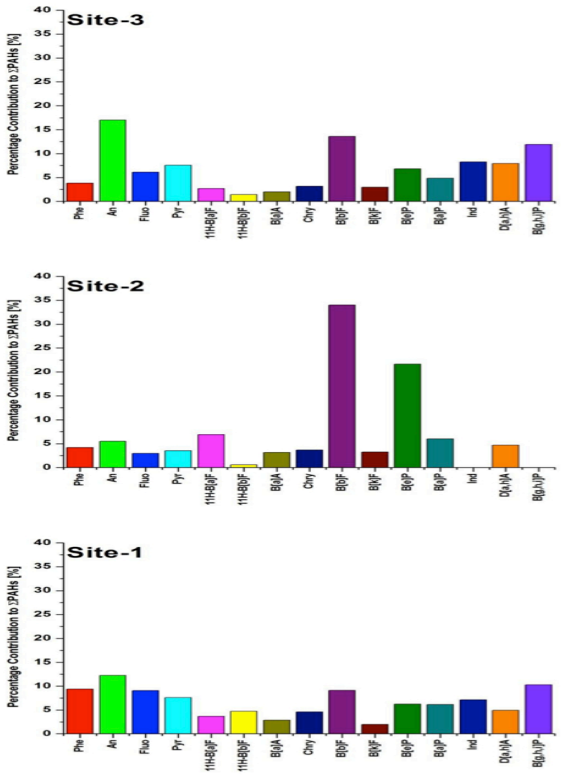

Figure 2. Percentage Contribution of PAH Congeners at Three Sampling Sites from February 18th-21st 2008

Trace gaseous species and water-soluble ionic species analysis

A chemiluminescence $NO/NO_2/NO_x$ Analyzer: Model 200E coupled with state-of-the-art microprocessor technology (Teledyne Technologies Incorporated, USA) was used to detect $NO/NO_2/NO_x$ in this study. The analytical capability of Model 200E ranges from 50 ppb to 20 ppm with the instrumental detection limit of 0.4 ppb. A CO Analyzer: Model 300E (Teledyne Technologies Incorporated, USA) was used for monitoring CO in this study. 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. Three-hour water-soluble ionic species in PM_{10} were also sampled over the monitoring campaign. The operation and QA/QC of instrument and extraction procedure have been previously described (Lai et al., 2007; Tao et al., 2007). For more details, the reader is referred to the aforementioned studies. Seven water-soluble ionic species (WSIS), namely Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+ and Ca^{2+}, in PM_{10} 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 these publications.

Meteorological parameters and statistical analysis

A versatile sensor suite, Davis Vantage Pro2, was employed to record all meteorological parameters, namely barometric pressure, temperature, humidity, rainfall, wind speed, wind direction and UV/solar radiation, every hour. In addition, PM_{10} mass loadings were measured gravimetrically operated by electronic microbalance Mettler Toledo AB204-S (Columbus (Ohio), USA). In addition, 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. All statistical analysis, such as t-Test, ANOVA and PCA were conducted by using SPSS software version 13.0.

Results

All atmospheric PAHs in PM_{10} were identified successfully from February 18th to 21st 2008 (n=72). Table 1 summarizes the concentrations of selected 15 PAHs measured in the 72 samples taken at Baiyoke Suit Hotel and Baiyoke Sky Hotel, which are encompassed by Phetchaburi Road and Rachaprarop Road. These two roads pass from east to west and north to south through Bangkok City respectively, and therefore form main arteries for traffic into and out of the city center on a daily basis. The percentage contributions of 5-6 ring PAHs are 46%, 70% and 56% for Site-1, Site-2 and Site-3 respectively. Statistical description of PAH compositions along with its percentage contributions in each sampling height is displayed in Table 1. PAH mass concentrations at Site-1 ranged from 39.0±60.8 pg m^{-3} (11H-B[b]F) to 472±495 pg m^{-3} (An), and at Site-2 they ranged from N.D. (Ind and B[g,h,i]P) to 2,023±2,638 pg m^{-3} (B[b]F) whilst at Site-3 they varied from 128±83.0 (B[k]F) to 742±932 pg m^{-3} (An). The average concentrations of ΣPAHs (i.e. sum of 15 PAHs) at Site-1, Site-2 and Site-3 were 6,076±6,479 pg m^{-3}, 5,951±7,957 pg m^{-3} and 2,776±2,573 pg m^{-3} respectively.

The average 15 PAH concentration was significantly lower at Site-3 (185±126 pg m^{-3}) in comparison with those detected at Site-1 (405±178 pg m^{-3}, $p<0.001$) and Site-2 (458±560 μg m^{-3}, $p<0.1$). As previously mentioned, the distributions of PAHs at Site-2 are mainly dominated by 5-6 ring PAHs such as B[b]F and B[e]P with a mean concentrations of 2,023±2,638 pg m^{-3} and 1,287±2,633 pg m^{-3} in that order, followed by relatively high contributions of 11H-B[a]F and B[a]P also making an important contribution of 411±530 pg m^{-3} and 358±262 pg m^{-3} respectively. It is crucial to mention that for Site-2, B[b]F alone, with the mean concentration of 2,023±2,638 pg m^{-3} comprises 34% of the ΣPAHs.

On the other hand, the 3-4 ring PAHs are found mainly at Site-1 with percentage contribution of 54%, for instance. An (742±932 pg m^{-3}), Phe (571±565 pg m^{-3}) and

Table 1. Statistic Description of PAH concentrations (pg n^{-3}) in PM_{10} (n=72) and its Percentage Contributions to ΣPAHs

	Phe	An	Fluo	Pyr	11H-B[a]F	11H-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	106±91.1	472±495	169±148	209±341	75.2±90.9	39.0±60.8	54.7±40.4	87.2±55.5	378±238	82.3±116	189±88.9	135±85.5	229±213	220±329	331±180
Site-2	248±231	326±350	178±114	211±168	411±530	33.9±31.8	187±115	217±158	2,023±2,638	192±145	1,287±2,633	358±262	N.D.	279±580	N.D.
Site-1	571±565	742±932	550±1,039	461±419	222±175	289±495	174±138	279±185	554±535	128±83.0	380±270	374±268	434±550	299±297	624±528
Percentage Contribution to ΣPAHs															
Site-3	3.82±3.54	17.0±19.2	6.09±5.74	7.53±13.3	2.71±3.53	1.40±2.37	1.97±1.57	3.14±2.16	13.6±9.27	2.96±4.50	6.81±3.46	4.85±3.32	8.26±8.28	7.93±12.8	11.9±7.00
Site-2	4.17±2.91	5.48±4.40	2.99±1.43	3.55±2.11	6.91±6.66	0.570±0.400	3.13±1.44	3.65±1.99	33.9±33.2	3.23±1.82	21.6±33.1	6.02±3.30	N.D.	4.69±7.23	N.D.
Site-1	9.40±8.71	12.2±14.4	9.06±16.0	7.59±6.46	3.65±2.69	4.76±7.64	2.86±2.13	4.59±2.86	9.12±8.23	2.00±1.28	6.25±4.17	6.16±4.14	7.15±8.49	4.93±4.59	10.3±8.15

Table 2. Atmospheric Concentrations of PAH (pg n^{-3}) in PM_{10} 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
22011	2	Ulsan	Korea[a]	2	ND	5	7	6	47	162	89	NA	2126	40	3,797	10
2012	5	Jeju Island	Korea[b]	172±118	14±8	282±196	210±147	54±40	179±124	244±164	169±113	NA	96±68	175±119	13±10	122±81
2011	5	Zaragoza	Spain[c]	2,300	500	1,100	1,100	300	400	500	100	300	300	1,100	1,100	100
2007	11	Kanazawa	Japan[d]	NA	NA	NA	900±500	400±300	600±400	1,000±700	400±300	NA	700±500	NA	NA	1,300±1,000
2008	9	Lancaster	UK[e]	53,700	1,700	4,380	3,160	750	930	NA	1,500	NA	10	NA	1,500	1,500
2008	10	Valencia	Spain[f]	80	10	180	160	160	190	270	190	NA	150	190	150	200
2009	9	Stuttgart	Germany[g]	40	20	1,170	1,710	850	860	610	660	580	910	430	NA	590
2009	3	Merced	Mexico[h]	561±240	133±50	1,438±630	1,702±780	2,174±1,320	3,132±1,790	3,412±1,960	2,858±1,440	NA	4,004±2,430	5,660±3,150	887±210	7,174±3,610
2009	9	Marseille	France[i]	NA	NA	64,000	31,400	2,450	2,830	360	192	ND	6,730	ND	NA	432
2011	9	Zelzate	Belgium[j]	17,000	149,000	6,400	4,000	1,250	1,960	3,400	900	1,050	950	1,370	680	1,150
2011	11	Stuttgart	Germany[k]	2,030	330	5,050	4,920	2,870	2,100	1,920	1,750	1,800	2,170	1,340	260	1,560
2011	2	Delhi	India[l]	800±400	2,400±1,400	1,700±1,200	4,100±2,100	3,200±1,800	4,400±1,500	8,800±3,500	9,600±3,600	NA	6,900±2,100	13,800±3,500	9,800±4,600	12,500±5,300
2011	3	Helsinki	Finland[m]	2,690	790	5,650	5,850	1,620	1,080	2,790	2,790	NA	1,670	220	NA	1,230
2011	Shenyang	Shenyang	China[n]	4,100	4,300	400	4,400	9,400	6,900	6,800	5,400	NA	5,100	NA	NA	3,500
2011	5	Wellington	New Zealand[o]	4,800	2,100	14,100	18,200	9,700	10,500	900	900	NA	1,700	1,500	200	3,200
2011	5	São Paulo	Brazil	1,600±1,700	1,200±1,000	600±100	2,500±2,800	1,000±500	400±100	800±700	1,700±900	800±200	700±200	1,100±800	900±100	4,300±2,100

[a]Vu et al., 2011, [b]Choi et al., 2012, [c]Callén et al., 2011, [d]Takamura et al., 2007, [e]Halsall et al., 2008, [f]Viana et al., 2008, [g]Bari et al., 2009, [h]Torres et al., 2009, [i]Haddad et al., 2009, [j]Vercauteren et al., 2011, [k]Bari et al., 2011, [l]Singh et al., 2011, [m]Vesteniús et al., 2011, [n]Li et al., 2011, [o]Ancelet et al., 2011, [p]Vasconcellos et al., 2011

Fluo (550±1,039 pg m^{-3}) constructs 12.2%, 9.40% and 9.06% of the ΣPAHs respectively. B[a]P concentrations in all sites ranged from 135 pg m^{-3} to 374 pg m^{-3} with an average of 289 pg m^{-3}, this value is approximately four times lower than the value of the guideline limits of annual B[a]P concentration (i.e. 1 ng m^{-3} or 1,000 pg m^{-3}) proposed by World Health Organization (WHO). However, the average value of 289 pg m^{-3} is slightly higher than the proposed value of 250 pg m^{-3} by the UK Expert Panel of Air Quality Standard (UK EPAQS, 1998). In addition, the atmospheric concentrations of B[a]P explained 6.16%, 6.02% and 4.85% of the ΣPAHs, determined gravimetrically at level-1, level-2 and level-3 in that order.

As illustrated in Table 2, the highest B[a]P concentrations were in New Delhi, India (6,900±2,100 pg m^{-3}), followed by Marseille, France (6,730 pg m^{-3}) and Merced, Mexico (4,004±2,430 pg m^{-3}), while average B[g,h,i]P concentrations were also the highest in New Delhi, India (12,500±5,300 pg m^{-3}), followed by Merced, Mexico (7,174±3,610 pg m^{-3}) and São Paulo, Brasil (4,300±2,100 pg m^{-3}), respectively. Interestingly, the level of B[a]P measured at Site-1 (374±268 pg m^{-3}) was approximately two and 37 times higher than those of Valencia, Spain (150 pg m^{-3}) and Lancaster, UK (10 pg m^{-3}) respectively, but comparable to the average B[a]P concentration observed at Zaragoza, Spain (300 pg m^{-3}). The average B[g,h,i]P concentration at Site-1 (624±528 pg m^{-3}) was in the same order of those observed at Stuttgart, Germany (590 pg m^{-3}), Marseille, France (432 pg m^{-3}), Valencia, Spain (200 pg m^{-3}) and Zaragosa, Spain (100 pg m^{-3}). In addition, the average atmospheric contents of Phe (571±565 pg m^{-3}), An (742±932 pg m^{-3}), Fluo (550±1,039 pg m^{-3}), Pyr (461±419 pg m^{-3}), B[a]A (174±138 pg m^{-3}), Chry (279±185 pg m^{-3}), B[b]F (554±535 pg m^{-3}), B[k]F (128±83.0 pg m^{-3}), B[e]P (380±270 pg m^{-3}), Ind (434±550 pg m^{-3}), D[a,h]A (299±297 pg m^{-3}) detected at Site-1 were comparable to those of Merced, Mexico (561±240 pg m^{-3}), Helsinki, Finland (790 pg m^{-3}), São Paulo, Brasil (600±100 pg m^{-3}), Jeju Island, Korea (210±147 pg m^{-3}), Valencia, Spain (160 pg m^{-3}), Valencia, Spain (190 pg m^{-3}), Zaragosa, Spain (500 pg m^{-3}), Zaragosa, Spain (100 pg m^{-3}), Zaragosa, Spain (300 pg m^{-3}), Stuttgart, Germany (430 pg m^{-3}) and Stuttgart, Germany (260 pg m^{-3}) respectively.

Discussion

Diurnal variation of PAHs

Little information is known about the possible variation of PAHs in the tropical atmosphere between day and night. Many factors such as fluctuation of source strength, ambient temperature variation, chemical reactions with trace gaseous species and OH radicals could change the concentrations of particulate PAHs. It should be emphasized that PAHs taken from 24-hour samples cannot describe those factors, which govern the diurnal fluctuations. Thus it is important and interesting to acquire such data, especially for a very large city like Bangkok where air pollutants are known to be mainly a mixture of traffic emissions combined with industrial and cooking activities. Since all sampling sites are situated in "Pratunam (or Watergate in Thai)", one of the largest night market areas in Bangkok, it appears reasonable to consider the daily ΣPAHs mass concentration maximum at 2100-0000 (Day1-Site-1, Day3-Site-2, Day2-Site-3), 0000-0300 (Day3-Site-1) and 0300-0600 (Day2-Site-1, Day1-Site-3) as

consequences of continuous nighttime traffic emissions coupled with lower nocturnal mixing layer, which can appreciably increase atmospheric chemical compositions, as documented by Wilson and Stockburger (1990) and Beyrich (1997). It is worth mentioning that the maximum peak detected during the period of 0900-1200 at Day1-Site-2, Day2-Site-2 and Day3-Site-3 reflects the crucial impact of morning rush hours on enhancements of particulate ΣPAHs. The decreased wind speed and stabilized nocturnal boundary layer around midnight influenced by vertical temperature profile detected by weather balloon coupled with radiosonde, can decelerate atmospheric dispersion and hence increase the contents of nighttime ΣPAHs. By contrast, the midday minimum ΣPAHs concentrations during the period of 1200-1500 (Day3-Site-1, Day1-Site-2, Day2-Site-2, Day3-Site-2, Day1-Site-3) and 1500-1800 (Day1-Site-1, Day2-Site-1, Day2-Site-3, Day3-Site-3) can be governed by i) the relatively low vehicle density during the daytime, ii) the expansion of mixing layer in midday which causes the dilution effects, iii) the greater dispersion triggered by relatively high wind speed in midday and iv) the fact that noodle stalls and barbecue peddlers were for the most part closed during the period of 1200-1500.

Apart from meteorological conditions that might govern both vertical distributions and diurnal variations, it is also crucial to address the issue of positive sampling artifacts, particularly during the nighttime with relatively low temperature. Several factors govern the sampling artefacts in both particulate and gaseous three-to-four ring PAHs (i.e. Phe, An, Fluo, Pyr, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry), which are categorized as semi-volatile organic compounds (SVOCs). The adsorption of gaseous SVOCs onto a filter can cause positive biases in the measured particle-phase concentrations, and negative biases in the measured gas-phase concentrations (McDow and Huntzicker, 1990; Hart and Pankow, 1994; Turpin and Huntzicker, 1994). In order to investigate the sampling artefact effect, gas/particle partitioning can be parameterised using the coefficient K_p (m^3 μg^{-1}):

$$K_p = c_p / c_g \quad \textbf{Equation 3}$$

Where c_p is the measured particle-phase concentration (μg μg^{-1}) and c_g is the measured gas-phase concentrations (μg m^{-3}) respectively. The length of time over which sampling take place, the filter type of interest, the ambient temperature are the main factors which control the K_p values and therefore the sampling artefacts (Mader and Pankow, 2000a; 2000b).

To minimize the sampling artefacts, the monitoring time should be kept to a minimum to avoid fluctuations in temperature and concentration during sampling and thus the observatory period of this study was selected as three hours. The selection of filter type is also one of the most significant factors in controlling the measured gas/particle partitioning in ambient air. Mader and Pankow (2000a and 2000b) investigated the sampling artefacts in Teflon membrane filters (TMFs) and quartz fibre filters (QFFs). It is well known that the TMFs have less surface area than the QFFs, thus the QFFs can be expected to be more absorptive than the TMFs. It was therefore assumed that the proportion of SVOCs adsorbed on QFFs are large compared to that adsorbed to TMFs (Mander and Pankow, 2000a; 2000b). By normalizing a gas/filter Kp value by the surface area a_f (m^2 g^{-1}) of the filter yields.

$$K_{p,s}[m] = [K_p(m^3 \mu g^{-1})] / [10^{-6}(g \mu g^{-1}) \times a_f(m^2 g^{-1})] \quad \textbf{Equation 4}$$

Log $K_{p,s}$ values for PAHs on QFFs were on average a factor of two higher than those for PAHs found on TMFs. This result can also be explained by the larger surface area and higher energy surface of the QFFs resulting in a greater adsorptive affinity. The effects of temperature T (K) on the measured $K_{p,s}$ values were studied over the range 285-299 K. A 10° increase in T resulted in decreases in the $K_{p,s}$ values of PAHs, PCDFs and PCDDs by factors of 2.4, 3.1 and 3.4 respectively (Mader and Pankow, 2000). Since QFFs was selected for this study and hence it is important to take the "filter type" effect into consideration when compare the PAH data with those collected by TMFs and/or GFFs (Glass Fibre Filters).

Table 3. Average Daytime (i.e. 0600-1800) and Nighttime (i.e. 1800-0600) PAH Concentrations in PM_{10} Collected at Site-1, Site-2 and Site-3 and T-Test Results ($p<0.05$)

	Site-1			Site-2			Site-3		
	Daytime	Nighttime	T-Test	Daytime	Nighttime	T-Test	Daytime	Nighttime	T-Test
Phe	675±842	527±484	NS	306±157	215±271	NS	168±129	75±57	NS
An	592±559	865±1,168	NS	47	420±363	NS	364±536	562±489	NS
Fluo	319±163	743±1,397	NS	169±132	185±100	NS	172±202	166±94	NS
Pyr	299±174	583±509	NS	205±225	217±92	NS	485±544	84±34	NS
11H-B[a]F	200	229±213	NS	388±595	434±503	NS	101±120	52±47	NS
11H-B[b]F	31±23	522±602	S	21±17	47±39	NS	45±73	34±52	NS
B[a]A	192±170	162±119	NS	164±110	215±121	NS	53±47	57±35	NS
Chry	314±150	248±216	NS	206±157	228±165	NS	78±57	97±54	NS
B[b]F	225±270	853±549	S	2,669±3,732	1,431±679	NS	359±253	395±234	NS
B[k]F	102±72	133±90	NS	217±162	171±132	NS	101±167	65±28	NS
B[e]P	300±209	459±308	NS	895±890	1,679±3,665	NS	151±95	227±66	NS
B[a]P	242±216	506±255	S	357±269	360±268	NS	124±112	146±50	NS
Ind	174±225	695±662	S	N.D.	N.D.	NS	205±247	249±191	NS
D[a,h]A	368±364	231±212	NS	43±67	594±862	NS	203±360	268±260	NS
B[g,h,i]P	453±483	859±523	NS	N.D.	N.D.	NS	298±224	353±151	NS
ΣPAHs	3080±1917	6,450±2,738	S	4791±4621	4,883±4,375	NS	2,009±1,270	2,282±906	NS

Table 4. Average PAH Concentrations of All Sampling Sites at Different Monitoring Periods and ANOVA Test Results

Sampling Period	Phe	An	Fluo	Pyr	11H-B[a]F	11H-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	ΣPAHs
0600 - 0900	273±102	1044±827	279±157	466±367	281±281	32.9±24.1	192±167	222±136	680±662	111±70.0	420±170	291±203	326±249	390±415	677±478	3,921±1,218
0900-1200	92.3±94.2	300±321	297±210	281±323	60.8±13.3	45.1±80.2	120±97.8	153±74.4	2,311±4,359	143±164	763±1,025	313±245	307±348	301±390	582±491	5,223±5,159
1200-1500	607±708	385±623	88.7±73.1	96.1±62.5	414±680	31.5±34.2	53.2±36.1	103±102	556±850	241±251	211±315	141±183	79.2±98.1	79.1±137	220±173	1,896±1,237
1500-1800	319	403±198	220±194	261±218	50.7±45.0	19.0±15.2	125±128	223±248	662±761	127±165	325±389	193±243	66.4±59.3	158±342	131±92.8	2,132±2,137
2100-0000	243±454	606±453	766±1,649	407±571	144±163	253±416	124±142	162±193	1,092±841	137±106	1,768±4,105	375±274	536±778	474±745	299±228	6,286±5,308
0000-0300	272±303	470±527	224±120	225±121	330±615	27.7±23.9	139±121	278±174	873±641	118±102	386±321	260±240	378±247	377±181	752±666	3,785±2,482
0300-0600	341±363	1,419±1,749	211±157	299±381	102±113	308±576	171±121	172±129	723±575	101±83.5	389±158	340±238	291±245	97.8±89.2	425±223	3,849±2,675
1800-2100	327±405	279±315	217±60.5	288±271	252±314	272±520	92.8±62.1	117±116	957±626	138±132	474±419	365±322	674±692	318±313	624±379	4,129±2,329
ANOVA Test	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

*S: Significant at p<0.05, **NS: None-Significant at p<0.05

T-Test and ANOVA

T-Test was conducted to investigate if there are any significant differences between the average daytime (i.e. 0600-1800) and nighttime (i.e. 1800-0600) PAH concentrations in PM_{10} collected at Site-1, Site-2 and Site-3. As illustrated in Table 3, the average nighttime ΣPAHs at Site-1 was approximately two times higher than those of daytime with the confidence level of 95%, whilst no significant differences between the average daytime and nighttime PAHs were observed in other sampling sites. In particular, there are only four PAH congeners at Site-1 namely 11H-B[b]F, B[b]F, B[a]P and Ind that are significantly higher during nighttime. Therefore, it seems rationale to interpret the relatively high PAH contents from 1800-0600 at Site-1 as results of heavy traffic congestion, charcoal burning from noodle stalls, barbecue peddlers and the reduction of mixing layer growth rate during nighttime. As the altitude increases within urban boundary layer, the mixing rate of air pollutants enhances and thus triggers the dilution effects. Hence, there are no significant differences between the average daytime and nighttime of any PAH congeners detected at Site-2 and Site-3.

Further statistical examinations on average PAH contents at eight different sampling periods (i.e. 0600-0900, 0900-1200, 1200-1500, 1500-1800, 2100-0000, 0000-0300, 0300-0600, 1800-2100) were performed by using PAH data at all sampling sites and analyzed by ANOVA technique as illustrated in Table 4. Although the highest and lowest levels of ΣPAHs were detected at the period of 2100-0000 (6,286±5,308 pg m^{-3}) and 1200-1500 (1,896±1,237 pg m^{-3}) respectively, there is no significant difference among average PAH levels at eight different sampling periods. This reflects that PAHs remain fairly homogeneous throughout the air mass at all sampling heights during the monitoring period. The fact that the maximum of average ΣPAHs content was observed at 2100-0000 raises public concern over the potential human health effects of exposures to PAHs through nighttime activities at the heart of Bangkok Metropolitan. In addition, the vertical expansion of air mass during 1200-1500 appears responsible for the minimum value of average ΣPAHs from midday to afternoon.

In order to investigate the effect of photodecomposition on PAH contents at different altitudes, PAHs were compared and defined as sum of 3-4 ring PAHs (sum of Phe, An, Fluo, Pyr, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry; PAHs (3,4)) and 5-6 ring PAHs (sum of B[b]F, B[k]F, B[e]P, B[a]P, Ind, D[a,h]A, B[g,h,i]P; PAHs (5,6)) for medium and high MW PAHs respectively. In spite of the fact that PAHs (5,6) contents were higher than those of PAHs (3,4) at all sampling altitudes, no statistically significant differences were observed during daytime (i.e. 0600-1800) at the confidence level of 95% (see Table 5). Hence, it seems logical to assume that photolysis plays a minor role in removal process of particulate PAHs during the monitoring period, particularly at the air mass adjacent to ground level. Interestingly, the average contents of PAHs (5,6) were significantly higher than those of PAHs (3,4) at Site-2 and Site-3 during nighttime (i.e. 1800-0600) at the confidence level of 90%. Since there are only two major PAH emission sources close to the observatory sites, namely vehicular traffic exhausts and cooking emissions, it appears reasonable to consider noodle stalls and barbecue peddlers from night markets as major contributors of PAHs at nighttime.

Evaluation of traffic contribution on PAHs level at high altitude

The impact of traffic emission to particulate PAH concentrations at high altitude can be investigated by using a similar concept as conducted by Nielsen et al. (1996). Since site-3 locates only 290 meters higher than Site-1, it appears reasonable to ignore the contributions to PAH aerosol concentrations caused by non-traffic sources and atmospheric chemical and/or physical processes. Thus the only difference in particulate PAH concentrations between Site-1 and Site-3 could be attributed to traffic emissions. A similar concept had been introduced to Copenhagen and Birmingham as investigated by Nielsen et al. (1996), Lim et al. (1999), then followed by Laurie (2002). In order to apply Nielsen method, firstly the significance of B[*e*]P as an indicator of PAH pollutions was tested by calculating correlation coefficients of individual particulate PAHs against B[*e*]P. Secondly, the traffic emission profiles of PAHs were produced by using the method of Nielsen et al. (1996). Finally, the evaluations of PAH traffic contributions

coming from vehicular exhaust gases were estimated by using the methods of B[*g,h,i*]P/B[*e*]P ratios (Lim et al., 1999; Laurie, 2002).

Several studies suggested that B[*e*]P can be used as an indicator of PAH pollutions due to its high stability in atmospheric environment (Nielsen et al., 1996; Menichini et al., 1999; Wan et al., 2006). In this study, B[*e*]P was also selected as a profile index because of its relative stability in the atmosphere, which ensures that the differences in PAH profile between two sites were the result of traffic and not caused by atmospheric chemical reaction. The average of correlation coefficients and its significance levels of individual PAHs with B[*e*]P for both Site-1 and Site-3 were calculated. Most of individual PAHs showed appreciable correlations with B[*e*]P, supporting the concept of using B[*e*]P as an indicator of PAHs pollution in urban air. For instance, the correlation coefficients between B[*e*]P and B[*a*]P, Ind, D[*a,h*]A, B[*g,h,i*]P were higher than 0.7, whilst those of Phe, An, Fluo, Pyr were lower than 0.2. Three-to-four ring PAHs were not significantly correlated with B[*e*]P at both sites, as would be reflected to the different atmospheric loss mechanism (e.g. chemical reactions with OH and NO_3 radicals, photo-degradation and wet/dry depositions). The poor correlation between low molecular weight PAHs and B[*e*]P had been previously reported at the University of Birmingham monitoring sites, namely Bristol Road Observatory Site (BROS) and Elms Road Observatory Site (EROS), by Lim (1999) and Laurie (2002) indicated another potential source/sink of these compounds.

To obtain a PAH traffic emission profile, delta (δ)PAHs was plotted against δB[*e*]P where δPAHs and δB[*e*]P are the differences of individual PAH concentrations and B[e]P taken at two sampling sites respectively. Traffic emission profiles were established by slopes of linear regression analysis of the δPAHs values against B[*e*]P values with the y-axis forced to zero. Nielsen (1996) and Lim (1999) had made the assumption of this method that i) appreciable positive correlation between δPAHs and B[*e*]P should be observed and ii) traffic emissions are the major sources of atmospheric PAHs in urban air. By contrast to the study from an individual vehicle in tunnel, which provided only PAHs data originated from an individual car, this method provides practical information related to more realistic traffic emission sources in urban air. For the current data an alternative index of high MW PAHs, B[*g,h,i*]P, is considered to be a suitable indicator and was used in two methods for the evaluation of traffic emission. This assumption can be supported by the high δB[*g,h,i*]P/δB[*e*]P ratio of 1.52 coupled with high B[*g,h,i*]$P_{-Site\text{-}1}$/B[*g,h,i*]$P_{-Site\text{-}3}$ ratio of 1.79. Moreover, several studies supported the assumption that the majority of particulate B[*g,h,i*]P is related to traffic emissions (Greenberg et al., 1985; Lodovici et al., 2003; Kalaiarasan et al., 2009). In order to estimate the influence of vehicular emissions on level of PAH contents at both sampling sites, calculations were performed using Method 1 and Method 2 as described below.

Method 1

Mean ***B[g,h,i]P*** concentration at Site-1 and Site-3 were 494 pg m^{-3} and 276 pg m^{-3} respectively, and ***δB[g,h,i]P/δB[e]P*** from the traffic emission profile is 1.52. Thus the concentration of ***B[e]P*** from traffic (***$B[e]P_{traffic}$***) is

Table 5. Statistical Description of Atmospheric Concentration of PAHs (3,4) (i.e. sum of Phe, An, Fluo, Pyr, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry) and PAHs (5,6) (i.e. sum of B[b]F, B[k]F, B[e]P, B[a]P, Ind, D[a,h]A, B[g,h,i]P) Concentrations of All Sampling Sites and t-Test Results

	Site-1		Site-2		Site-3	
	PAHs (3,4) (pg m^{-3}, n=24)	PAHs (5,6) (pg m^{-3}, n=24)	PAHs (3,4) (pg m^{-3}, n=24)	PAHs (5,6) (pg m^{-3}, n=24)	PAHs (3,4) (pg m^{-3}, n=24)	PAHs (5,6) (pg m^{-3}, n=24)
Day Time	1,454±1,000	1,626±1,429	1,002±792	3,789±4,765	773±856	1,235±1,226
t-Test	NS (p<0.05)		NS (p<0.05)		NS (p<0.05)	
	NS (p<0.10)		S (p<0.10)		NS (p<0.10)	
Night Time	3,245±2,862	3,206±1,530	1,235±738	3,649±4,472	780±583	1,503±598
t-Test	NS (p<0.05)		NS (p<0.05)		S (p<0.05)	
	NS (p<0.10)		S (p<0.10)		S (p<0.10)	

*NS (Not Significant) and S (Significant)

Table 6. Statistical Description of Incremental Lifetime Cancer Risk of the Occupational Exposure (*ILCR*) of Each Individual PAH Congener at All Sampling Sites

PAH Congener	TEF[a]	CSF[b] (kg d mg^{-1})	Site-1	Site-2	Site-3
B[a]P	1.00	3.900	$9.62\times10^{-7}\pm6.89\times10^{-7}$	$9.21\times10^{-7}\pm6.75\times10^{-7}$	$3.46\times10^{-7}\pm2.20\times10^{-7}$
B[a]A	0.10	0.390	$4.47\times10^{-8}\pm3.55\times10^{-8}$	$4.80\times10^{-8}\pm2.95\times10^{-8}$	$1.41\times10^{-8}\pm1.04\times10^{-8}$
Chry	0.01	0.039	$7.17\times10^{-9}\pm4.76\times10^{-9}$	$5.58\times10^{-9}\pm4.06\times10^{-9}$	$2.24\times10^{-9}\pm1.43\times10^{-9}$
B[b]F	0.10	0.390	$1.42\times10^{-7}\pm1.38\times10^{-7}$	$5.20\times10^{-7}\pm6.79\times10^{-7}$	$9.71\times10^{-8}\pm6.13\times10^{-8}$
B[k]F	0.10	0.390	$3.13\times10^{-8}\pm2.13\times10^{-8}$	$4.94\times10^{-8}\pm3.72\times10^{-8}$	$2.12\times10^{-8}\pm2.98\times10^{-8}$
Ind	0.10	0.390	$1.12\times10^{-7}\pm1.42\times10^{-7}$	ND	$5.89\times10^{-8}\pm5.48\times10^{-8}$
D[a,h]A	1.00	4.100	$8.10\times10^{-7}\pm8.04\times10^{-7}$	$7.54\times10^{-7}\pm1.57\times10^{-6}$	$5.59\times10^{-7}\pm1.27\times10^{-6}$
Average			$3.01\times10^{-7}\pm2.62\times10^{-7}$	$3.28\times10^{-7}\pm4.28\times10^{-7}$	$1.62\times10^{-7}\pm1.81\times10^{-7}$
Total			$2.11\times10^{-6}\pm1.83\times10^{-6}$	$2.30\times10^{-6}\pm2.99\times10^{-6}$	$1.14\times10^{-6}\pm1.27\times10^{-6}$

[a]TEF: Toxic Equivalency Factor (Nisbet and LaGoy, 1992), [b]CSF: Cancer Slope Factor

Table 7. Principal Component Analysis of PAH Congeners, Water-Soluble Ionic Species, Trace Gaseous Species and Meteorological Parameters Observed at All Monitoring Sites

	Principal Component (PC)		
	PC1	PC2	PC3
Phe	-0.310	-0.030	**0.950**
An	0.301	0.232	**0.925**
Fluo	**0.974**	-0.104	-0.204
Pyr	**-0.963**	-0.119	-0.241
11H-B[a]F	0.223	-0.532	**0.817**
11H-B[b]F	**0.971**	0.231	-0.056
B[a]A	-0.243	0.241	**-0.940**
Chry	**-0.862**	-0.130	-0.491
B[b]F	**-0.925**	0.358	-0.124
B[k]F	**0.846**	0.339	0.411
B[e]P	**0.803**	0.246	0.543
B[a]P	**0.996**	0.038	0.076
Ind	**-0.711**	0.684	0.167
D[a,h]A	**0.996**	-0.059	0.059
B[g,h,i]P	**0.934**	0.356	-0.032
CO	0.314	-0.607	**0.730**
NO_2	-0.408	**-0.910**	0.072
O_3	-0.574	**0.773**	-0.271
Cl^-	0.063	**0.997**	-0.045
NO_3^-	0.183	**0.983**	0.017
SO_4^{2-}	-0.590	**0.807**	-0.037
Na^+	**0.713**	0.667	-0.215
NH_4^+	-0.378	**0.917**	-0.124
K^+	0.382	**0.921**	0.080
Ca^{2+}	0.282	**0.938**	0.200
Temperature	0.462	**0.779**	-0.424
Relative Humidity	-0.038	**-0.872**	0.488
Atmospheric Pressure	0.025	**-0.933**	-0.359
Solar Radiation	-0.446	-0.675	-0.588
Wind Speed	-0.093	0.175	**0.980**
Total of Variance%	**43.2**	**37.2**	**19.6**

calculated as:

$$B[e]P_{traffic}=B[g,h,i]P_{conc.}/(\delta B[g,h,i]P/\delta B[e]P) \quad \textbf{Equation 5}$$

$=494/1.52=325$ pg m^{-3} at Site-1

$=276/1.52=182$ pg m^{-3} at Site-3

The percentages of ***B[e]P*** originating from Site-1 and Site-3 can be given as follows:

$$\%B[e]P_{traffic}=B[e]P_{traffic}/B[e]P_{conc.}\times 100\% \quad \textbf{Equation 6}$$

$=(325/380)\times 100=86\%$ for Site-1

$=(182/189)\times 100=96\%$ for Site-3

Further investigation on impacts of vehicular exhaust emissions at high altitude was attempted by applying Nielsen's method by using the value of ***B[g,h,i]P/B[e]P*** (0.8) as an indicator of non-traffic PAH emission. ***B[g,h,i]P/B[e]P*** ratio of 0.8 deduced from the ratio observed in long range transported polluted air coming from the Continent in Denmark (0.89), the ratio in air samples collected from a Danish village (0.97) and 'pre-traffic' investigation of PAH taken in Copenhagen in 1954-55 (0.87). Thus, the percentage of traffic contribution at a given site can be calculated by solving the following equation in Method 2.

Method 2

$$B[g,h,i]P/B[e]P_{site}=B[g,h,i]P/B[e]P_{traffic}\times fractional\ traffic\ contribution+B[g,h,i]P/B[e]P_{non\text{-}traffic}\times(1-fractional\ traffic\ contribution) \quad \textbf{Equation 7}$$

By input the $B[g,h,i]P/B[e]P_{traffic}$ ratio of 1.52, the $B[g,h,i]P/B[e]P_{non\text{-}traffic}$ ratio of 0.8 as mentioned above and the $B[g,h,i]P/B[e]P_{site}$ ratio of 1.30 and 1.46 for Site-1 and Site-3 into the equation, the fractional traffic contribution were calculated as 69% and 91% for Site-1 and Site-3 in that order. The percentage $PAH_{traffic}$ calculated from Method 2 using data set of Laurie, Lim and Nielsen were 109%, 81% and 84% for the traffic site (BROS) and 79%, 62% and 29% for the urban background site (EROS) respectively. The difference from those values reported by Nielsen, Lim and Laurie can be explained by the differences in sampling locations, vehicle fleet composition and the early years of monitoring in 1990, when the regulations of using catalytic converters in passenger cars were not introduced. Despite these discrepancies observed in previous studies, the results in both methods emphasize the fact that most of PAH aerosols at Site-1 and Site-3 was dominated by vehicular exhausts. It is also worth mentioning that the estimated values of Site-3 were higher than those of Site-1 about 10% and 22% for Method 1 and Method 2 respectively. This can be explained by more complicated PAH emission sources at ground level (e.g. cooking emissions from noodle stalls and barbecue peddlers) overwhelmed air mass at Site-1 whilst Site-3 was plausibly governed by traffic-originated PAHs from all mobile exhausts around Bangkok City.

Occupational exposure to PAHs

In spite of numerous investigations implying that indoor PM_{10} concentrations, PAHs and VOCs were gradually lower than outdoor concentrations, the adequate positive correlations between indoor and outdoor concentrations were detected, indicating that indoor concentrations were to some extent dependent on ambient concentrations (Colome et al., 1992; Ohura et al., 2009; Masih et al., 2010). To the best of our knowledge, there is no available study related to the assessment of health risk associated with the exposure to particulate PAHs of workers and residents living in high buildings of Thailand. Hence, it is crucial to conduct the health risk assessment by using the concept of *B[a]P* equivalent concentration and incremental individual lifetime cancer risk (*ILCR*) as previously reported by Xia et al. (2010) and Chen et al. (2006), respectively. It is common to express the carcinogenic risk of a PAH mixture in form of its B[*a*]P equivalent concentration ($B[a]P_{eq}$) by using the toxicity equivalency factors (TEFs) as developed by Nisbet and Lagoy (1992). TEFs were applied to assess the carcinogenic potency of PAH mixtures in PM_{10}. The $B[a]P_{eq}$ of PM_{10} (BEC) was computed according to Equation (8).

$$BEC_i=\sum_{i=1}^{n} C_i\times TEF_i \quad \textbf{Equation 8}$$

Where: C_i=concentration of PAH congener ***i*** in PM_{10};

TEF_i=toxicity equivalency factors of PAH congener *i*.

Since there are no reports of TEFs for 11H-B[a]F and 11H-B[b]F, the carcinogenic potencies of 13 PAHs (i.e. Phe, An, Fluo, Pyr, B[a]A, Chr, B[b]F, B[k]F, B[e]P, B[a]P, Ind, D[a,h]A and B[g,h,i]P) were estimated as the sum of each individual $B[a]P_{eq}$. The total $B[a]P_{eq}$ concentrations (i.e. sum of $B[a]P_{eq}$ of 13 PAHs) for all sampling sites are 441±484 pg m^{-3}, 896±1,164 pg m^{-3} and 824±717 pg m^{-3} for Site-1, Site-2 and Site-3, respectively. Surprisingly, the total $B[a]P_{eq}$ results showed the potential health risk to cancer due to inhalation exposure is of concern for residents living in Site-2 and Site-3. Two main factors, namely building configurations and wind direction, can be attributed to these relative high $B[a]P_{eq}$ results at higher altitudes. It is also worth mentioning that the total $B[a]P_{eq}$ concentrations for both observatory sites were close to, or vaguely below the maximum permissible risk level of 1,000 pg m^{-3} of B[a]P.

Further estimations on incremental individual lifetime cancer risk (*ILCR*) were conducted by using the model proposed by Chen et al. (2006), which can be defined as follows:

$$ILCR=\left[\left[C_a\left(CSF_{B[a]P}(BW/70)^{1/3}\right)\times IR_{air}\times EF\times ED\right]/(BW\times AT)\right]\times cf \quad \textbf{Equation 9}$$

Where: ***ILCR***=Incremental individual lifetime cancer risk; $CSF_{B[a]P}$=Inhalation cancer slope factor (mg kg^{-1} $day^{-1})^{-1}$; C_a=$B[a]P_{eq}$ concentration (ng m^{-3}); IR_{air}=Inhalation rate (m^3 $hour^{-1}$)=20 m^3 day^{-1} (US EPA, 1991); ***cf***=conversion factor=10^{-6}; ***EF***=Exposure frequency=250 day $year^{-1}$ a, upper-bound value; ***ED***=Exposure duration=70 years (US EPA, 1989); ***BW***=Body weight=57 kg (Average body weight of Asian people) (Walpole et al., 2012); ***AT***=Averaging time for carcinogenic=70 years for carcinogen×365 day/years=25,550 day (US-EPA, 1989), (Note: [a]Adapted from Human Health Evaluation Manual (1991)).

The calculated *ILCR* levels in three different altitudes are summarized in Table 6. The estimated *ILCR* of the sum of B[a]P, B[a]A, Chry, B[b]F, B[k]F, Ind and D[a,h]A were constantly highest at Site-2 followed by Site-1 and Site-3 with values of $2.30\times10^{-6}\pm2.99\times10^{-6}$, $2.11\times10^{-6}\pm1.83\times10^{-6}$ and $1.14\times10^{-6}\pm1.27\times10^{-6}$ respectively. These results are also in good agreement with those average values of *ILCR* detected at Site-2, Site-1 and Site-3 with the values of $3.28\times10^{-7}\pm4.28\times10^{-7}$, $3.01\times10^{-7}\pm2.62\times10^{-7}$ and $1.62\times10^{-7}\pm1.81\times10^{-7}$ respectively. It should be emphasized that both the average and sum of predicted *ILCR* of seven PAHs display the maximum value at Site-2, which is consistent with those trend of the estimated $B[a]P_{eq}$ of PM_{10} (i.e. 13 PAHs) calculated by using Equation 8. Again, the building configuration coupled with wind directions appears responsible for this phenomenon. According to the USEPA, a one in a million chance of additional human cancer over a 70-year lifetime (*ILCR*=10^{-6}) is the level of risk comparable to daily risk exposure (e.g. diagnostic X-rays, fishing, etc.) and thus considered acceptable or negligible (Asante-Duah, 2002). Supplementary lifetime cancer risk of one in ten thousand or larger (*ILCR*=10^{-4}) can be considered as harmful and may request elevated priority for paying attention to inhalation respiratory health problems (Xia et al., 2010). The average values of *ILCR* for all sampling sites fell within the range of 10^{-7}-10^{-6}, being close to the acceptable risk level (10^{-6}) but much lower than the priority risk level (10^{-4}).

Principal component analysis

As illustrated in Table 7, the principal component patterns for Varimax rotated components of three observatory sites composed of three components, which account for 43.2%, 37.2% and 19.6% for the total of variances of PC1, PC2 and PC3 respectively. The contribution of PC1 and PC2 explains 80% of total variance, and moreover PC1 (43.2% of variation) is two times higher than PC3 (19.6%). The main cluster (PC1) contains dominantly PAHs (3,4) (i.e. Fluo, Py, 11H-B[b]F, Chry) and PAHs (5,6) (i.e. B[b]F, B[k]F, B[e]P, B[a]P, Ind, D[a,h]A, B[g,h,i]P) and could be conditionally named "*mix*" since they show strong positive correlation coefficients for Fluo, 11H-B[b]F, B[k]F, B[e]P, B[a]P, D[a,h]A, B[g,h,i]P and negative correlation coefficients of Pyr, Chry, B[b]F, Ind. It is well known that both cooking emissions and vehicular exhausts are major sources of PAHs and thus the strong correlation coefficients of PAHs (5,6) observed in PC1 can be attributed to those emissions derived from transportation, noodle stalls and barbecue peddlers. The strong positive loading on secondary aerosols (i.e. Ca^{2+}, K^+, NH^{4+}) implied that dust particles from nearby building construction and agricultural activities related particles, which were conveyed to Site-2 by long-range transportation, are probably two main sources found in PC2. There are also moderate loadings of O_3 as well as Na^+ and Cl^-, which can be explained as a production of sea spray aerosols from the Gulf of Thailand. PC3 displays high loadings of Ph and An, which are present in high concentrations in vehicular emissions, and moderate loadings of CO. The positive correlations of these three parameters suggest that fuel combustion from transportation was a dominated source in PC3. Finally, the negative loadings of solar radiation can be attributed to higher boundary layer and photochemical activities in daytime, whilst the positive loading of wind speed suggests that wind velocity during nighttime promotes re-suspension of soil dust.

In conclusion, all selected 15 PAHs in PM_{10} measured in the 72 samples were quantified successfully from February 18th to 21st 2008. The nighttime traffic emissions coupled with lower nocturnal mixing layer was responsible for the highest peak of PAHs observed during midnight, whilst the lowest peak observed during midday can be attributed to the relatively low vehicle density, the expansion of mixing layer and the greater dispersion triggered by relatively high wind speed. Besides these meteorological conditions, there are "sampling artefacts" and "filter type" that can significantly influence the variation of particulate PAHs. Nielsen's method highlights the importance of traffic contribution on PAH content levels, particularly at higher altitude. The average values of *ILCR* for all sampling sites fell within the range of 10^{-7}–10^{-6}, being close to the

acceptable risk level (10^{-6}). This indicates a potential risk of developing lung cancer and other respiratory diseases for workers and residents living in high buildings located at Pratunam area. PCA results show 62.8% contribution of both traffic and cooking emissions (i.e. PC1 + PC3) at all observatory sites, emphasizing that anthropogenic sources are the main contributors of PAHs in Bangkok's atmosphere.

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