RESEARCH ARTICLE

Temporal and Spatial Distribution of Particulate Carcinogens and Mutagens in Bangkok, Thailand

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Abstract

To investigate the level of genotoxicity over Bangkok atmosphere, PM_{10} samples were collected at the Klongchan Housing Authority (KHA), Nonsree High School (NHS), Watsing High School (WHS), Electricity Generating Authority of Thailand (EGAT), Chokchai 4 Police Station (CPS), Dindaeng Housing Authority (DHA) and Badindecha High School (BHS). For all monitoring stations, each sample covered a period of 24 hours taken at a normal weekday every month from January-December 2006 forming a database of 84 individual air samples (i.e. 12×7=84). Atmospheric concentrations of low molecular weight PAHs (i.e. phenanthrene, anthracene, pyrene and fluoranthene) were measured in PM_{10} at seven observatory sites operated by the pollution control department of Thailand (PCD). The mutagenicity of extracts of the samples was compared in *Salmonella* according to standard Ames test method. The dependence of the effects on sampling time and on sampling location was investigated with the aid of a calculation of mutagenic index (MI). This MI was used to estimate the increase in mutagenicity above background levels (i.e. negative control) at the seven monitoring sites in urban area of Bangkok due to anthropogenic emissions within that area. Applications of the AMES method showed that the average MI of PM_{10} collected at all sampling sites were 1.37±0.10 (TA98; +S9), 1.24±0.08 (TA98; -S9), 1.45±0.10 (TA100; +S9) and 1.30±0.09 (TA100; -S9) with relatively less variations. Analytical results reconfirm that the particulate PAH concentrations measured at PCD air quality monitoring stations are moderately low in comparison with previous results observed in other countries. In addition, the concept of incremental lifetime particulate matter exposure (*ILPE*) was employed to investigate the potential risks of exposure to particulate PAHs in Bangkok atmosphere.

Keywords: Polycyclic aromatic hydrocarbons (PAHs) - Ames test - PM_{10} - mutagens - carcinogens - Bangkok

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Introduction

In 1775, the British surgeon, Percival Pott, was the first to consider PAHs as toxic chemicals with the high incidence of scrotal cancer in chimney sweep apprentices (IARC, 1985). Occupational exposure of workers by inhalation of PAH-both volatile and bound to respirable particulate matter- and by dermal contact with PAH-containing materials, occurs at high levels during coke production, coal gasification, and iron and steel founding. Coke oven workers have a 3- to 7- fold risk increase for developing lung cancer (IARC, 1984; 1987). PAHs are a class of very stable organic molecules made up of only carbon and hydrogen and contain two to eight fused aromatic rings. PAHs can be released to the atmosphere by imperfect combustions of hydrocarbon fuels from traffic exhausts, industrial activities, domestic heating, forest fires and biomass/agricultural waste burnings (Li et al., 1999; Okuda et al., 2002; Yang et al., 2002; Rajput et al., 2011; Riva et al., 2011; Slezakova et al., 2011; Lu et al., 2012). These molecules were oriented horizontal to the surface, with each carbon having three neighboring atoms much like graphite. There are hundreds of PAH compounds in the environment, but only 16 of them are included in the priority pollutants list of US EPA (US-EPA, 2003). Many PAHs have also been identified as cancer-inducing chemicals for animals and/or humans (IARC, 1983).

The experimental evidences in rats suggest that human exposures to PAHs, especially B[*a*]P are high risk factors for carcinogenic and mutagenic effects (Loli et al., 2004; Wester et al., 2012). Several epidemiological meta-analyses highlight that heavy exposures to mixtures of PAHs entail a substantial risk to developmental neurotoxicity (Hood et al., 2011; Qiu et al., 2011; Crépeaux et al., 2012). For this reason, the monitoring of PAHs in environmental media is

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a reasonable approach to assess the risk for adverse health effects. Since the fate of PAHs in the natural environment is mainly governed by its physiochemical properties, the study of general properties of the compounds is of great concern. Like PAHs, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) comprise a cluster of persistent organic pollutants (POPs) that form almost inevitably in all combustion processes (Thompson et al., 2003; Lavric et al., 2004; 2005). Generally, there are 75 different PCDD congeners, which have different toxicities depend upon the positions and number of the chlorine atoms. 2,3,7,8-tetrabromodibenzo-p-dioxin (2,3,7,8-TBDD) is considered as the most toxic dioxin congener according to the World Health Organization toxic equivalent (WHO-TEQ) scheme (Hornung et al., 1996). As a consequence, numerous studies have been focused on the contamination of dioxin congener in various environmental compartments (Draper et al., 1988; Ok et al., 2002; Mai et al., 2007).

In spite of several studies focusing on the fate of PAHs and dioxins around the world, the chemical compositions, temporal and spatial distribution of these congeners in aerosols are still inadequately investigated, especially in Thailand. Bangkok, as a capital of Thailand, is the 73rd largest city in the world with the approximate population of 12 million people, covering administrative area of 1,568.7 km^2 with 50 districts under the authority of the Bangkok Metropolitan. Over the past few years, numerous studies have been raising concerns over the increased air quality problems associated with carcinogenic substances in airborne particles of Bangkok's atmosphere (Chetwittayachan et al., 2002; Muttamara and Leong, 2002; Boonyatumanond et al., 2007; Hoshiko et al., 2011). According to our best knowledge, there is still no report showing both temporal and spatial distribution of PAHs in Bangkok except for only a few roadside measurements (Chetwittayachan et al., 2002; Ruchirawat et al., 2002; 2005; 2007; Boonyatumanond et al., 2007). Thus, it appears difficult to conduct the comprehensive evaluation of adverse health impact caused by exposure to particulate PAHs for Bangkok citizens.

Overall, the principal objectives of this study are to i) conduct investigations into the temporal and spatial distribution of PAH aerosols collected at the seven pollution control department (PCD) observatory sites, ii) analyze the PAH contents and explain the influences of meteorological parameters over the behavior of PAH compositions in PM$_{10}$, iii) calculate the mutagenicity index (MI) for the estimation of mutagenic contents in PM$_{10}$ and iv) perform the assessment of health risk associated with the exposure to particulate PAHs of residents living adjacent to PCD air monitoring stations by using the concept of the incremental lifetime particulate matter exposure (*ILPE*) as previously reported by Hu et al. (2007).

Materials and Methods

Air sample observatory sites

Seven air sample observatory sites, namely Klongchan Housing Authority (KHA; 13°49'11.761" N 100°34'33.190" E), Nonsree High School (NHS; 13°42'28.937" N 100°32'50.443" E), Watsing High School (WHS; 13°41'3.218" N 100°26'45.554" E), Electricity Generating Authority of Thailand (EGAT; 13°43'39.205" N 100°29'11.776" E), Chokchai 4 Police Station (CPS; 13°47'33.474" N 100°35'45.879" E), Dindang Housing Authority (DHA; 13°46'59.544" N 100°32'25.618" E) and Badindecha High School (BHS; 13°46'10.745" N 100°36'52.433" E) were selected for the investigation of PAH contents and mutagenic index (MI) in PM$_{10}$ (Figure 1). It is remarkable and should be stressed that CPS, DHA, EGAT were situated adjacent to roadsides, whilst KHA, NHS, WHS and BHS were located at the residential zones. Therefore, CPS, DHA, EGAT and KHA, NHS, WHS, BHS can be considered as representatives of "traffic emissions" and "urban residential background" respectively. Intensive monitoring campaigns were performed at all observatory sites simultaneously at a normal weekday every month from January-December 2006 forming a database of 84 individual air samples.

PM$_{10}$ sample collection

Graseby-Anderson high volume air samplers TE-6001 were employed to achieve unmanned 24-hour samplings for PM$_{10}$. A total of 84 air samples were acquired using high volume yielding sample volumes of approximately 1,632 m^3 for each 24 h sample. PM$_{10}$ were collected on 20×25 cm Whatman glass fiber filters (GFFs) 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 GFF samples were wrapped by DCM rinsed aluminum foil, sealed in plastic bags and preserved in refrigerator at 4^{o}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. 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" (US-EPA, 1999).

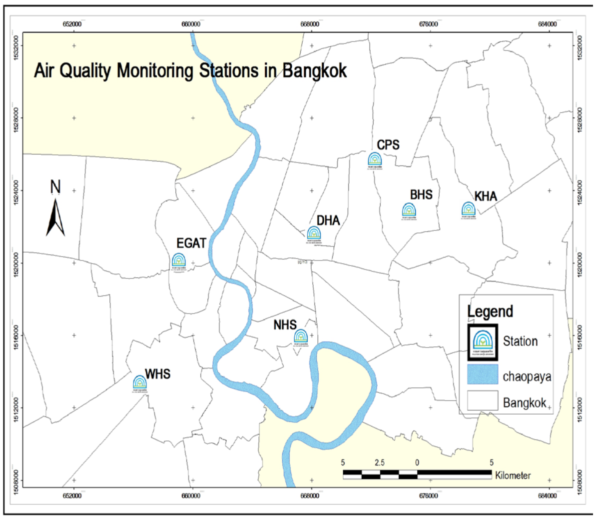

Figure 1. Map of Pollution Control Department (PCD) Air Sample Observatory Sites for this Study

PAHs analysis

All organic solvents (i.e. DCM and Hexane) are HPLC grade, purchased from Fisher Scientific. A cocktail of PAHs Norwegian Standard (NS 9815: S-4008-100-T) (phenanthrene (Phe), anthracene (An), fluoranthene (Fluo) and pyrene (Pyr); each 100 µg mL^{-1} in toluene: unit: (1×1 mL) and a recovery Internal Standard PAHs (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 standard (Gogou et al., 1996; Pongpiachan, 2006).

The analysis, calibrations and QA/QC procedures were performed by using a 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) at the laboratory of Inter-Department of Environmental Science, Faculty of Graduate Studies, Chulalongkorn University. The target compounds were separated on a 60 m length x0.25 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 a duration of 0.50 min. This data acquisition technique can be employed in both gathering qualitative spectral data (Scan) and analyzing quantitative data (SIM). Quantification of the compounds is based upon the Internal Standard (IS) method as described by Pongpiachan et al. (2009).

Mutagenicity assay

Mutagenicity assays were performed in accordance with the preincubation technique using the *Salmonella typhimurium* strain TA98 and TA100 (Ames et al., 1975; Yahagi et al., 1977). The TA98 and TA100 strain were kindly provided by Prof. Dr. Usanee Vinitketkumnuen (Faculty of Medicine, Chiang-Mai University, Thailand). In each assays, a positive and a negative control were conducted. The positive controls in the absence of metabolic activator (-S9) were 2-aminofluorine (2-AF) for TA98 and TA100. Each determination was made in triplicate and at least two independent experiments were carried out to confirm the results (Gatehouse et al., 1994).

Trace gaseous species and statistical 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. In addition, all statistical analysis, such as *t*-Test, Analysis of Variance (ANOVA), Pearson Correlations and Principal Component Analysis (PCA) were conducted by using SPSS software version 13.0.

Results

All particulate PAHs and MI in PM_{10} were analyzed successfully at a normal weekday every month from

Table 1. Average Values of Phe, An, Pyr and Fluo in PM_{10} (pg m^{-3}) Obtained from This Study and Other Observatory Sites Around the World

Site Description	Monitoring Period	References	Ph	An	Fluo	Pyr
CPS: *BK, TH.	January-December 2006	This Study	491±183	44±25	67±61	101±80
DHA: *BK, TH.	January-December 2006	This Study	540±275	85±45	131±51	234±184
EGAT: *BK, TH.	January-December 2006	This Study	401±127	60±24	77±27	91±50
WHS: **BK, TH.	January-December 2006	This Study	337±194	31±23	65±46	84±65
KHA: **BK, TH.	January-December 2006	This Study	287±177	25±23	43±46	40±37
NHS: **BK, TH.	January-December 2006	This Study	120±145	14±14	85±48	73±25
BHS: **BK, TH.	January-December 2006	This Study	276±141	97±110	144±135	151±141
NY, USA	August, 2006	Jouraeva et al., 2006	48,800	2,810	51,000	32,400
Divinopolis, BR	November, 2011	Menezes et al., 2011	629	370	670	1,300
Delhi, IN	November, 2008	Ray et al., 2008	376	319	848	1,045
Ulsan, KR	October, 2010	Lee et al., 2010	230	170	5,060	10,370
New Taipei, TW	August, 2012	Chuang et al., 2012	530	300	1,220	1,040
Coruna, ES	November, 2010	Prieto-Blanco et al., 2010	23	46	37	44
Steinheim, DE	September, 2012	Barrado-Olmedo et al., 2012	160	18	255	250
Brno, CZ	April, 2004	Ciganek et al., 2004	200	2,130	5,240	5,390
Srpska, BA	July, 2010	Lammel et al., 2010	13,900	590	3,690	2,840
Distrito Federal, MX	October, 2012	Amador-Munoz et al., 2012	135	21	253	322
Florence, IT	December, 2011	Martellini et al., 2012	150	190	240	260
Shenyang, CN	July, 2010	Kong et al., 2010	48,460	510	5,160	2,170

*Traffic Site, **Urban Residential Zone

January-December 2006 (i.e. n=84). Table 1 summarizes the average and standard deviation values of Phe, An, Pyr and Fluo measured in PM_{10} taken at seven PCD air quality observatory stations (Figure 2). During the observation period, the average concentrations of Phe, An, Fluo and Pyr were 348±144 pg m^{-3}, 47±26 pg m^{-3}, 84±31 pg m^{-3} and 109±63 pg m^{-3} in that order. As illustrated in Table 1, the highest Phe concentrations were in New York, USA (48,800 pg m^{-3}), followed by Shengyang, China (48,460 pg m^{-3}) and Srpska, Bosnia and Hercegovina (13,900 pg m^{-3}), while average Pyr concentrations were the highest in New York, USA (32,400 pg m^{-3}), followed by Ulsan, Korea (10,370 pg m^{-3}) and Brno, Czech Republic (5,390 pg m^{-3}), correspondingly. In this study, An contents (47±26 pg m^{-3}) was in the range between those of Coruna, Spain (46 pg m^{-3}) and Ulsan, Korea (170 pg m^{-3}), whilst Fluo (84±31 pg m^{-3}) values was in the same order to those of Coru˜na, Spain (37 pg m^{-3}). Although the temporal and spatial distribution of PAH congeners obtained from this study were quite similar to some extent, there were some significant differences in binary ratios between average PAHs measured at traffic roadsides (i.e. the average of PAHs detected at CPS, DHA, EGAT) and urban residential zones (i.e. the average of PAHs detected at WHS, KHA, NHS, BHS) (Figure 3). For instance, the binary ratios of $Phe_{traffic}/Phe_{urban}$, $An_{traffic}/An_{urban}$, $Fluo_{traffic}/Fluo_{urban}$ and $Pyr_{traffic}/Pyr_{urban}$ were 1.91±0.76, 1.78±0.82, 1.18±1.06 and 1.68±1.90 respectively. Since all binary ratios were higher than one, it seems reasonable to ascribe this trend as a consequence of overwhelming influence of vehicular exhausts on PCD air quality monitoring stations.

The mutagenicity of extracts of the samples was compared in the *Salmonella typhimurium* according to standard AMES test method. The dependence of the effects on sampling time and locations was investigated with the aid of a calculation of mutagenic index (MI). This MI was used to estimate the increase in mutagenicity above background levels at the seven monitoring sites in urban area of Bangkok due to anthropogenic emissions within that area as described in Equation 1.

MI=(Number of Colony in Sample)/(Number of Colony in Negative Control) **Equation 1**

The applications of the AMES method showed that the average MI of PM_{10} collected at all sampling sites were 1.37±0.10 (TA98; +S9), 1.24±0.08 (TA98; -S9), 1.45±0.10 (TA100; +S9) and 1.30±0.09 (TA100; -S9) with relatively low standard deviations. Interestingly, the binary ratios of $MI_{traffic}/MI_{urban}$ for TA98 (-S9), TA98 (+S9), TA100 (-S9) and TA100 (+S9) were 0.998±0.793, 0.998±0.794, 0.998±0.795 and 0.998±0.796 respectively. It is worth mentioning that there were no binary ratios of $MI_{traffic}/MI_{urban}$ for all strains higher than one, highlighting the fact that there is no contribution from vehicular exhausts on


DHA (Dindang Housing Authority)

KHA (Klongchan Housing Authority)


NHS (Nonsree High School)

WHS (Watsing High School)


EGAT (Electricity Generating Authority of Thailand)

CPS (Chokchai 4 Police Station)


BHS (Badindecha High School)

Figure 2. Seven PCD Air Sample Observatory Sites Namely, DHA, KHA, NHS, WHS, EGAT, CPS and BHS

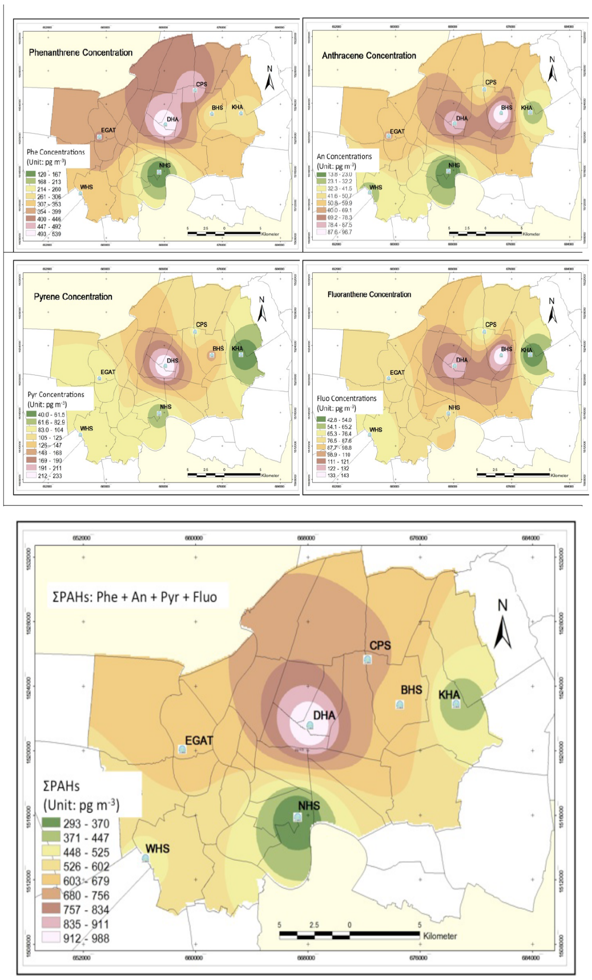

Figure 3. Spatial Distribution of Phe, An, Pyr, Fluo and TPAHs at DHA, KHA, NHS, WHS, EGAT, CPS

mutagenic contents in Bangkok's atmosphere. In addition, statistical comparisons of two data sets reveal that there were no significant differences between MI measured at the traffic and urban groups ($p<0.001$).

Discussion

Diagnostic binary ratios of PAHs, relating the ambient concentration of PAHs to their sources is essential to the development of control strategies to mitigate their adverse health and environmental effects. PAH profiles have been used in quantitative apportionment estimation for the ongoing phasing out of lead from gasoline in many countries (Gordon, 1988). Khalili et al. (1995) determined the chemical composition (source fingerprint) of the major sources of airborne PAHs in the Chicago metropolitan area, from 1990-1992. They found that two and three ring PAHs were responsible for 98%, 76%, 92% and 80% of the total concentration of the measured 20 PAHs from coke ovens, diesel engines, highway tunnels, petrol engines and wood combustion samples respectively. Six ring PAHs such as indeno[*1,2,3-c,d*]pyrene and benzo[*g,h,i*]pyrene were mostly below the detection limit and were only detected in the highway tunnel, diesel and petrol engine samples. By using an air passive sampler, the study found that the ratio of 1-methylphenanthrene/phenanthrene collected in the city centre of Bangkok and urban background sites in Thailand are 0.88 and 0.46 respectively (Söderström et al., 2003). Rogge et al. (1993) suggested that traffic congestion could increase the alkyl-PAHs emissions compared to the un-substituted PAHs emissions, due to the slower movement of the vehicles and lower engine temperatures that occur under such conditions. This indicates that the major source of atmospheric PAHs in Bangkok city center is traffic emission, as does the results in Birmingham (UK) reported by Harrison et al. (1996). The binary ratio method for PAH source identification, involves comparing ratios between pairs of frequently found PAH compound characteristics of different sources. Stationary source combustion emissions from the use of coal, oil and wood are low in coronene relative to benzo[*a*] pyrene, while mobile source combustion emissions from diesel and petroleum use are high in benzo[*g,h,i*]perylene and coronene relative to benzo[*a*]pyrene (Stenberg et al, 1979). The ratio of these PAHs can be used to distinguish between traffic dominated PAH profiles and other sources (Brasser, 1980; Mainwaring and Stirling, 1981).

In this study, cross-plots between ratios An/(An+Phe) and Fluo/(Fluo+Pyr) were employed to identify the potential sources of particulate PAHs in Bangkok atmosphere (Yunker et al., 2002; 2003). These binary ratios could indicate the contribution of petrogenic and pyrogenic sources to Bangkok's atmosphere during the observation period. Obviously, these binary diagnostic ratios are quite useful and provide valuable information to identify the potential sources of PAHs. However, these An/(An+Phe) and Fluo/(Fluo+Pyr) ratios, as well as other diagnostic ratios, should be used with great caution as physiochemical processes can alter PAH distribution pattern during their transport from the emission source to the receptor site. In order to minimize the above-mentioned uncertainties, the plots of two-dimensional diagnostic ratios can be used as a tool to extract potential sources of PAHs. As displayed in Figure 4, the clearest features are: (i) petrogenic, fossil fuel, grass wood and coal combustions responsible for 44% of particulate PAHs in Bangkok's atmosphere (ii) 50% and 25% of PAHs observed in CPS were dominated by petrogenic and fossil combustions respectively; (iii) BHS was almost completely dominated by pyrogenic combustions, suggesting that vehicular exhausts from traffic roads might be insignificant in this area; and (iv) 2D plots of BHS were highly deviated from the group, reflecting biomass burnings as other important sources of PAHs.

Pearson correlations and principal component analysis, pearson correlation coefficients between PAH contents and physicochemical parameters were calculated and displayed in Table 2. The relatively high Pearson correlation coefficients between An vs Fluo ($R=0.71$) and Fluo vs Pyr ($R=0.81$) can be interpreted in two ways namely i) An, Fluo and Pyr share similar emission sources, which can be plausibly derived from vehicular exhausts (He et al., 2010), ii) these three PAH isomers have comparable physico-chemical properties and thus similar atmospheric behavior. Furthermore, the considerably strong Pearson correlation coefficients between TA98 (-S9) vs TA100 (-S9) ($R=0.73$) and TA 98 (+S9) vs TA100 (+S9) ($R=0.69$) emphasize the validity of *Salmonella typhimurium* tester strains TA98 and TA100 as indicators of mutagenic contents in PM_{10}. As illustrated in Table 3, the principal component patterns for Varimax rotated components of seven air quality observatory sites with 19 parameters composed of five principal components, which

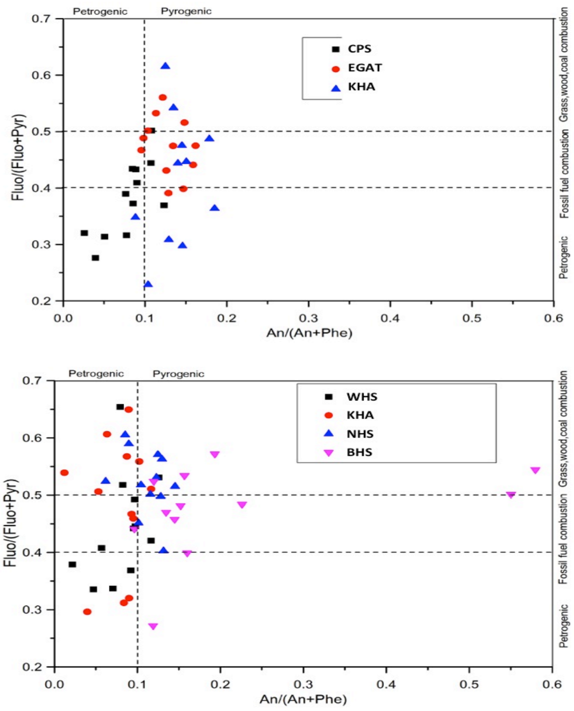

Figure 4. Two-dimensional Plots of Binary Diagnostic Ratios between An/(An+Phe) and Fluo/(Fluo+Pyr) in PM_{10} Collected at CPS, EGAT, KHA (Roadside Measurements) and WHS, KHA, NHS, BHS (Urban Residential Zone)

Table 2. Pearson Correlation Coefficients between PAH Contents and Physicochemical Parameters Obtained from This Study

Y	PM_{10}	Phe	An	Fluo	Pyr	CO	O_3	NO_2	SO_2	Temp	RH	SR	AP	Rain	WS	TA98 (-S9)	TA98 (+S9)	TA100 (-S9)	TA100 (+S9)
PM_{10}	1																		
Phe	0.487	1																	
An	0.292	0.446	1																
Fluo	0.43	0.364	**0.707**	1															
Pyr	0.548	0.515	0.554	**0.812**	1														
CO	0.497	0.584	0.441	0.445	0.556	1													
O_3	-0.012	-0.155	-0.138	-0.132	-0.264	-0.226	1												
NO_2	0.582	0.445	0.293	0.256	0.324	**0.688**	0.085	1											
SO_2	-0.152	-0.202	-0.255	-0.227	-0.253	-0.103	-0.069	0.035	1										
Temp	0.052	-0.211	-0.051	-0.077	-0.02	-0.146	0.176	-0.051	0.065	1									
RH	-0.383	-0.16	-0.037	-0.016	-0.05	-0.054	-0.334	-0.275	0.165	-0.384	1								
SR	-0.199	-0.306	-0.325	-0.295	-0.221	-0.357	0.183	-0.199	0.022	0.556	-0.455	1							
AP	0.274	0.013	0.137	0.12	0.112	0.175	0.405	0.419	-0.041	0.338	-0.253	0.161	1						
Rain	-0.22	0.138	0.225	0.162	0.162	0.172	-0.462	-0.185	0.06	-0.287	**0.636**	-0.423	-0.351	1					
WS	-0.208	-0.112	-0.135	-0.126	-0.231	-0.297	0.131	-0.156	0.042	0.079	-0.135	0.239	0.074	-0.184	1				
TA98(-S9)	0.53	0.243	0.36	0.377	0.404	0.346	0.006	0.386	-0.242	0.1	-0.312	-0.057	0.176	-0.112	-0.148	1			
TA98(+S9)	0.455	0.294	0.303	0.305	0.349	0.351	0.043	0.385	-0.217	0.036	-0.205	-0.061	0.216	-0.077	-0.157	**0.86**	1		
TA100(-S9)	0.25	0.176	0.269	0.228	0.351	0.245	-0.272	0.207	-0.192	0.007	-0.095	-0.034	-0.108	0.074	-0.075	**0.728**	**0.631**	1	
TA100(+S9)	0.321	0.291	0.281	0.286	0.346	0.372	-0.216	0.342	-0.303	0.044	-0.139	-0.076	0.06	0.026	-0.155	**0.73**	**0.693**	**0.742**	1

*Temp: Air Temperature (°C); RH: Relative Humidity (%); SR: Solar Radiation (W m^{-2}); AP: Atmospheric Pressure (hPa); Rain: Precipitation (mm $month^{-1}$); WS: Wind Speed (m s^{-1}); TA98 (-S9): Mutagenic Index of TA98 without S9; TA98 (+S9): Mutagenic Index of TA98 with S9; TA100 (-S9): Mutagenic Index of TA100 without S9; TA100 (-S9): Mutagenic Index of TA100 with S9

Table 3.Principal Component Analysis of PAH Congeners, Mutagenic Indexes, Trace Gaseous Species and Meteorological Parameters Observed at All PCD Air Quality Observatory Sites

	Principal Component (PC)				
	PC1	PC2	PC3	PC4	PC5
PM_{10}	0.312	0.410	0.314	0.540	-0.013
Phe	0.155	0.514	0.058	0.393	-0.302
An	0.158	**0.793**	-0.065	0.104	-0.081
Fluo	0.133	**0.878**	-0.070	0.113	-0.009
Pyr	0.226	**0.822**	-0.125	0.255	0.068
CO	0.205	0.445	-0.055	**0.690**	-0.165
O_3	-0.141	-0.149	**0.767**	-0.104	-0.082
NO_2	0.225	0.180	0.327	**0.783**	-0.106
SO_2	-0.312	-0.442	-0.283	0.446	0.304
Temp	0.037	0.018	0.217	-0.039	**0.855**
RH	-0.221	-0.089	**-0.695**	-0.042	-0.337
SR	0.033	-0.227	0.299	-0.301	**0.711**
AP	-0.048	0.156	0.575	0.319	0.257
Rain	-0.068	0.189	**-0.781**	0.008	-0.228
WS	-0.118	-0.060	0.263	-0.404	0.085
TA98 (-S9)	**0.867**	0.230	0.156	0.182	0.042
TA98 (+S9)	**0.825**	0.161	0.160	0.217	-0.041
TA100 (-S9)	**0.877**	0.115	-0.194	0.018	0.056
TA100 (+S9)	**0.864**	0.168	-0.062	0.133	-0.001
Total of Variance (%)	30.1	16.8	10.2	7.00	5.84

*Temp: Air Temperature (°C); RH: Relative Humidity (%); SR: Solar Radiation (W m^{-2}); AP: Atmospheric Pressure (hPa); Rain: Precipitation (mm $month^{-1}$); WS: Wind Speed (m s^{-1}); TA98 (-S9): Mutagenic Index of TA98 without S9; TA98 (+S9): Mutagenic Index of TA98 with S9; TA100 (-S9): Mutagenic Index of TA100 without S9; TA100 (-S9): Mutagenic Index of TA100 with S9

account for 30.1%, 16.8%, 10.2%, 7.00% and 5.84% for the total of variances of PC1, PC2, PC3, PC4 and PC5 respectively (Table 3). The contribution of PC1 and PC2 explains 47% of total variance, and moreover PC1 is almost two times and three times higher than PC2 and PC3 respectively. The main cluster (PC1) contains dominantly TA98 (-S9), TA98 (+S9), TA100 (-S9) and TA100 (+S9) with relatively high correlation coefficients of 0.87, 0.83, 0.88 and 0.86 respectively. Since these four parameters are typical indicators of mutagens, it seems reasonable to conclude that 30% of PM_{10} was dominated by mutagenic substances. It is also well known that Phe, An, Fluo and Pyr are typical biomarkers of vehicular exhausts (Nelson, 1989; McKenzie et al., 2005) and thus the relatively high loadings of these four PAH congeners can be attributed to traffic emissions in PC2 (i.e. 17% of traffic contribution). Finally, the negative loadings of relative humidity and precipitation coupled with positive loading of O_3 detected in PC3 suggest that raining during observation period promotes wet deposition with the total variance of 10%.

Incremental lifetime particulate PAHs exposure (*ILPE*), to assess the health risks associated with the occupational exposure to particulate PAHs of outdoor workers close to PCD air quality monitoring stations, the incremental lifetime particulate PAHs exposure (*ILPE*) model was employed and defined as,

$$ILPE=C\times IR\times t\times EF\times ED \qquad \textbf{Equation 2}$$

ILPE=Incremental lifetime particulate PAHs exposure (ng), ***C***=PAH concentrations (pg m^{-3}), ***IR***=Inhalation rate (m^3 h^{-1}), ***t***=Daily exposure time span (6 h d^{-1}, for two shifts), ***EF***=Exposure frequency (250 d $year^{-1}$ [a], upper-bound value), ***ED***=Exposure duration (25 years[a], upper-bound value), Note: [a]Adapted from Human Health Evaluation Manual (US EPA, 1991).

According to the methods for derivation of inhalation dosimetry (US EPA, 1994), the inhalation rate of male and female outdoor workers were estimated as 0.89 and 0.49 m^3 h^{-1} respectively. The *ILPE* model was adapted from the probabilistic incremental lifetime cancer risk (ILCR) model, which was used to assess traffic policemen exposure to PAHs during their work time in China (Hu et al., 2007). The estimated *ILPE* levels in outdoor workers are summarized in Table 4. The predicted *ILPE* of PAH isomers were consistently highest at traffic observatory sites with the average values of 15,938±2,355 ng, 2,107±699 ng, 3,059±1,144 ng and 4,739±2,653 ng for Phe, An, Fluo and Pyr accumulated in male outdoor workers over exposure duration of 25 years respectively. It is worth mentioning that the estimated *ILPE* of PAH congeners at traffic observatory sites were constantly 1.91±0.76, 1.78±0.82, 1.18±1.06 and 1.68±1.90 times higher than those of urban residential sites. These results emphasize higher risk particularly for outdoor workers (e.g. police men, construction workers, lottery sellers, flower sellers, etc.) who experiencing prolonged exposure to particulate PAHs in comparison with those living in residential zones.

In conclusions, since PAHs are continuously released into the atmosphere, raising concerns over the safety of urban residents and those who are working at roadsides, it is therefore crucial to monitoring particulate PAHs in Bangkok. This will expand the database, and thus amend the scope of long-term temporal trend analysis of PAHs in urban atmosphere. Moreover, one should keep in mind that air quality compliance measurements should be conducted at multiple monitoring sites within the city. Therefore, a more comprehensive air-monitoring network requires to be developed in order to provide a more precise risk assessment of human exposures within the Bangkok metropolitan area. In this study, PCA results show 47% contribution of both mutagenic and carcinogenic emissions (i.e. PC1+PC2) at all observatory stations, underlining that anthropogenic sources are the main contributors of PAHs and other chlorinated dioxins in Bangkok's atmosphere. The average values of *ILPE* for all sampling sites indicate a higher potential risk of developing lung cancer and other respiratory diseases for outdoor workers at roadsides than those who living in urban residential zones of Bangkok metropolitan area.

Table 4. Incremental Lifetime Particulate PAHs Exposure (*ILPE*) of Male and Female Outdoor Workers at Traffic Roadsides (i.e. CPS, DHA, EGAT) and Urban Residential Zones (i.e. WHS, KHA, NHS, BHS)

	Ph	An	Fluo	Pyr
Male-*ILPE* (ng)				
Traffic	15,938±2,355	2,107±699	3,059±1,144	4,739±2,653
Urban	8,361±3,099	1,182±855	2,602±1,080	2,814±1,394
Female-*ILPE* (ng)				
Traffic	8,775±1,297	1,160±385	1,684±630	2,609±1,461
Urban	4,603±1,706	651±471	1,432±595	1,549±767
Traffic/Urban	1.91±0.76	1.78±0.82	1.18±1.06	1.68±1.90

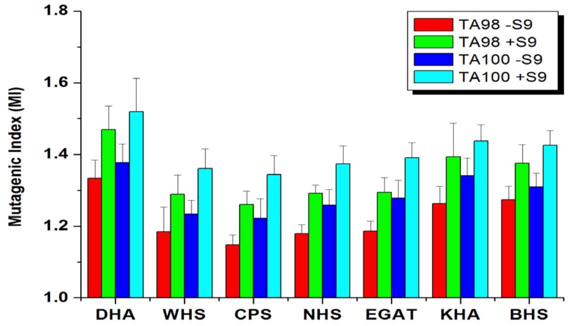

Figure 5. Average MI of TA98 (-S9), TA98 (+S9), TA100 (-S9) and TA100 (+S9) at DHA, WHS, CPS, NHS, EGAT, KHA and BHS

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