



## Diurnal Variations of Particle-bound PAHs at a Traffic Site in Xiamen, China

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### ABSTRACT

To improve our current understanding of the fate of particle-bound PAHs, which include potent mutagens and carcinogens, diurnal measurements of these compounds were carried out from 23 Oct to 31 Dec 2008 at a busy traffic site in Xiamen, China. The sum of 19 PAH concentrations showed a just noticeable day-night difference in the warmer period (from 23 Oct to 25 Nov) to a remarkable day-night difference in the colder period (from 26 Nov to 31 Dec). However, the average profiles of the 19 PAHs in the warmer and colder periods were very similar for both day and night samples. Atmospheric mixing seemed to have more influence on the diurnal variations in PAHs than photodecomposition resulting from solar radiation, because PAH concentrations showed negative correlation with air temperature but significantly positive correlation with the ratios of reactive to stable PAHs, such as benz[a]anthracene to chrysene and benzo[a]pyrene to benzo[e]pyrene. Based on the diagnostic ratios of indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[g,h,i]perylene and fluoranthene to fluoranthene plus pyrene, the results showed that no significant differences were observed in PAHs sources between the warm and cold periods and a combination of grass, wood or coal combustion and petroleum sources in airborne particles might be the most significant contributors of PAHs. Gas-phase PAHs were calculated based on the theoretical gas/particle partitioning coefficients for 19 PAHs and a high fraction of daily exposure was attributed to particle-phase PAHs in most cases. The excess lifetime cancer risk in colder period was generally higher than in the warmer period. The total uncertainties were computed based on the simpler average error transfer formula.

**Keywords:** PAHs, Diurnal variations; Risk assessment; Uncertainty analysis; Xiamen.

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that are widely distributed in the environment. Some higher-molecular-weight PAHs with four or more rings are predominantly (> 80%) adsorbed onto particulate matter at ambient temperatures in the atmosphere (Bi *et al.*, 2003; Terzi and Samara, 2004). These compounds are reported to be probable human carcinogens (ATSDR 1995; IARC, 2008) and mutagens (Hakura *et al.*, 2005). Hence, from a human health perspective the fate of these compounds associated with particulate matter is of major concern for assessing health impact, since the most potent genotoxic compounds are those primarily associated with particles (Grimmer *et al.*, 1987; IARC, 1989; Nielsen *et al.*, 1996). In urban areas without coal heating boilers, PAHs are released into the atmosphere mainly from vehicle emissions (Riddle *et al.*, 2007; Zhang *et al.*, 2008; Shi *et al.*, 2009). PAHs associated with airborne particles are always subject

to a number of physical and chemical processes such as dry and wet deposition, gas-particle phase partitioning, photochemical transformations and reactions with other pollutants (Bi *et al.*, 2003; Vione *et al.*, 2006; Sahu *et al.*, 2008; Miet *et al.*, 2009). After dry and wet deposition, the photo-induced reaction is considered to be the next most important mechanism in removing PAHs from the atmosphere (Reisen and Arey, 2005).

The occurrence and fate in the atmosphere of PAHs associated with particles have been extensively studied on a 24-h sampling scale, and the levels of particle-bound PAHs are often shown to be affected by various meteorological factors such as temperature, wind direction, wind speed, humidity, solar radiation, atmospheric stability as well as atmospheric oxidant concentrations and local emissions during the sampling period (Kavouras *et al.*, 1999; Tzapakis and Stephanou, 2003, 2007). Measurements of PAHs at 12-h day and night sampling intervals were carried out in order to study their diurnal variations and removal mechanism (Arey *et al.*, 1998; Albinet *et al.*, 2007; Hien *et al.*, 2007). A few studies have employed shorter time periods (less than 4 h) to investigate the fate of the short-lived highly toxic nitro-PAHs (Reisen and Arey, 2005; Marr *et al.*, 2006; Tzapakis and Stephanou, 2007). Considering the significant differences of sunlight, OH and NO<sub>3</sub> radicals, O<sub>3</sub>, and

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convective instability between day and night (McLaren *et al.*, 2004), the particle-bound PAHs in the atmosphere are also expected to present a diurnal variation. The diurnal variations of particle-bound PAHs are also expected to reflect their photostability and removal pathways.

To this end, we conducted field measurements of the diurnal atmospheric variations of PAHs on PM<sub>10</sub> particles in order to expand our knowledge of the atmospheric fate of PAHs including their deposition flux in urban areas. In addition, such diurnal variation measurements meet the needs for more accurate inhalation risk assessment.

## METHODS

### Sampling and Measurements

The variation of particle-bound PAHs was studied at a coastal urban site (E 118°05'25", N 24°26'08") in the south of Xiamen Island (Fig. 1). The sampling site was located on the roof of Ocean building (the mean sea level elevation is ~25 m and generally higher than its neighborhood) at Xiamen University near a major road with high traffic volume. Sampling was carried out from Oct 23 to Dec 31 2008 (dry season) using a High-Volume Air Sampler (GMW PM10VOL, Thermo Scientific Co., USA) equipped with a PM<sub>10</sub> size-selective inlet at a constant flow rate of 1.13 m<sup>3</sup>/min. The day samples were collected from 08:00 to 19:00, and the night samples were taken from 20:00 to 07:00 (local time). For analysis, the sampling period was broken into two parts, a warmer period for 23 Oct to 25 Nov (temperatures between 19 and 26.5°C) and a colder period from 26 Nov to 31 Dec (temperatures between 14.3 and 17.8°C). A total of 100 air samples were collected during the sampling period. The intensive sampling schedule at the site was part of a three-year Big Xiamen Bay (including Xiamen, Kinmen, part of Zhangzhou and Quanzhou) Air Quality Monitoring Project. After sampling, the glass fiber filter was removed from the sampler, folded with the particulate matter inside, replaced in its aluminum foil envelope, and stored in a freezer (−18°C) until analysis.

Quasi-weekly mean meteorological parameters (wind speed, wind direction, temperature, relative humidity, and atmospheric pressure) were measured at the sampling station using an automatic weather station (Table 1). During the sampling period, the total rainfall was 8.0 mm (with 0.8, 3.4 and 3.8 mm on the night of Dec 29, the day of Dec 30 and the night of Dec 30).

### Sample Analysis and Quality Assurance

Prior to analysis, a quarter of the filter papers were cut into 1 cm<sup>2</sup> squares, put into a centrifuge tube, and spiked with a known amount of naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub> and 4-nitro-p-terphenyl (AccuStandard Inc., USA) to serve as internal standards. Samples were prepared according to the modified US EPA method 3550B (ultrasonic extraction) and method 3630C (silica gel clean-up) (USEPA, 1995; Wu *et al.*, 2009). All filters were ultrasonically extracted three times for 30 min in dichloromethane (DCM) after soaking overnight. The extracted samples were then concentrated to ~10 mL by rotary evaporation, an additional 15 mL hexane added into the flask and evaporation repeated with the hexane to ensure complete removal of DCM. Approximately 1 mL of the concentrated solution was transferred to a silica gel column (1 cm id and 20 cm length), and was successively eluted with 40 mL hexane: DCM (6:4), followed by 30 mL DCM to obtain the PAH and nitro-PAH fractions. PAH fractions were evaporated under a nitrogen stream down to a volume of 200 μL. Nineteen PAHs, naphthalene (Nap), acenaphthylene (Acpy), acenaphthene (Acp), fluorine (Flu), phenanthrene (Phe), athracene (Ant), fluoranthene (Flua), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pery), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), benzo[g,h,i]perylene (BgP) and coronene (Cor), were identified and quantified using GC/MS with an electron impact (EI) ion source and selective

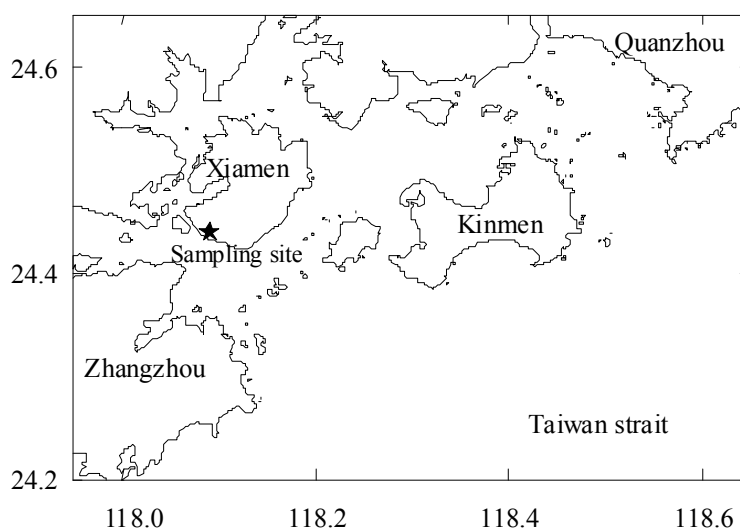


Fig. 1. Map of Xiamen Island with the sampling station indicated.

**Table 1.** Ambient meteorological conditions during the intensive sampling period.

Parameter	Temperature (°C)		Relative humidity (%)		Wind speed (m/s)		Prevailing wind direction		Pressure (mbar)	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
23 Oct–27 Oct	26.5	25.0	63.4	66.4	2.3	1.9	N, NE	N, NE	1011.0	1011.6
28 Oct–1 Nov	25.7	24.0	60.0	65.8	2.8	2.7	NE, E	NE	1011.9	1011.9
2 Nov–9 Nov	24.0	22.5	62.5	67.0	2.7	2.5	NW, N	E, NE	1013.5	1014.0
10 Nov–14 Nov	23.0	21.5	61.3	65.5	2.5	2.2	NW, NE	N, NE	1014.0	1015.0
15 Nov–25 Nov	21.1	19.0	63.9	68.0	2.6	2.0	NW, N, NE	NW, N, N	1015.1	1016.3
26 Nov–30 Nov	17.8	14.9	40.0	48.1	2.7	2.3	N	N, NE	1018.1	1019.0
1 Dec–8 Dec	16.7	15.2	58.2	62.6	2.4	2.1	N	N	1016.7	1017.3
9 Dec–14 Dec	17.7	16.0	58.1	63.8	2.2	1.9	NW, NE	NW, N, NE	1013.5	1014.5
16 Dec–25 Dec	15.9	14.3	66.0	71.9	2.5	2.0	NW, E	NW	1016.3	1016.9
26 Dec–31 Dec	15.6	14.5	71.4	75.7	2.0	1.9	N, E, NE	NW, N, NE	1015.6	1016.0

ion monitoring (SIM) mode (Agilent 6890GC-5973MSD). For PAHs analyses an HP-5MS capillary column (0.25 mm id × 30 m, 0.25 μm film thickness, 5% phenyl methyl polysiloxane) was used with injection in the splitless mode and ultra pure helium (99.999+%) was used as the carrier gas. The oven temperature for analysis of PAHs was programmed from an initial temperature of 60°C to a final temperature of 300°C at the rate of 5 °C/min and held isothermally for 20 min. Conditions for the mass spectrometer were as follows: GC/MS interface temperature was 280°C and electron energy was 70 eV. It should be noted that, using our analysis technique, in no case was separation obtained between BbF and BkF, so the paired unresolved peaks were quantified together when making a calibration curve. All the standard solutions used for PAHs were purchased from AccuStandard (J&K, China). Recoveries of five PAH surrogate standards were as follows: 76 ± 12% for naphthalene-d8, 82 ± 7% for acenphthene-d10, 80 ± 8% for phenanthrene-d10, 92 ± 12% for chrysene-d10, and 72 ± % for perylene-d12 (n = 5). Field and laboratory blank samples were also analyzed along the samples to check for any background contamination from artificial contaminants, reagents and glassware during the sampling and analysis procedure. Only trace Nap (20.6 ± 5.3 ng/sample), Acp (6.3 ± 2.7 ng/sample) and Phe (30.8 ± 3.7 ng/sample) were found in the field and laboratory blank. Two pairs of replicate samples were analyzed with each set of 20 samples to detect the precision of the analytical method. The results showed that the average relative deviation (RSD) ranged from 0.7% (COR) to 7.1% (Acpy) with an average value of 5.2 ± 2.4%. The reported concentrations of particle-bound PAHs were corrected by blank values and recovery rates.

## RESULTS AND DISCUSSION

As can be seen from Fig. 1, the sampling site was located at the farthest south of Xiamen Island and so, when the wind was from the southeast, the site was influenced by clean sea air. The island was mainly influenced by the northeast monsoon during the intensive sampling period and the air masses reaching the sampling site had a similar origin, mostly from the northeast and north. Table 1 presents the atmospheric conditions during the sampling period. The

monthly average temperature decreased from 25.5°C in October to 17.7°C in November and 15.7°C in December. Wind speeds were relatively stable. Atmospheric pressure, temperature and relative humidity showed clear diurnal variations and were likely to have influenced the concentrations of atmospheric pollutants such as PM<sub>10</sub>, NO<sub>x</sub> and O<sub>3</sub>. The lower temperature along with higher atmospheric pressure in winter would limit vertical mixing and trap pollutants close to the surface, the process called inversion.

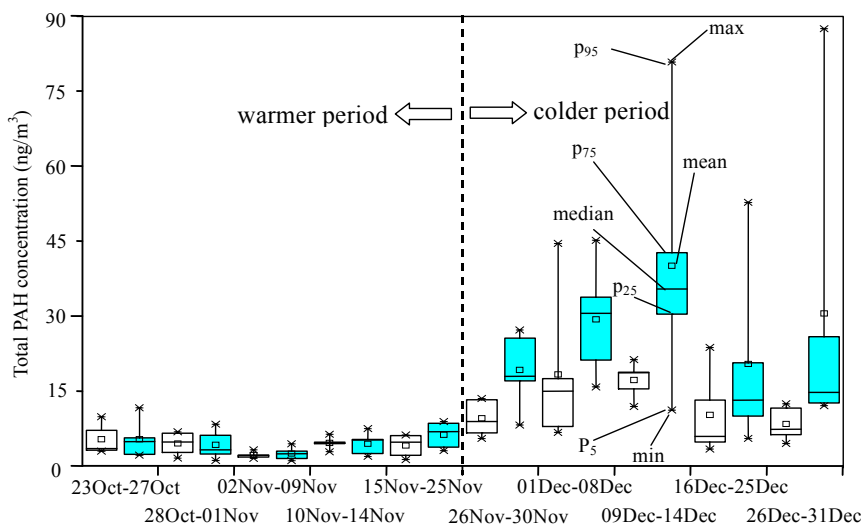
### Concentrations and Trends of Particle-bound PAHs

In all samples, the high molecular weight PAHs, including BbF, BkF, BeP, BaP, Pery, IP, DBA, BgP and Cor, were the most abundant and comprised 72.4 ± 4.5% (day) and 74.5 ± 4.0% (night) of the total PAHs. The low molecular weight PAHs including Nap, Acpy, Acp and Flu were the least abundant, accounting for only 0.9 ± 0.4% (day) and 0.8 ± 0.5% (night) of the total. For the two- to four-ring PAH, a large fraction is predominately in the vapor phase in air and the volatilization of these compound from filters or the adsorption of gas phase PAH to filters can introduce negative or positive errors to the measured particle-phase concentrations. In our study, the concentration of most PAHs on the backup filter was typically < 3% that on the primary filter except Nap (14.7%) and Acp (20.6%). Thus, particle-bound PAHs concentrations were not corrected for filter adsorption since the five- to seven-ring PAHs were the most abundant compounds. Additionally, the “blow-off” artifact of PAHs from particles collected on the filters will also lead to an underestimation of the PAHs concentrations in the particulate phase. The average profiles of PAHs on the particles were consistent with other studies (Kavouras *et al.*, 1999; Bi *et al.*, 2003). The average total PAH concentration showed a just noticeable day-night difference in the warmer period but a significant day-night difference in the colder period (Fig. 2). The average air temperature had significantly negative correlation with day PAHs ( $r = -0.70$ ,  $p < 0.05$ ), night PAHs ( $r = -0.81$ ,  $p < 0.01$ ), night PM<sub>10</sub> ( $r = -0.77$ ,  $p < 0.01$ ) and significantly positive correlation with the ratio of day to night PAHs ( $r = 0.92$ ,  $p < 0.01$ ) except day PM<sub>10</sub> ( $r = -0.54$ ) and the ratio of day to night PM<sub>10</sub> ( $r = 0.52$ ) (Fig. 3). These indicated that air temperature might be the most important factor in

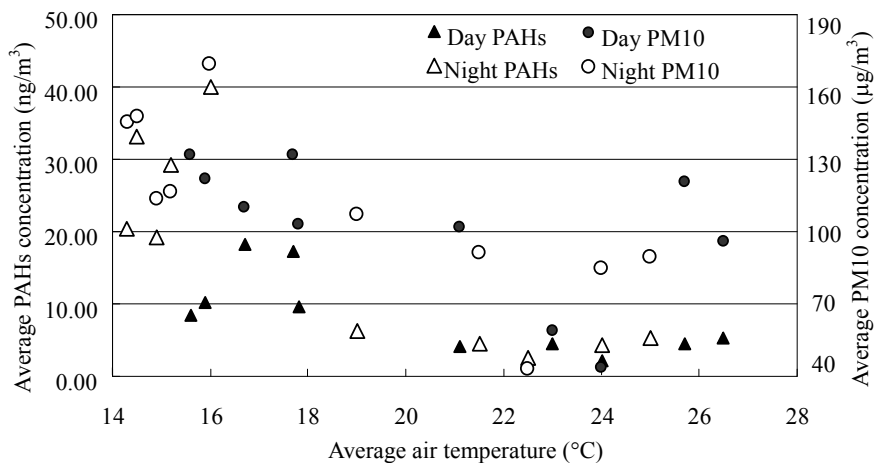
determining the concentration and the day-night variation of particle-bound PAHs. Because PAHs were mainly from the fuel combustion, especially from vehicle exhaust in urban area in subtropical zone without heating season (Bi *et al.*, 2003; Li *et al.*, 2006a), PAHs emissions from local vehicle and industrial activities would not vary greatly depending on the relative stable traffic volume and industrial activities during the sampling period in Xiamen. Although the PAH content of a fuel (Lin *et al.*, 2006a), biodiesel blends (Lin *et al.*, 2006b; Yuan *et al.*, 2007) and the Mn-based additive (Yang *et al.*, 1998) had a strong influence on PAH and particulate matter emission from vehicles, there is at present no data for fuel quality assumed in Xiamen. However, the input of PAHs from upwind (north and northeast) sources might change due to the coal combustion in heating season although the wind direction did not change much (Table 1) (Guo *et al.*, 2003). Thus, the increased levels during the colder period (from

26 Nov to 31 Dec) could be attributed to (1) lower air temperature, (2) lower atmospheric mixing height, (3) lower photolysis activity, (4) less removal due to dry/wet deposition, or (5) long-range transport from north and northeast China.

The invasion of a strong cold air mass from the north on 26 Nov 2008 caused a great decrease in the daily temperature from 20 to 14°C and an increase in the atmospheric pressure from 1016 to 1019 mbar. The lower air temperature and high atmospheric pressure were expected to inhibit vertical diffusion and dilution and trap atmospheric pollutants close to the surface. Surface layer temperature inversions are very common during the cold season and they strongly influence atmospheric pollution in Xiamen (Li *et al.*, 2006b). Under the low temperature and high particle concentration conditions (Table 1 and Fig. 3), the gas-particle partitioning of PAHs was also favored in the particulate phase, enhancing condensation of particulate PAHs (Subramanyam *et al.*, 1994).



**Fig. 2.** Day-night variations of average total PAH concentrations during the sampling period. The values of the maximum, the 95th, 75th, 50th (median), 25th, and 5th percentile, and the minimum are illustrated by box-whisker symbols and the arithmetic means are presented as “□”. Night samples are indicated by the cyan color.



**Fig. 3.** Variations of average day PAHs, night PAHs, day PM<sub>10</sub> and night PM<sub>10</sub> with average air temperature in the periods defined in Table 1 and Fig. 2.

However, the high molecular weight ( $\geq 228$ ) PAHs are almost completely associated with particles (Bi *et al.*, 2003), and the increased particle-bound PAHs in the cold period could not be explained by changes in gas-particle partitioning. The significant positive correlations found in our study between particle-bound PAHs and  $PM_{10}$  (Table 2) can support the above deduction. Although the use of PAH isomer ratios such as BaA/Chr and BaP/BeP for source reconciliation is criticized (Zhang *et al.*, 2005), they are widely used to study the aging process of atmospheric aerosols with higher values indicating freshly emitted air masses (Li *et al.*, 2006a; Ding *et al.*, 2007; Esen *et al.*, 2008). Our results showed significantly positive correlation ( $p < 0.01$ ) between total PAH concentration and BaA/Chr and BaP/BeP during the sampling period (Fig. 4) suggesting that the particles collected in the colder period had experienced less of an aging process (lower solar radiation and/or just been emitted from local vehicle exhaust) than those collected in the warmer period. According to other study (Yunker *et al.*, 2002), the ratios of Flua to Flua + Py  $> 0.5$  was considered as an indication of grass, wood and coal combustion, and the ratios of IP/IP + BgP between 0.2 and 0.5 indicating petroleum combustion. Fig. 5 shows that black triangle for warmer period samples were just weakly separated from empty dot for colder period samples, possibly indicating a combination of emission sources (i.e. petroleum and coal combustion) of PAHs in the two periods. The above aging and diagnostic ratios indicate that the major sources of particulate PAHs in colder period were not from north and northeast air transport but tended to be local emissions. However, the influence of grass, wood, and

coal combustion on the particle-bound PAHs tended to increase in the colder periods in comparison with that in the warmer period suggesting that air mass from north and northeast upwind in the colder period had only limited influence on particle-bound PAHs in Xiamen.

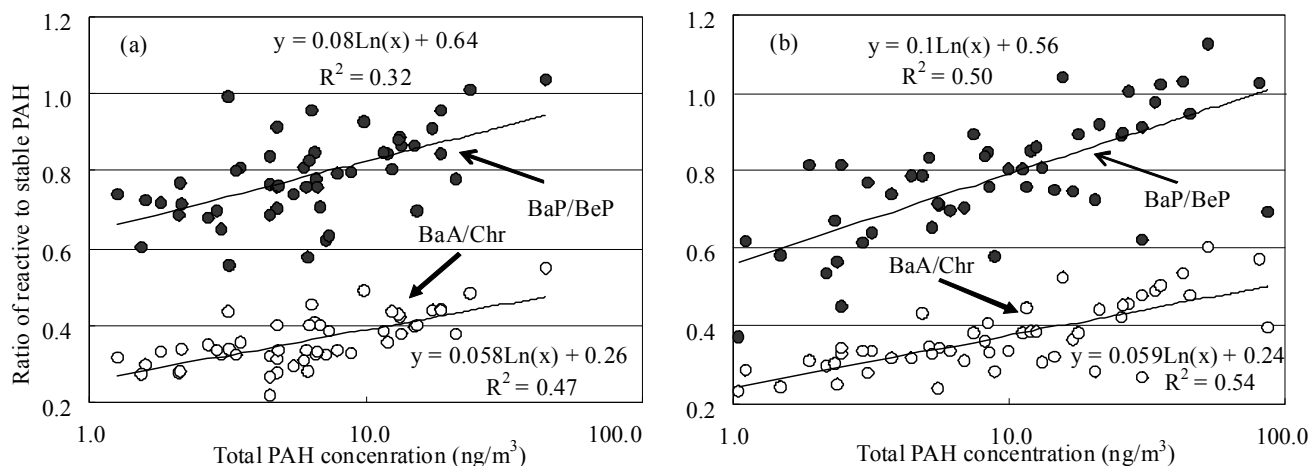
It is evident that, in the day, the photodecomposition process alone was unable to cause a significant decrease of particle-bound PAHs in the colder period because the day-night difference was just noticeable during the warmer period while the effects of photolysis on the particle-bound PAHs should be stronger than those during the colder period based on the ratios of reactive to stable PAHs in Fig. 4. Li *et al.* (2006b) also reported that the diurnal variation of number density of particles was small in warm seasons and large in cold seasons in Xiamen. The particles were quickly diluted under unstable conditions and the particle-bound PAHs showed just noticeable diurnal variations in the warmer period. However, low temperature and high atmospheric pressure would trap pollutants allowing them to build up in the colder period. The increased day-night differences in the colder period might be explained to a large extent by the inversions being more often during the night than during the day. Moreover, a decline in PAHs emissions at night (with lower traffic volume relative to that in the day), relatively stable wind speed and direction between day and night (Table 1), and the very similar profiles of 19 PAHs between the warmer and colder periods samples (Fig. 6) suggested that the diurnal shift of temperature inversion was the most critical factor among physical losses due to dry deposition, chemical losses due to photochemical reaction and changes in sources of particle-bound PAHs in causing the significant diurnal variation of particle-bound PAHs.

**Table 2.** Pearson's correlation coefficient between  $PM_{10}$ , nitro-PAH and PAH concentrations ( $n = 50$ ).

	$PM_{10}$ (Day)	$PM_{10}$ (Night)	PAHs (Day)
$PM_{10}$ (Night)	0.562**		
PAHs (Day)	0.537**	0.485**	
PAHs (Night)	0.375*	0.559**	0.646**

\*\* Correlation is significant at the 0.01 level (1-tailed).

\* Correlation is significant at the 0.05 level (1-tailed).



**Fig. 4.** Correlations between total PAH concentrations and BaP/BeP and BaA/Chr in the day (a) and night (b) samples.

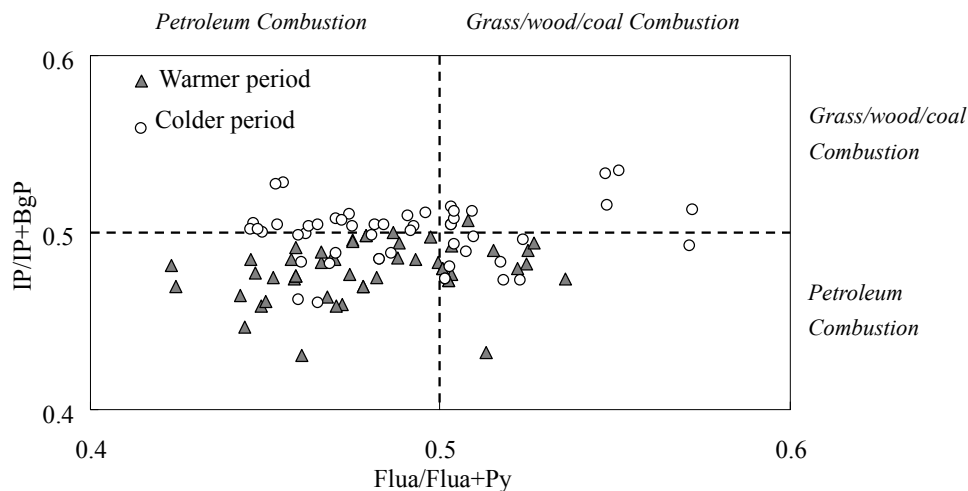


Fig. 5. PAHs cross-plot for the ratio of Flua to Flua + Py vs. IP to IP + BgP.

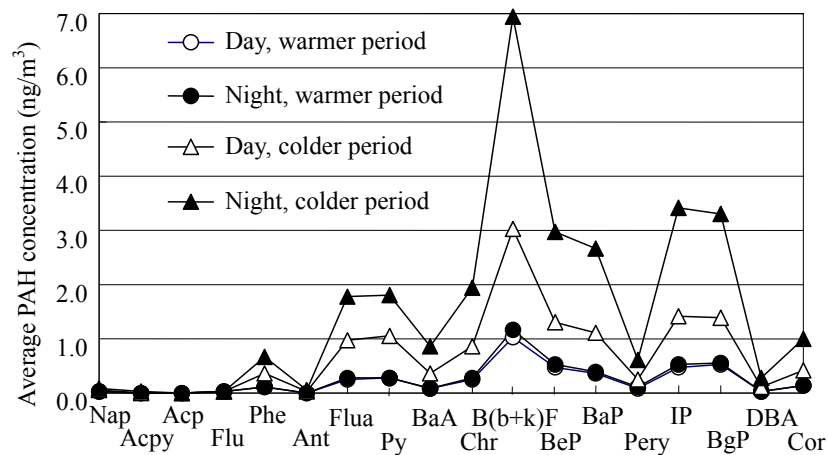


Fig. 6. Comparison of average concentration of 19 PAHs in different samples.

content and composition), and atmospheric conditions (temperature and humidity) (Bidleman, 1988; Pankow, 1998; Lohmann and Lammler, 2004). Recently, both soot-air ( $K_{SA}$ ) and octanol-air ( $K_{OA}$ ) partitioning coefficients have been used to describe the partitioning of PAHs between gas and particle phases (Lohmann and Lammler, 2004)

$$K_p = 10^{-12} \left( f_{OM} \frac{\gamma_{oct} MW_{oct}}{\gamma_{OM} MW_{OM} \rho_{oct}} K_{OA} + f_{BC} \frac{\partial_{atm-BC}}{\partial_{soot} \rho_{BC}} K_{SA} \right) \quad (1)$$

where  $\partial_{atm-BC}$  and  $\partial_{soot}$  denotes the available surfaces of atmospheric BC and diesel soot, respectively, and other parameters are illustrated in Table 3. Assuming the ratios of  $\gamma_{oct}/\gamma_{OM}$ ,  $MW_{oct}/MW_{OM}$ , and  $\partial_{atm-BC}/\partial_{soot}$  are equal to 1, it is possible to calculate  $K_p$  values ( $m^3/\mu g$ ) of PAHs (Table 3). Then, the gas-phase concentration of each PAH can be predicted using the following equation (Pankow, 1987)

$$K_p = \frac{F/TSP}{A} \quad (2)$$

In Eq. (2), F and A denotes the measured fractions of

particle- and gas-phase of PAHs, respectively. In our study, a ratio of 1.15 was assumed for TSP/PM<sub>10</sub>.

A toxicity equivalency factor (TEF), developed based on Nisbet and LaGoy (1992), was used in the assessment of airborne PAHs (Table 4). Results showed that the mean daily exposure dose of BaP<sub>eq</sub> (BaP equivalent) was due mainly to particle-phase except the period from 23 Oct to 27 Oct and from 2 Nov to 9 Nov and BaP<sub>eq</sub> values exceed the WHO (1987) air criterion (1 ng/m<sup>3</sup>) in most cases indicating that the air pollution by airborne PAHs at this site was serious. Furthermore, the levels of human exposure to airborne PAHs at night were relatively higher than during the day (especially in the colder period). At the guideline value of 7.3 (mg/kg/day)<sup>-1</sup> for the oral cancer slope factor (CSF) of BaP (USEPA, 1999), the excess lifetime cancer risk (ELCR) is then computed as

$$ELCR = CDI[mg/kg/d] \times CSF[(mg/kg/d)^{-1}] \quad (3)$$

In Eq. (3), CDI (chronic daily intake) is obtained by combining data from daily BaP<sub>eq</sub>, inhalation rate (20 m<sup>3</sup>/d) and body weight (70 kg/adult). According to USEPA (1999),

**Table 3.** Physicochemical properties of selected PAHs and particle properties, namely molecular weight (MW), octanol-air ( $K_{OA}$ ) and soot-air ( $K_{SA}$ ) partitioning coefficients, organic matter ( $f_{OM}$ ) and black carbon ( $f_{BC}$ ) fractions, density of octanol ( $\rho_{oct}$ ) and black carbon ( $f_{BC}$ ), calculated gas-particle partitioning coefficient ( $K_p$ ).

	MW (g/mol) <sup>a</sup>	Log $K_{OA}$ <sup>b</sup>	Log $K_{SA}$ <sup>b</sup>	$F_{OM}$ <sup>c</sup>	$f_{EC}$ <sup>c</sup>	$\rho_{oct}$ (g/mL) <sup>d</sup>	$\rho_{BC}$ (g/mL) <sup>d</sup>	$K_p$ (m <sup>3</sup> /μg)
Nap	128.18	5.07	6.82	0.114	0.070	0.82	1	4.8E-07
Acey	152.2	6.26	8.04	0.114	0.070	0.82	1	7.9E-06
Acp	154.2	6.36	8.14	0.114	0.070	0.82	1	1.0E-05
Flu	166.23	6.80	8.60	0.114	0.070	0.82	1	2.9E-05
Phe	178.24	7.60	9.40	0.114	0.070	0.82	1	1.8E-04
Ant	178.24	7.70	9.50	0.114	0.070	0.82	1	2.3E-04
Flua	202.26	8.60	10.50	0.114	0.070	0.82	1	2.3E-03
Py	202.26	8.70	10.60	0.114	0.070	0.82	1	2.9E-03
BaA	228.3	10.02	11.91	0.114	0.070	0.82	1	5.8E-02
Chr	228.3	10.20	12.10	0.114	0.070	0.82	1	9.0E-02
B(b + k)F	252.32	11.20	13.13	0.114	0.070	0.82	1	9.6E-01
BeP	252.32	11.20	13.13	0.114	0.070	0.82	1	9.6E-01
BaP	252.32	11.10	13.00	0.114	0.070	0.82	1	7.2E-01
Pery	252.32	11.20	13.13	0.114	0.070	0.82	1	9.6E-01
IP	276.34	12.39	14.35	0.114	0.070	0.82	1	1.6E+01
DBA	278.36	12.49	14.45	0.114	0.070	0.82	1	2.0E+01
BgP	276.34	12.39	14.35	0.114	0.070	0.82	1	1.6E+01
Cor	300.36	13.56	15.55	0.114	0.070	0.82	1	2.5E+02

<sup>a</sup> Mackay *et al.* (1992).<sup>b</sup> Lohmann and Lammel (2004), data not given in the reference were calculated through the linear relationship between MW and  $K_{OA}$  or  $K_{SA}$ .<sup>c</sup> mean values of EC (or BC) and OM ( $f_{OM}/f_{OC} = 1.2$ ).<sup>d</sup> Dachs, J. and Eisenreich, S.J. (2000) and Lohmann and Lammel (2004).**Table 4.** BaP equivalents (ng/m<sup>3</sup>) and increased risk level of cancer\*.

Sampling period	BaP <sub>eq</sub> (ng/m <sup>3</sup> )				Exposure BaP <sub>eq</sub> (ng)		CDI (×10 <sup>-6</sup> mg/kg/d)	ELCR (×10 <sup>-6</sup> )
	D (g)	D (p)	N (g)	N (p)	D	N		
23 Oct–27 Oct	1.05 ± 0.37	0.82 ± 1.53	1.33 ± 0.39	0.82 ± 1.86	18.71 ± 18.90	21.50 ± 22.52	0.57 ± 0.59	4.19 ± 4.32
28 Oct–1 Nov	0.20 ± 0.05	0.66 ± 1.30	0.28 ± 0.07	0.62 ± 1.78	8.58 ± 13.48	8.97 ± 18.55	0.25 ± 0.46	1.83 ± 3.34
2 Nov–9 Nov	0.52 ± 0.15	0.31 ± 0.84	0.23 ± 0.08	0.35 ± 1.28	8.26 ± 9.86	5.75 ± 13.51	0.20 ± 0.33	1.46 ± 2.44
10 Nov–14 Nov	0.15 ± 0.04	0.69 ± 0.92	0.15 ± 0.04	0.67 ± 1.27	8.33 ± 9.57	8.11 ± 13.02	0.23 ± 0.32	1.71 ± 2.36
15 Nov–25 Nov	0.53 ± 0.15	0.59 ± 1.44	0.71 ± 0.21	0.89 ± 1.17	11.12 ± 15.91	16.00 ± 13.86	0.39 ± 0.43	2.83 ± 3.10
26 Nov–30 Nov	1.13 ± 0.34	1.31 ± 1.04	1.37 ± 0.39	2.77 ± 1.03	24.32 ± 13.81	41.40 ± 14.18	0.94 ± 0.40	6.85 ± 2.92
1 Dec–8 Dec	1.38 ± 0.41	2.72 ± 2.22	1.59 ± 0.50	4.77 ± 1.02	40.98 ± 26.28	63.60 ± 15.30	1.49 ± 0.59	10.91 ± 4.34
9 Dec–14 Dec	1.24 ± 0.35	2.49 ± 0.65	1.21 ± 0.32	6.54 ± 1.80	37.28 ± 10.05	77.57 ± 21.20	1.64 ± 0.45	11.98 ± 3.26
16 Dec–25 Dec	0.85 ± 0.29	1.55 ± 1.79	1.26 ± 0.31	3.31 ± 1.45	23.97 ± 20.81	45.61 ± 17.57	0.99 ± 0.55	7.26 ± 4.00
26 Dec–31 Dec	1.16 ± 0.34	1.25 ± 0.88	1.38 ± 0.41	4.69 ± 1.60	24.08 ± 12.20	60.73 ± 20.17	1.21 ± 0.46	8.85 ± 3.38

\* Pery, BeP and Cor were given a TEF value of 0.001, 0.01 and 0.001 respectively in the calculation of BaP equivalents. An adult inhales about 20 m<sup>3</sup>/day of air daily

a one in a million chance of the increased risk of a 70 kg adult developing cancer over a 70 year lifetime is the level of risk considered acceptable. The data in Table 4 showed that the increased cancer risks in the colder period were significantly higher than those in the warmer period. Even though the highest value of ELCR in the colder period was much lower than the serious level of one in thousand according to USEPA (1999), the local public health department should take steps to improve air quality and reduce airborne PAHs exposure.

### Uncertainty Analysis

It must be emphasized that there are substantial uncertainties associated with the determination of  $K_p$  (Lohmann and Lammel, 2004) according to Eq. (1) due to the propagation of error for  $\rho_{oct}$ ,  $\rho_{BC}$ ,  $f_{OM}$ ,  $f_{BC}$ ,  $K_{OA}$ ,  $K_{SA}$ , etc. For the purposes of uncertainty analysis we will use average error transfer formula to quantify a total error for the computed value. The average deviations for  $\rho_{oct}$  and  $\rho_{BC}$  were assumed 0.08 g/mL and 0.10 g/mL, respectively (around 10% of the average value). The average deviations

for  $f_{OC}$  and  $f_{BC}$  were given the values of 0.019 and 0.013, respectively, according to the carbon measurements in Big Xiamen Bay Air Quality Monitoring Project. The deviations for  $K_{OA}$  and  $K_{SA}$  were not accessible and their errors propagations were considered as zero. According to the report of Bruhn *et al* (2003), a value of 0.15 was assigned to the random and analytical error of  $PM_{10}$ . However, additional error of particle-phase PAHs due to the filter adsorption plus 0.15 was assigned to the average deviation of F.

The total error for the computed ELCR values was considerably larger, especially in the warmer period (Table 4). There was a significantly negative correlation between the relative average deviation of ELCR and airborne PAHs concentration ( $r = -0.92$ ,  $P < 0.01$ ) and ratio of gas- to particle-phase PAHs ( $r = -0.77$ ,  $p < 0.01$ ) indicating that the gas-phase PAHs put severe constraints on the airborne PAHs risk assessment. In light of this, the gas- and particle-phase PAHs measurements should be carried out at the same time in the future in order to get accurate information about airborne PAHs.

## CONCLUSIONS

In this study, the diurnal concentrations of particle-bound PAHs were measured at a traffic site. Significant night over day predominance for PAHs was observed, especially for those samples measured in the colder period. An important role in the diurnal distributions of PAHs seems to be played by thermal inversions occurring at night instead of photodegradation. Thermal inversions following low temperature and high atmospheric pressure in the colder period are responsible for the enhanced concentrations of PAHs in Xiamen while air mass input from north and northeast upwind had only limited influence. However, a rural or remote area without intensive industrial activities and heavy traffic, such as Kinmen, are more likely to suffer from upwind air pollutants in the colder period. Daily exposure of airborne PAHs in most cases was mainly attributed to particle-bound PAHs and the uncertainties of ELCR were influenced by the airborne PAHs and the ratio of gas- to particle-phase PAHs to a certain extent. Considering the significant day-night differences of PAH concentrations between the warmer and the colder period, it is necessary to take into consideration the coupled effects of air temperature and photolysis when the local air quality is being assessed. For more precise atmospheric behavior research and health risk assessment purposes, 12-h and even intensive (< 4-h) sampling schedules, including gas- and particle-phase PAHs, CO, lead isotope,  $O_3$  and  $NO_x$  and solar radiation, are needed to improve our understanding of the fate of atmospheric PAHs.

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