



Polycyclic Aromatic Hydrocarbons in the Atmosphere of Two Subtropical Cities in Southeast China: Seasonal Variation and Gas/Particle Partitioning

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ABSTRACT

Eighteen polycyclic aromatic hydrocarbons (PAHs) were measured in the gas and particle phase from four sites in two cities, Quanzhou and Xiamen, in Southeast China during January (winter), March (spring), August (summer) and November (fall) 2010. The total concentration in the gas phase ranged from 10.7 ± 2.4 to 507.8 ± 57.0 ng/m³, while in the particle phase between 1.4 ± 0.5 and 46.5 ± 19.1 ng/m³. The levels of total PAHs (gas + particle) were lower than those recorded for Beijing, Shanghai and Guangzhou in China. The seasonal variations of particle phase PAHs were similar to those cities, with high levels in fall-winter and low levels in spring-summer. However, much higher levels of gas phase PAHs were found in summer. Results of correlation studies illustrated that total suspended particle concentrations, ambient temperature and atmospheric mixing height had significant impact on the concentrations of atmospheric PAHs and accounted for the observed seasonal variations. Phenanthrene and fluorine were the most abundant compounds in the urban atmosphere during the sampling period, accounting for approximately 38.9 ± 12.4 and $15.3 \pm 6.9\%$, respectively, of the total PAHs. A good positive relationship was obtained in the log-log plot of K_p (the gas to particle partitioning coefficient) against P_L^0 (the sub-cooled vapor pressure) with a shallow slope (from -0.836 to -0.6742) greater than -1 . Potential sources of PAHs were investigated using diagnostic ratios, which reflected the major sources such as vehicular emissions and coal combustion, although other sources such as direct emissions from industrial activities and evaporation from urban soil and road dust also contributed. The cancer risk from residential oral exposure to atmospheric PAHs in Quanzhou was higher than that in Xiamen, which was much higher than the US EPA risk management criterion (1×10^{-6}) during the fall-winter sampling period.

Keywords: Gas-particle partitioning; Seasonal variation; PAHs; Risk assessment.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants existing extensively in the atmosphere and mainly formed and emitted as a result of incomplete combustion of organic matter such as fossil fuel and biomass. PAHs have been extensively studied in the urban atmosphere over the past two decades mainly due to the public health effects associated with their carcinogenic and/or mutagenic properties (Lee *et al.*, 2001; Kameda *et al.*, 2005; Chen and Liao, 2006).

PAHs are semi-volatile organic compounds, which can occur in both the vapor and particulate phase in the atmosphere. The partitioning of a given compound between

the particulate and the gas-phase depends on the vapor pressure of the compound, the organic composition of an atmospheric aerosol and the ambient temperature (Sitaras *et al.*, 2004). For example, low molecular weight PAHs (MW ≤ 178) tend to remain in the vapor phase while the higher molecular weight ones (MW ≥ 228) are mostly associated with particulates (Cincinelli *et al.*, 2007; Spezzano *et al.*, 2009). Thus, it is important to understand the occurrence and potential sources of PAHs in both the particulate and gaseous phases in order to fully understand the occurrence of these compounds in the atmosphere.

To understand the total PAH concentrations in the particulate phase and gaseous phase, reliable sampling and analytical methods are necessary. A combination of glass/quartz/Teflon filter and sorbent cartridge (PUF or XAD-2 or PUF/XAD-2/PUF sandwiches) is widely used to collect particle-phase and gas-phase PAHs, respectively (Odabasi *et al.*, 1999; Terzi and Samara, 2004; Akyüz and Çabuk, 2010; Zhao *et al.*, 2011). Generally, the XAD-2 has a higher collection efficiency for volatile PAHs than PUF, as well

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as a higher retention efficiency (Lee *et al.*, 2004). However, XAD-2 cartridges are difficult to handle in the field and the flow rate is not very stable as compared to PUF. Because the collection of PAHs on quartz fiber filters is prone to both positive and negative artifacts, and 2- and 3-ring PAHs may break through the PUF plug, an air sampler with a backup filter and split PUFs is sometimes carried out in order to minimize the sampling artifacts and save cost and time (Hart and Pankow, 1994; Simick *et al.*, 1997; Kavouras *et al.*, 1999; Turpin *et al.*, 2000; Fernández *et al.*, 2002). The value measured on the backup filter and PUF can be used to correct the adsorption of gaseous PAHs to the front filter and the breakthrough of gaseous PAHs in the front PUF. In a critical review, Lohmann and Lammel (2004) note the contribution of adsorption and absorption to the gas-particle partitioning of PAHs, and that 4–20% of the PAHs were found on the back up filter during studies. However, the same corrections cannot be applied at all sites because the filter adsorption is sensitive to ambient temperature. Furthermore, only after both filters have reached equilibrium with adsorbed gas-phase PAHs is this correction valid (Mader and Pankow, 2001). Thus, caution should be taken when interpreting and comparing results from different studies because of the different sampling methods used. Presently, there are no “truly perfect” methods to simultaneously measure gas and particle PAHs and the sample must be collected under conditions that minimize the potential for sampling artifacts.

Because the ambient atmospheric concentrations of PAHs are influenced by local emission sources (Caricchia *et al.*, 1999; Lee *et al.*, 2008), atmospheric dynamics (Ravindra *et al.*, 2008), solar irradiation (Tham *et al.*, 2008), ambient temperature (Ravindra *et al.*, 2008; Tham *et al.*, 2008), and seasonal variations of PAH concentrations, with highest values in winter (Lee *et al.*, 2008; Xie *et al.*, 2009) are observed in many urban, rural and remote areas. The two coastal cities, Xiamen and Quanzhou, in Southeast China, as the important economic engine of the Economic Zone on the Western Coast of the Taiwan Strait, have experienced rapid urbanization and industrial expansion resulting in increased utilization of fossil fuels in vehicles. Based on data from the Fujian Provincial Bureau of Statistics in 2009 (www.stats-fj.gov.cn), the number of registered vehicles has shown a steady increase and reached 2.7 million, out of which 70% are motor cycles. Expanding car ownership, heavy traffic, and low-grade gasoline have made vehicles the leading source of air pollution in this area as in many other major cities in China. Although PAHs may be contributed from many sources, vehicle exhausts are considered to be the primary source in the major cities of Southeast China (Li *et al.*, 2006; Liu *et al.*, 2010; Chen *et al.*, 2011; Zhao *et al.*, 2011). Several studies conducted in the Xiamen area during the last decade focused primarily on the particulate phase PAHs (Hong *et al.*, 2007; Wu *et al.*, 2009, 2010, 2012), while extremely limited data are available concerning the gaseous phase distribution of these compounds (Liu *et al.*, 2011; Zhao *et al.*, 2011). The EPA federal reference method for ambient single filter-adsorbent PAHs (US EPA, 1999) used by Zhao *et al.* (2011) may underestimate the gas

phase PAHs and influence the gas-particle partitioning coefficient (K_p) of the PAHs, especially for 2- and 3-ring PAHs (Liu *et al.*, 2011). The main object of the present work was to study the seasonal variation of particulate and gaseous PAHs in the two cities using the filter-filter plus PUF-PUF method, and to identify their pollution sources using PAH diagnostic ratios and multivariate statistical analysis.

METHODS

Sampling Program and Collection

Air samples (both gas and particle) were taken at four sampling sites in Xiamen and Quanzhou (Fig. 1). The first site, A1, was located on the roof (ca. 21 m height) of the Quanzhou Environmental Protection Bureau (24°53.91'N, 118°35.86'W) and representative of an urban and traffic mixture area. The second site, A2, was located on the roof of a building (ca. 30 m height) at Anhai Chenggong Primary School in Jinjiang city, a county-level city of Quanzhou City (24°43.33'N, 118°27.95'W) and representative of a traffic and industrial area. The third site, A3, was located on the roof of a building (ca. 15 m height) at Xiamen Dadeng Middle School (24°33.61'N, 118°19.82'W) and representative of a tourism and sub-rural area of Xiamen. The fourth site, A4, was located on the roof (ca. 18 m height) of Xiamen University Oceanography Building (24°26.16'N, 118°05.41'W) and representative of an urban and traffic area of Xiamen. Four field campaigns were carried out in the winter (January 20–25, 2010), spring (March 3–8, 2010), summer (August 10–15, 2010), and fall (November 24–29, 2010). The sampling dates were chosen based on the local weather forecast so that there were no rain events in the seven days. The daily temperature during the four sampling periods varied from $12.6 \pm 2.4^\circ\text{C}$ in winter, to $16.2 \pm 3.3^\circ\text{C}$ in spring, $30.0 \pm 0.4^\circ\text{C}$ in summer and $19.1 \pm 0.8^\circ\text{C}$ in fall. Each 24 h sampling period was divided into two intervals, the daytime and nighttime sampling periods, depending on the local sunrise and sunset times. The sampling durations were short (around 12 h) to reduce PAH volatilization losses from the filter during sampling. Based on the breakthrough test in section 2.4, the levels of low-molecular weight PAHs adsorbed on primary filter and PUF were greater than the detection limit and the highest breakthrough ratio of naphthalene (backup to backup plus primary) didn't exceed 50% using 12 h sampling strategy. Therefore, the sampling duration of 12 h was able to capture enough volatilized PAHs and avoid the possible breakthrough. In a word, the data measured in different seasons could represent to a great extent the general pollution levels of atmospheric PAHs in each season.

The collection method for atmospheric particle and gas samples was modified from US EPA TO-13A (US EPA, 1999). The atmospheric particle (total suspended particle, TSP) and gas samples were simultaneously collected with a middle-volume GPS-1 polyurethane foam (PUF) sampler (Thermo Electron Corporation, USA) at a rate of ~160 L/min. Two 102 mm diameter quartz fiber filters (QFFs, Pallflex Tissuequartz 2500 QAT-UP), one placed directly

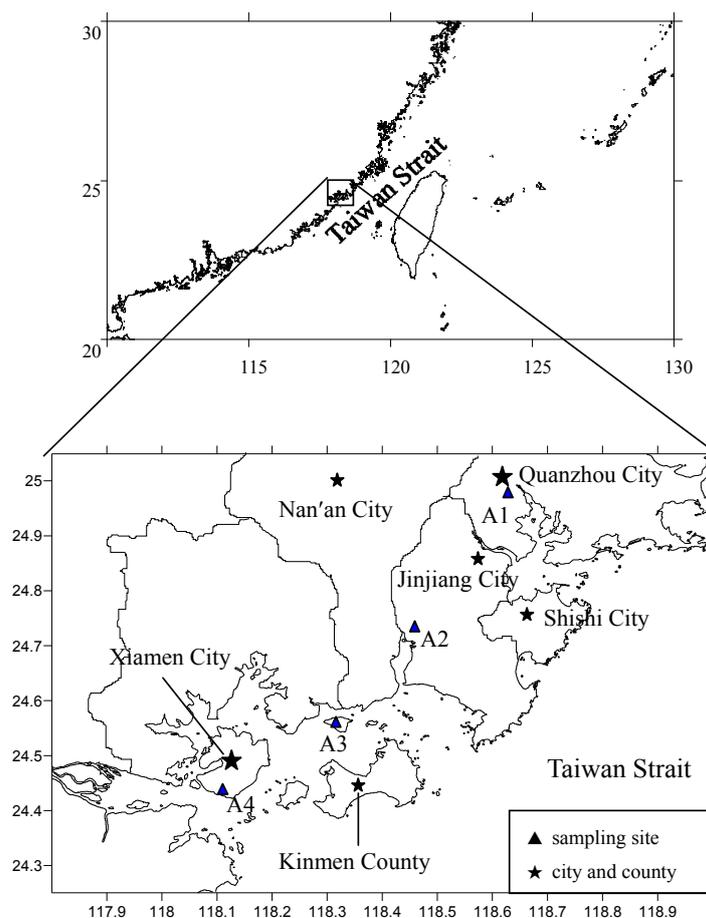


Fig. 1. Map of sampling sites in southeast China.

on top of the other (in tandem, front/backup pair), were used to collect particulate samples and to correct for compound-specific adsorption. The gas samples were trapped with two pre-cleaned PUF plugs (65 mm diameter, 40 mm length and 0.22 g/cm^3 in density) in tandem (front/backup pair). QFFs were pre-weighed using a Mettler Toledo AE240 microbalance ($\pm 0.01 \text{ mg}$) in a temperature (25°C) and relative humidity (65%) controlled laboratory after being baked at 600°C for 4 h in a muffle furnace. A baked (at 450°C for 4 h) aluminum foil bag was used to store the clean filters. PUFs were extracted in a Soxhlet apparatus with acetone for 24 hours at approximately 6 cycles per hour before initial use. When PUFs were reused, dichloromethane (DCM) was used as the cleanup solvent. After extraction cleanup, PUFs were dried at reduced pressure in a vacuum drier in order to avoid interference from the laboratory air. The dried PUFs were stored in acetone rinsed glass vials with Teflon-faced rubber liners in the screw caps. After sampling, both front and backup filters were folded and wrapped in their aluminum foil bags and weighed individually. The net difference between pre- and post-sampling filter weights was used to calculate the ambient TSP concentration. The net weight difference between pre- and post-sampling for backup filter could also be used to correct the weighing error of the front filter. For the two PUFs in tandem, they were stored in their glass vials individually and $\sim 1 \text{ mL}$ DCM

was injected into each vial to prevent bacterial growth. On arrival, the sealed foil bags and vials were kept in a refrigerator at -20°C until analysis.

The levels of criteria air pollutants, such as NO_2 , SO_2 , CO and O_3 (42i, 43i, 48i and 49i, Thermo Electron Co., USA), from the air quality automatic monitoring station near site A4 were provided by the Xiamen Environmental Protection Bureau during the sampling time. The meteorological factors, temperature, relative humidity, wind direction and wind speed, were monitored using an automatic weather station (PH-1, XPH Co., China) at site A4.

PAH Analysis

The extraction and cleanup methods for PAHs in QFFs and PUFs were modified from USEPA TO-13A, method 3550B (ultrasonic extraction) and 3630C (silica gel cleanup) (EPA, 1995, 1999). Before extraction, $10 \mu\text{L}$ of a $20 \mu\text{g/mL}$ deuterated PAH solution (surrogate) containing naphthalene-d8 (Nap-d8), acenaphthene-d10 (Acp-d10), phenanthrene-d10 (Phe-d10), chrysene-d12 (Chr-d12) and perylene-d12 (Pery-d12) was spiked directly to the QFFs and PUFs.

The QFF samples were immersed in DCM overnight and extracted ultrasonically three times, each time with DCM. These extracts were then combined and evaporated to approximately 10 mL using a rotary evaporator. After adding 15 mL of n-hexane, the extract volumes were reduced again

to around 1 mL for solvent exchange and further purified on a silica gel column. PUF cartridges were Soxhlet extracted with DCM for at least 16 h and the solvent in the PUF was squeezed into the flask after extraction to enhance the recovery. The procedure of concentrating and solvent exchange was the same as that carried out for the filter samples. Both sample extracts were transferred to a silica gel column packed with approximately 10 grams of silica gel (type 60, 70–230 mesh) with 1 g anhydrous sodium sulfate on the top. The column was eluted with 25 mL n-hexane and 40 mL n-hexane/DCM (6:4 v/v). Both fractions were combined and reduced to ~200 μ L under a gentle stream of ultra-pure nitrogen gas. Next, 10 μ L of 10 μ g/mL hexamethylbenzene solution (internal standard) was added to the tube and the supernatant was transferred to a vial insert for GC/MS analysis.

Eighteen PAHs (AccuStandard Inc., USA), including Nap, acenaphthylene (Acpy), Acp, fluorine (Flu), Phe, anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), Chr, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[j]fluoranthene (BjF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenz[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP), were analyzed using an Agilent 6890 GC coupled with an Agilent 5973 MSD operated in selective ion monitoring mode. A 30 m \times 0.25 mm i.d. \times 0.25 μ m HP5-MS capillary column (Agilent Co., USA) was used to separate these compounds with an oven temperature program from 60°C to 300°C at a rate of 5 °C/min (held isothermally at the end temperature for 20 min). Injector and GC/MS interface temperatures were 250°C and 280°C, respectively. In mass spectrometry, electron impact ionization was carried out at the electron energy of 70 eV. It should be noted that BbF, BkF and BjF are difficult to separate from each other using HP-5MS column and these three compounds were quantified together as BbkjF when making a calibration curve.

Quality Control

Before sample analysis, PAHs recovery studies were undertaken to verify the method. Five deuterated PAH surrogate standard solution was added directly to pre-cleaned blank QFF and PUF and no great difference of recovery was found between QFF and PUF for each surrogate compound. The recoveries ($n = 6$) of five PAH surrogate

standards in blank PUF/QFF were as follows: $78 \pm 7\%/88 \pm 10\%$ for Nap-d8 (represent Nap), $85 \pm 6\%/90 \pm 8\%$ for Acp-d10 (represent Acpy, Acp and Flu), $90 \pm 8\%/93 \pm 4\%$ for Phe-d10 (represent Phe, Ant, Flua and Pyr), $92 \pm 12\%/95 \pm 9\%$ for Chr-12 (represent BaA and Chr), and $91 \pm 4\%/89 \pm 7\%$ for Pery-d12 (represent BbkjF, BeP, BaP, IP, BgP and DBA). To correct the effect of laboratory and field contamination, laboratory and field blank samples were also analyzed as regular samples. Only trace Nap (17.1 ± 6.4 ng/sample), Acp (3.8 ± 1.5 ng/sample) and Phe (20.1 ± 4.0 ng/sample) were detected on both filter and PUF blanks ($n = 6$), and both levels were less than 5% of the mass in the samples. Two pairs of duplicate samples were also treated with each set of regular samples and the differences between the duplicate samples were less than 10.8%. The reported concentrations of PAHs were corrected using blank values and recovery rates.

Correction of Sampling Artifacts

As mentioned previously, the sampling artifacts associated with QFF include the adsorption of gaseous PAHs to the QFF and volatilization of volatile PAH compounds from the QFF, and the sampling artifact associated with PUF is the possible breakthrough of volatile PAHs from the PUF. Based on the sampling scheme with backup QFF and PUF, the sampling artifacts were assessed using the fraction of PAHs detected on backup QFF and PUF to PAHs detected on backup plus primary QFF and PUF. During November when the ambient temperature was around 25°C, a high percentage mass (> 20%) on backup QFFs and PUFs was found for the most volatile PAHs (such as Nap, Acpy, Acp and Flu) and PAHs with five or more rings were not detected on any backup QFF and PUF (Fig. 2). Because the breakthrough ratios of Nap and Acpy were very high (~40%), it is possible that part of these two compounds may escape from the two-stage PUF system. Thus, sampling system with XAD-2 resin sandwiched between layers of PUF is prior to two-stage PUFs (Pizzoli *et al.*, 2004). However, the toxicity contribution of these two compounds escaped from the sampling system is not important and neglectable. The particle-gas partitioning parameter for two to three ring PAHs (Nap, Acpy and Acp) can be overestimated by a factor of as much as 10.5–19.8 without correcting for the gas adsorption to QFFs (Liu *et al.*, 2011). Therefore, PAHs detected on backup QFFs were subtracted from those in the

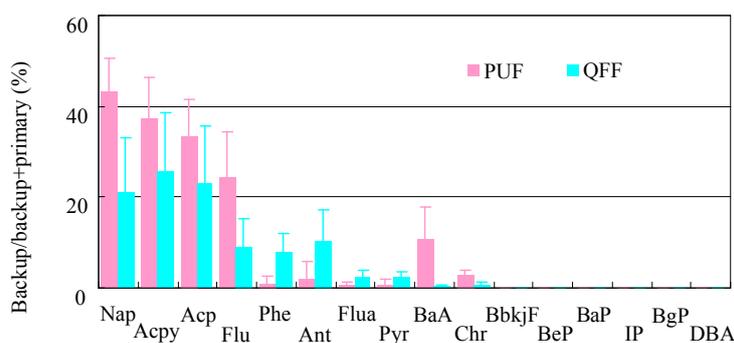


Fig. 2. Sampling artifacts assessment using backup QF and PUF.

primary QFFs and added to the gas phase concentration. Moreover, the levels of high molecular weight PAHs with rings ≥ 6 in PUFs were lower than their detections, which suggested that their gas-phase concentrations might be underestimated using this modified sampling method as compared with TO-13A. The nearly true gaseous concentrations were calculated as the contaminant mass detected on the primary and backup PUFs plus twice the contaminant mass detected on the backup QFF, while PAHs in the particle phase were calculated as the mass measured on primary QFF minus those on backup QFF (Hartt and Pankow, 1994). However, the backup filter could be contaminated by PAHs compounds associated with the primary filter because the primary filter was directly on the backup one. Thus, gas-phase PAHs may be overestimated while particle-phase PAHs may be underestimated. Nevertheless, the transport diffusion of PAHs from the primary filter to the backup one was limited and the contamination of backup filter by the primary one was not considered in the study. For further study, the two filters need to be fixed on different support in tandem without contact in order to avoid this kind of artifact. Anyway, the modified sampling and analytical system met the requirements for atmospheric PAHs monitoring in our study.

RESULTS AND DISCUSSION

Seasonal Variations of PAH Concentrations

The seasonal average concentrations of total 18 PAHs in the gas and particle phases varied widely (Fig. 3). The highest level of gas phase PAHs was found at A2 in summer ($507.8 \pm 57.0 \text{ ng/m}^3$) and the lowest level was found at A4 in spring ($10.7 \pm 2.4 \text{ ng/m}^3$). For the particle phase PAHs, however, the highest and lowest levels were found at A2 in fall ($46.5 \pm 19.1 \text{ ng/m}^3$) and A4 in spring ($1.4 \pm 0.5 \text{ ng/m}^3$). The atmospheric levels of PAHs in the two cities were generally lower than those reported in urban areas of Shanghai (Chen *et al.*, 2011), Guangzhou (Yang *et al.*, 2010), Turkey (Esen *et al.*, 2008) and Egypt (Hassan and Khoder, 2012), but were higher than those reported in Kaohsiung (Lai *et al.*, 2011), and in Xiamen by a previous study (Zhao *et al.*, 2011). However, a direct comparison of PAHs between

different cities should be done with caution because both the sampling sites and ambient meteorological factors could greatly affect PAH concentrations.

Fig. 3 reveals that the seasonal trends in PAH concentrations were different between the gas and particle phases. The average concentrations of particle phase PAHs at four sites in the two cities were higher in fall-winter than in spring-summer, which is similar to the results reported in other areas without domestic heating in winter (Yang *et al.*, 2010; Chen *et al.*, 2011; Lai *et al.*, 2011; Zhao *et al.*, 2011). Thus, the high particle phase PAH concentrations measured in fall-winter might not result from additional local fossil fuel usage for domestic heating purposes. As mentioned above, lower mixing height, less solar radiation and photo-oxidation, less rainfall (or high levels of ambient particles) and more gas-to-particle partitioning might result in higher levels of particle phase PAHs in winter. In this study, the seasonal variations of the daily solar radiation intensity and TSP concentrations during the sampling period conform to the observed trend of the particle phase PAHs (Fig. 4). However, higher levels of TSP found in fall-winter did not result from lower solar radiation intensity, but due to the less atmospheric convection in fall-winter. Moreover, particle phase PAHs were significantly correlated ($r = 0.692$, $P < 0.01$) with TSP indicating that the greater area available in the form of TSP was favorable for the adsorption of gas phase species in fall-winter and/or that both TSP and particle phase PAHs came from the same sources (Wu *et al.*, 2010). Additionally, the lower mixing height and possible input from north and northeast in the fall-winter should increase levels of PAHs associated with TSP (Fig. 5). The possibility that PAHs were being transported from upwind areas will be addressed later in the emission sources identification section using a diagnostic ratio.

The seasonal variation pattern of gas phase PAHs was not as clear as the particle phase PAHs trend, with lower concentration in spring and higher levels in other seasons. This can be partly interpreted in terms of particle-to-gas phase distribution and volatilization from the urban land of semi-volatile PAHs in summer and concomitant effects of atmospheric conditions characterized by lower mixing layers and decreased solar radiation in the winter and fall

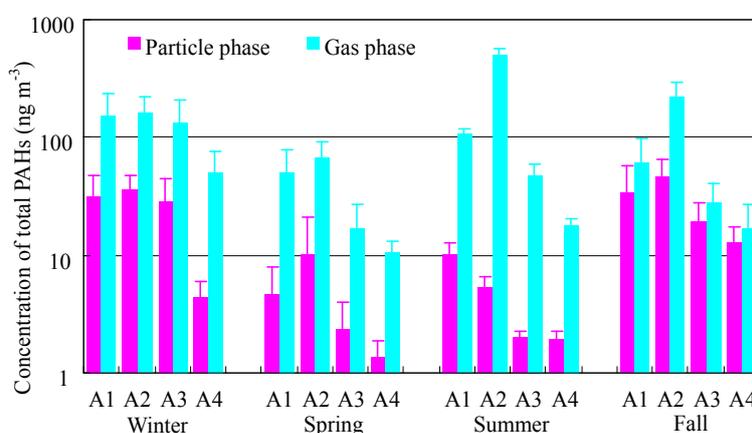


Fig. 3. Seasonal variation of total PAHs in the two cities.

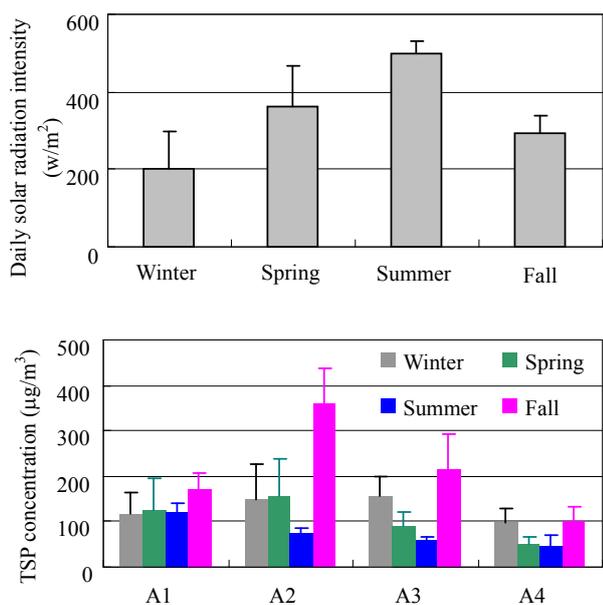


Fig. 4. Seasonal variations of daily solar radiation intensity and TSP concentration.

(Fig. 4). The highest net soil to air gas exchange of PAHs is reported in summer in North China because the temperature is higher in summer than in other seasons although the high temperature favors photochemical degradation (Wang et al., 2011).

Temperature dependence of gas phase PAHs is often investigated using the Clausius–Clapeyron plots of the natural logarithm of partial pressure of PAH ($\ln P$, atm) vs. inverse of temperature ($1/T$, K^{-1}) (Sitaras et al., 2004; Gaga et al., 2012). The temperature dependence was discussed for two compounds, Flu and Phe, with the highest concentrations in gas phase at site A4 due to the limited meteorological data available. The correlation between $\ln P$ and $1/T$ was statistically significant at the 0.01 level (2-tailed) for Flu and Phe (Fig. 6). A positive slope of 5113.6 obtained for Flu indicated that this compound was under the influence of freshly emitted PAHs, while a negative slope of -5095.9 obtained for Phe indicated the influence of volatilization of PAHs from soil, road dust and atmospheric particles (Sitaras et al., 2004; Vasilakos et al., 2007; Gaga et al., 2012).

Table 1 presents the correlations between the gas and particle phase PAHs and temperature (T), wind speed (WS),

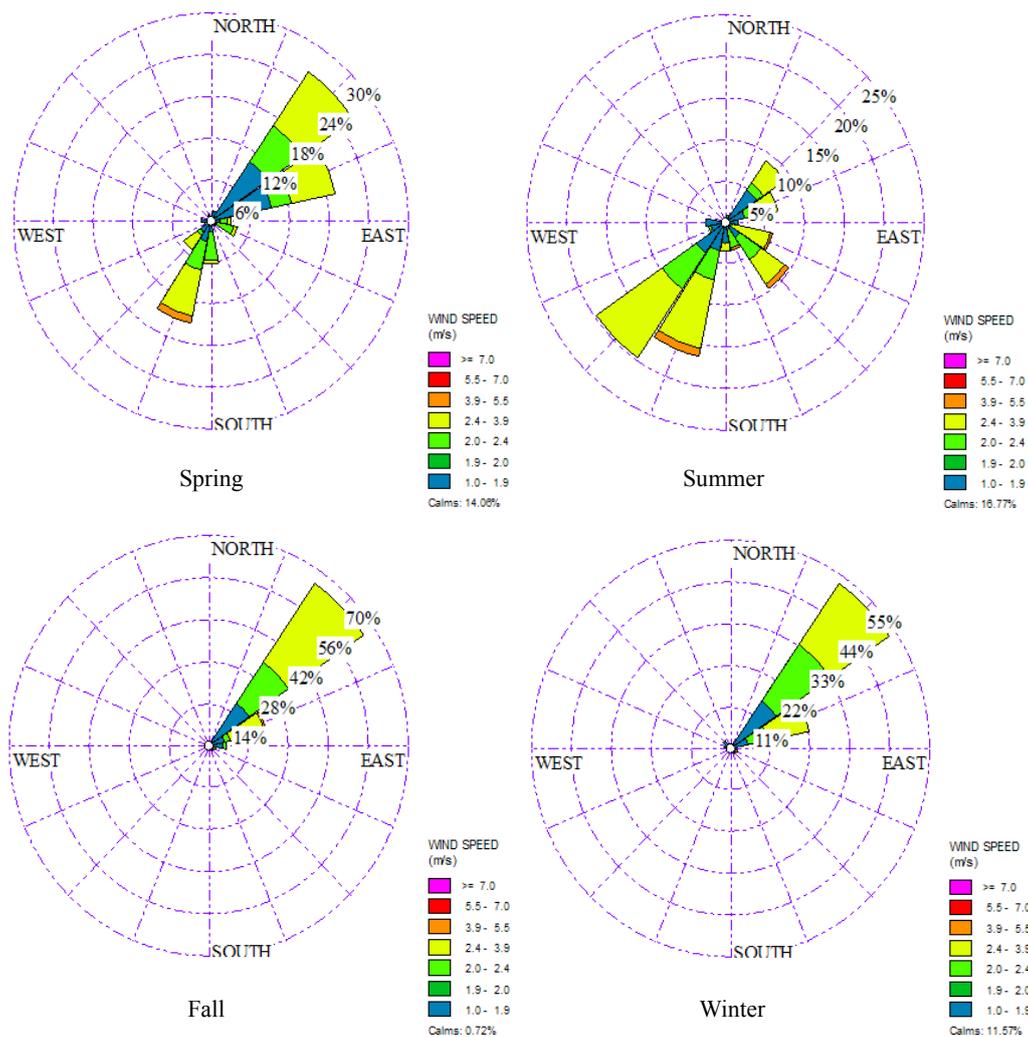


Fig. 5. Wind roses in different seasons at site A4.

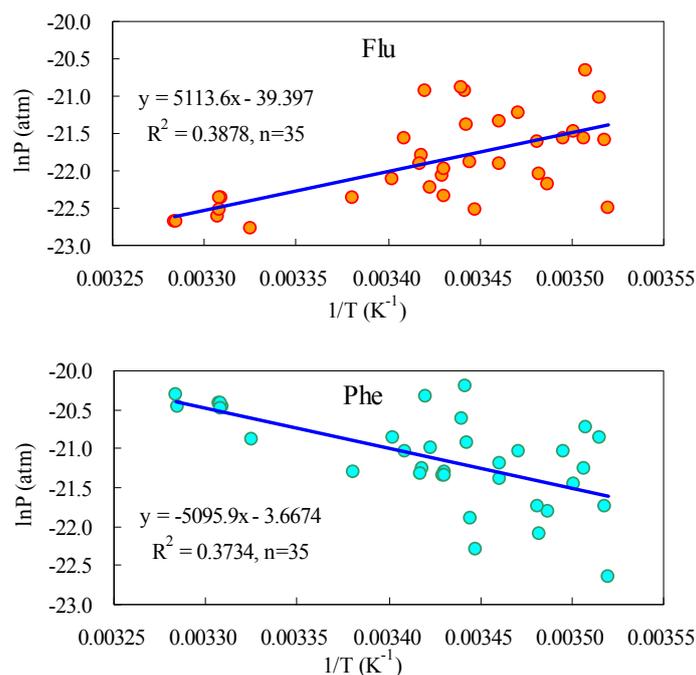


Fig. 6. Clausius–Clapeyron plots for Flu and Phe at Site A4 (not include samples in winter).

Table 1. Correlation coefficients for the relationships of selected PAHs concentrations with meteorological parameters and criteria air pollutants at site A4.

Gas phase, n = 35	T	WS	RH	NO ₂	O ₃	SO ₂	CO
Flu	-0.451**	-0.482**	-0.026	0.691**	-0.182	0.523**	0.518**
Phe	0.554**	-0.203	0.435**	0.187	-0.602**	-0.050	-0.217
Flua	0.239	-0.434**	0.326	0.484**	-0.471**	0.167	0.188
Pyr	0.270	-0.473**	0.541**	0.381*	-0.621**	-0.041	0.124
ΣPAH _g ¹	0.277	-0.331	0.281	0.404*	-0.519**	0.173	0.014
Particle phase, n = 29	T	WS	RH	NO ₂	O ₃	SO ₂	CO
Flua	-0.300	-0.248	-0.549*	0.747**	0.350	0.860**	0.567*
Pyr	-0.278	-0.322	-0.386	0.832**	0.185	0.832**	0.615*
BaA	-0.205	-0.172	-0.476*	0.69**	0.213	0.761**	0.414*
Chr	-0.300	-0.393	-0.239	0.813**	0.026	0.699**	0.575*
BbkjF	-0.307	-0.401*	-0.235	0.842**	0.009	0.722**	0.590*
BeP	-0.216	-0.192	-0.478*	0.648**	0.202	0.733**	0.366
BaP	-0.218	-0.200	-0.460*	0.665**	0.185	0.740**	0.385
IP	-0.144	-0.048	-0.543*	0.467*	0.259	0.656**	0.216
BgP	-0.210	-0.214	-0.446*	0.704**	0.141	0.764**	0.405
DBA	-0.290	-0.370	-0.285	0.772**	0.029	0.695**	0.477*
ΣPAH _p ²	-0.075	-0.198	-0.280	0.619**	0.065	0.644**	0.323

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

¹ total PAH concentration in gas phase.

² total PAH concentration in particle phase.

relative humidity (RH) and criteria air pollutants at site A4. The particle phase PAHs were strongly correlated with NO₂ and SO₂ while an insignificant correlation was observed between the gas phase PAHs (except Flu) and SO₂. NO₂ and SO₂ are mainly emitted from vehicular emissions and coal combustion, respectively, and therefore it can be assumed that both vehicular emissions and coal combustion can contribute to the particle phase PAHs. Furthermore a

strong negative correlation was measured between the gas phase PAHs and O₃ while no significant correlation was found between the particle phase PAHs and O₃ although surface reactions are more rapid than gas-phase reactions (Perraudin *et al.*, 2007). These results were expected since higher ambient O₃ concentrations usually occur when solar radiation is strong. Under the action of sunlight, photolysis of PAHs associated with particles was slow because the

dark carbonaceous material can absorb a substantial fraction of light, and therefore protect PAHs from photodegradation (Vione *et al.*, 2006). The positive correlation observed between Flu and CO but the negative correlation between Flu and T suggest that this compound was probably mainly a direct emission from fossil combustion (Li *et al.*, 2006). However, a significant positive correlation between Phe and T but an insignificant correlation between Phe and NO₂, SO₂ and CO indicates the importance of volatilization of the Phe from soil, road dust and atmospheric particles (Dimaski *et al.*, 2001; Li *et al.*, 2006). In conclusion, PAHs in the particle phase were more influenced by anthropogenic stressors than by meteorological parameters based on the data shown in Table 1, and both source emissions and meteorological factors had a strong influence on the seasonal variation of PAHs.

PAH Composition and Gas/Particle Distribution

Total PAH concentrations (gas + particle) were dominated by Phe followed by Flu, Flua and Pyr which accounted for 38.9 ± 12.4 , 15.3 ± 6.9 , 7.9 ± 2.35 and $5.5 \pm 1.9\%$ of the total ambient concentrations, respectively, during the sampling periods (Fig. 7). These results are similar to the ones reported by Chen *et al.* (2011) and Gaga *et al.* (2012). In particular, Phe contributed more than half of the total PAH concentrations in summer suggesting the strong volatilization fluxes of this compound from soil, road dust and atmospheric particles probably due to the high ambient temperature. PAH compounds with a molecular weight ≥ 228 were associated primarily with the particle phase due to their lower vapor pressure and contributed more to the total PAH concentration in fall and winter than in spring and summer. The distribution of PAH compounds between the gas and particle phases were often described by the partitioning coefficient,

$$K_p \text{ (m}^3/\mu\text{g)} = \frac{F/TSP}{A} \quad (1)$$

where F (ng/m³) and A (ng/m³) refer to the particle- and gas- phase concentrations of PAHs. The partitioning coefficient (K_p) of PAHs was also found to be highly correlated with sub-cooled vapor pressure (P_L^0) in a plot of $\log K_p$ versus $\log P_L^0$ (Yamasaki *et al.*, 1982). However, a slope of -1 in plots of $\log K_p$ versus $\log P_L^0$ is rarely observed for real samples probably because the compounds between the gas and particle phases are not at equilibrium and/or the partitioning is too complicated to be explained simply by the sub-cooled liquid vapor pressure (Simcik *et al.*, 1998; Lohmann and Lammel, 2004; Galarnéau *et al.*, 2006). In our study, the log-log plots of K_p versus P_L^0 were plotted and a linear regression equation was fitted in the form of

$$\log K_p = m_r \log P_L^0 + b_r \quad (2)$$

where m_r is slope and b_r is intercept, and the sub-cooled vapor pressure (P_L^0) was estimated for each PAH using the temperature regressions based on Odabasi *et al.* (2006) and

Lei *et al.* (2002)

$$\log(P_L^0/P_a) = m_L/(T/K) + b_L. \quad (3)$$

Table 2 lists the intercepts (b_r) and slopes of the regressions between the measured $\log K_p$ values of PAHs and the estimated sub-cooled liquid saturation vapor pressure $\log P_L^0$ from Eq. (3). These slope values are in line with the literature (Simcik *et al.*, 1998; Sitaras *et al.*, 2004; Tasdemir and Esen, 2007). The most likely reasons why the estimate of the slope deviates from -1 are probably the continuous input of freshly emitted PAHs from fossil combustion, the slow gas-to-particle sorption of PAHs, and the measurement artifacts and the particle composition (Pankow, 1998; Volckens and Leith, 2003; Lohmann and Lammel, 2004). In order to further investigate the influence of these factors on gas/particle partitioning, additional information including the atmospheric lifetime of PAHs, the chemical composition and the properties of aerosols is necessary.

Emission Source Identification

Although the PAH profiles can be used as a signature of potential emission sources, several factors such as emitted amounts, atmospheric oxidants and meteorological conditions (i.e., temperature, sunlight, wind speed and wind direction) could affect the shape of fingerprint to a great extent. Thus, PAHs used as tracers should be considerably less reactive when exposed to sunlight and atmospheric oxidants. Furthermore, both the concentration of the gas and particle phases of each compound should be used together to calculate the diagnostic ratio (Zhao *et al.*, 2011; Obiszewski and Namiesnik, 2012;). However, some ratios of reactive to stable PAHs, such as BaA to Chr (BaA/Chr), Ant to Phe (Ant/Phe), BaP to BeP (BaP/BeP), can be used to assess the aging process (Li *et al.*, 2006; Wu *et al.*, 2010, 2012; Obiszewski and Namiesnik, 2012). Diagnostic ratios of Flua to Flua plus Pyr (Flua/Flua + Pyr) and IP to IP plus BgP (IP/IP + BgP) are widely used in the literature due to them being more conservative than other ratios during transportation (Yunker *et al.*, 2002; Obiszewski and Namiesnik, 2012; Tobiszewski and Namieśnik, 2012; Wu *et al.*, 2012). Table 3 lists the typical diagnostic ratios which are widely used in the literature. The ratios of BaA/BaA + Chr, Ant/Ant + Phe, Flua/Flua + Pyr and IP/IP + BgP were calculated and shown in Fig. 8 to assess possible pollution sources of PAHs. The spot distribution of samples in summer and fall implied that grass/wood/coal combustion were the prevailing sources of PAHs while the distribution of samples in spring and winter indicated mixed emission sources of petroleum and grass/wood/coal combustion (Fig. 8(a)). However, it seems implausible that the sources of PAHs were different between fall and winter since the wind directions were almost the same in both seasons (Fig. 5) as were the possible external transportation and major local contribution from vehicular emissions and coal combustion. Similarly, the spot distributions of samples in summer and fall are separated from those in spring and winter suggesting seasonal variations of PAH emission sources. For samples of A2 in summer and fall, the Ant/Ant + Phe ratios were

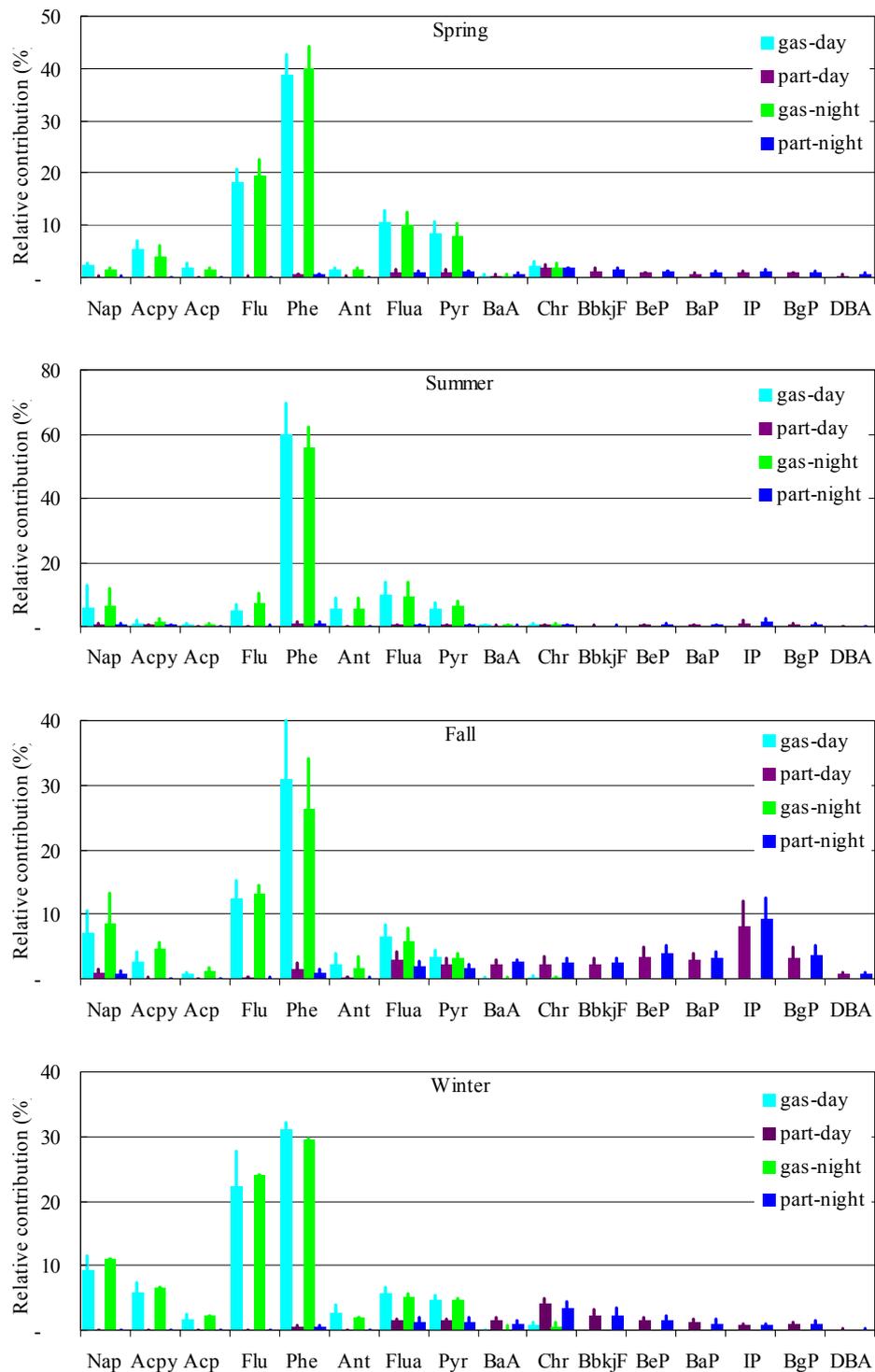


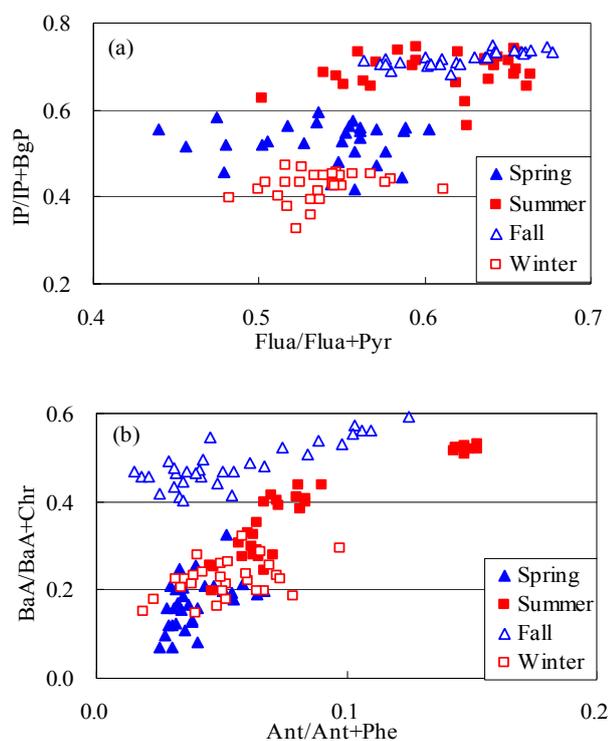
Fig. 7. Mean relative contribution of individual compound to the total (gas+particle) concentrations of PAHs in different seasons.

Table 2. Regression parameters for Eq. (1).

Site	m_r	b_r	R^2	Significance level (%)
A1	-0.7998	-4.4898	0.8227	99
A2	-0.8360	-4.8866	0.7696	99
A3	-0.6742	-4.2578	0.7309	99
A4	-0.7461	-3.9980	0.7673	99

Table 3. Some PAHs diagnostic ratios used for source identification.

PAH ratio	Value range	Source	Reference
Ant/Ant + Phe	< 0.1	Petrogenic	Pies <i>et al.</i> , 2008
	> 0.1	Pyrogenic	
BaA/BaA + Chr	0.2–0.35	Petroleum combustion	Yunker <i>et al.</i> , 2002
	> 0.35	Grass/wood/coal combustion	
	< 0.2	Petrogenic	Akyuz and Cabuk, 2010
	0.2–0.35	Coal combustion	
> 0.35	Vehicular emissions		
Flua/Flua + Chr	< 0.4	Petrogenic	De La Torre-Roche <i>et al.</i> , 2009
	0.4–0.5	Fossil fuel combustion	
	> 0.5	Grass/wood/coal combustion	Dvorská <i>et al.</i> , 2011
	< 0.35	Coal	
0.35–0.6	Almost source		
> 0.6	Biomass burning		
IP/IP + BgP	< 0.2	Petrogenic	Yunker <i>et al.</i> , 2002
	0.2–0.5	Petroleum combustion	
	> 0.5	Grass/wood/coal combustion	Dvorská <i>et al.</i> , 2011
	< 0.37	Bituminous coal	

**Fig. 8.** PAH cross-plots for the ratios of (a) Flua/Flua + Pyr vs. IP/IP + BgP and (b) Ant/Ant + Phe vs. BaA/BaA + Chr.

greater than 0.1 indicating petrogenic sources, while the ratio of BaA/BaA + Chr > 0.35 accounts for grass/wood/coal combustion (Yunker *et al.*, 2002) or vehicular emissions (Akyüz and Çabuk, 2010). Moreover, the loss rates of BaA and Ant through photodegradation are higher than Chr and Phe (Behymer and Hites, 1985) while higher ratios of BaA/BaA + Chr and Ant/Ant + Phe are found in summer and fall. Thus, it can be assumed that PAHs in summer and fall were more influenced by evaporation from urban soil and road dusts driven by the relatively higher ambient temperature.

High ratio of Ant/Ant + Phe indicating petrogenic origin has also been questioned because it is sensitive to environmental changes (Brändli *et al.*, 2008; Tobiszewski and Namieśnik, 2012). Nevertheless, the possibility of low molecular weight such as Ant and Phe from industrial activity in site A2 cannot be ruled out. The source identification using PAH concentrations in both the gas and particle phases were different from those using only particle phase concentration (Wu *et al.*, 2012) and evaporation of PAHs from urban soil and road dusts needs to be quantified in the future in order to improve the source identification of PAHs.

Owing to the limitation of PAHs diagnostic ratios in the emission source identification, principal component analysis (PCA) is often employed as an exploratory tool to identify possible sources of particulate PAHs (Li *et al.*, 2011; Wu *et al.*, 2012). In this study, the statistical analysis was carried out using SPSS for Windows 10.0 with the orthogonal transformation method with varimax rotation and an eigenvalue whose magnitude is greater than 1, is retained. Two or three principal components (PCs) were identified for each season, which accounted for 88.37–93.71% of the total variability (Table 4). PC1 was highly loaded with high molecular weight compounds including BbF, BeP, BaP, IP, BgP and DBA. According to the literature, vehicle emissions are considered to be enriched in BbF, BkF, BeP, BaP, IP, BgP, and DBA, while Phe, Ant, Flua, Py, BaA and Chr, are tracers for coal combustion (Miguel *et al.*, 1998; Khalili *et al.*, 1995; Kulkarni and Venkataraman, 2000). Thus, PC1, which accounted for 57.98–82.43% of the total variance, indicated that the main source of PAHs was vehicular exhausts. However, PC1 was also highly weighted in favor of BaA and Chr in spring, fall and winter, which reflected the contribution of coal combustion. PC2, with 12.17–31.75% of the total variance, was highly loaded with Flu, Phe, Ant, Flua and Pyr, suggested that the coal combustion was a major source of PAHs (Khalili *et al.*, 1995). But, the high variance contribution of PC2 (31.75%) in summer might be attributed to volatilization from soil and

Table 4. PCA analysis of PAHs in Xiamen and Quanzhou in different seasons*.

	Spring		Summer		Fall		Winter		
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC3
Nap		0.87							0.81
Acpy		0.75	0.84			0.82			0.83
Acp		0.92	0.86			0.76			0.88
Flu		0.91		0.76		0.89		0.70	
Phe		0.82		0.99		0.95		0.85	
Ant		0.81		0.99		0.97		0.88	
Flua	0.70	0.67		1.00		0.93		0.77	
Pyr	0.71			0.99		0.89		0.77	
BaA	0.92			0.98	0.81		0.82		
Chr	0.75			0.90	0.88		0.81		
BbjkF	0.94		0.94		0.90		0.83		
BeP	0.96		0.97		0.93		0.91		
BaP	0.92		0.99		0.92		0.87		
IP	0.95		0.98		0.94		0.86		
BgP	0.95		0.97		0.96		0.85		
DBA	0.95		0.98		0.94		0.90		
% of variance	78.63	13.59	59.62	31.75	79.58	14.13	69.48	12.17	6.72
Cumulative %	78.63	92.22	59.62	91.37	79.58	93.71	69.48	81.65	88.37

* Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Eigenvalue > 1.0 and factor loading ≥ 0.60 are listed.

road dust instead of direct emission from coal combustion. PC3, which accounted for 6.72% of the total variance in winter, was highly weighted with Acpy and Acp. As the two PAH compounds have no specific source meaning, PC3 was not attributed to the identified sources. PC1 and PC2 together explained > 80% of the variance (Table 4), implying that the PAHs measured at the sampling sites could be attributed to sources of vehicular emissions and coal combustion. The PCA result is a useful supplement for the source-diagnostic ratios.

Health Risk Assessment

Because PAHs are potentially carcinogenic to humans and different PAH compounds have different cancer potency, it is important to use toxic equivalency factors (TEFs) for the quantitative risk assessment of PAHs (Nisbet and LaGoy, 1992). In this study, more than half of the total BaP equivalents (BaP_{eq}) exceeded the national ambient air quality standard of 2.5 ng/m³ for the recommended daily exposure regulated by the Ministry of Environmental Protection of China (MEP, 2012). The excess lifetime cancer risk (ELCR) can be calculated using the following equation

$$\text{ELCR} = \text{CDI} [\text{mg/kg/d}] \times \text{CSF} [(\text{mg/kg/d})^{-1}] \quad (4)$$

In Eq. (4), CDI (chronic daily intake) is computed by multiplying the daily BaP_{eq}, inhalation rate (20 m³/d) and body weight inversion (1/70 kg). A CSF (cancer slope factor) is an estimate of possible increases in cancer cases in a population and a guideline value of 7.3 (mg/kg/day)⁻¹ of BaP is provided by USEPA (1999). Currently risks less than or equal to one-in-one million (1×10^{-6}) are considered an insignificant risk or negligible. The calculated values of

ELCR in Table 5 showed that the increased cancer risks in fall and winter were almost greater than 1×10^{-6} indicating that more effort is needed to limit the emission of PAHs from fossil combustion and/or reduce exposure to the local polluted air during these two seasons. It is important to note that the contribution of gas-phase PAHs to BaP_{eq} increased significantly in summer, especially at site A2 (around 70%) (Table 5). As has been mentioned, the gas-phase PAHs with very high atmospheric levels, around two orders of that of particle-phase PAHs (Fig. 3), at site A2 in summer might evaporate from urban soil and road dusts contaminated by vehicle exhausts and other emissions. The contaminant concentrations of PAHs in the urban soil and road dusts near site A2 as well as the possible direct emission of PAHs from petrochemical industry will be very helpful to test this hypothesis. Thus, it is necessary to monitor the gas-phase PAHs as a part of the risk assessment for exposure to polluted air, especially in summer, due to their significant contributions to BaP_{eq}.

CONCLUSIONS

In this study, we determined atmospheric PAHs in both the gas- and particle-phases using the filter-filter plus PUF-PUF method at two cities in different seasons. The measured concentrations (gas + particle) of PAHs were found to be lower than those reported from other cities in China such as Beijing, Shanghai and Guangzhou. PAHs appeared mainly in the gas phase with a small fraction in the particle phase. The low molecular weight PAHs were present mainly in the gaseous phase and PAH compounds with a molecular weight ≥ 228 were primarily associated with the particle phase. In all samplings, Phe and Flu dominated the PAH

Table 5. BaP_{eq} (ng/m³), contribution of gas-phase PAHs to the BaP_{eq} values (%), CDI (× 10⁻⁶ mg/kg/d) and increased ELCR (× 10⁻⁶).

Season	Content		A1	A2	A3	A4
Spring	BaP _{eq}	Day	0.47 ± 0.2	1.28 ± 0.47	0.31 ± 0.11	0.23 ± 0.06
		Night	1.21 ± 0.4	2.99 ± 1.87	0.33 ± 0.19	0.19 ± 0.06
	Gas contribution	Day	15.25	10.33	8.7	10.28
		Night	6.04	4.57	9.21	11.48
	CDI	Daily	0.24 ± 0.09	0.61 ± 0.33	0.09 ± 0.04	0.06 ± 0.02
	ELCR	Daily	1.76 ± 0.62	4.45 ± 2.44	0.67 ± 0.32	0.44 ± 0.12
Summer	BaP _{eq}	Day	1.30 ± 0.11	1.65 ± 0.29	0.28 ± 0.02	0.22 ± 0.05
		Night	1.96 ± 0.26	2.05 ± 0.22	0.18 ± 0.04	0.22 ± 0.02
	Gas contribution	Day	14.39	74.78	43.67	30.87
		Night	11.9	70.17	53.29	24.59
	CDI	Daily	0.47 ± 0.05	0.53 ± 0.07	0.07 ± 0.01	0.06 ± 0.01
	ELCR	Daily	3.4 ± 0.39	3.87 ± 0.54	0.48 ± 0.07	0.46 ± 0.08
Fall	BaP _{eq}	Day	2.59 ± 0.56	6.36 ± 1.18	3.15 ± 0.25	1.62 ± 0.4
		Night	8.61 ± 2.64	9.63 ± 2.06	3.2 ± 1.14	2.33 ± 0.46
	Gas contribution	Day	2.78	5.44	1.82	0.94
		Night	1.26	3.71	2.25	1.28
	CDI	Daily	1.6 ± 0.46	2.28 ± 0.46	0.91 ± 0.2	0.57 ± 0.12
	ELCR	Daily	11.68 ± 3.33	16.67 ± 3.38	6.62 ± 1.46	4.12 ± 0.9
Winter	BaP _{eq}	Day	3.75 ± 1.46	6.12 ± 0.68	5.36 ± 0.26	0.62 ± 0.06
		Night	3.51 ± 0.48	3.62 ± 0.51	5.53 ± 2.18	0.33 ± 0.06
	Gas contribution	Day	5.62	4.15	5.95	6.35
		Night	6.11	5.76	3.6	3.75
	CDI	Daily	1.04 ± 0.28	1.39 ± 0.17	1.55 ± 0.13	0.13 ± 0.02
	ELCR	Daily	7.57 ± 2.02	10.16 ± 1.24	11.35 ± 2.55	0.98 ± 0.12

* TEF values of PAHs were obtained from Nisbet and LaGoy (1992) and BeP was given a TEF value of 0.01.

spectrolemum with 38.9 ± 12.4 and $15.3 \pm 6.9\%$ relative contribution, respectively. TSP concentrations, ambient temperature and atmospheric mixing height were probably the most important factors influencing the seasonal variations of PAHs. PAH levels in the particle phase showed higher values in fall-winter while the lowest levels of PAHs in the gas phase were found in spring instead of summer, probably due to the temperature-related influence in air-soil/road gas exchange of PAHs. Regressions of $\log K_p$ vs. $\log P^0_L$ for the four sampling sites gave satisfactory correlation for individual samples suggesting that P^0_L is the most important factor controlling the gas/particle partitioning of PAHs. The atmospheric lifetime of PAHs, particle chemical and physical composition, and accurate source identification of PAHs need to be further investigated in order to know why the m_r slopes might deviate from -1 in the future. Based on the diagnostic ratios it could be concluded that vehicular emissions and coal combustion were by far the major sources of PAHs which is consistent with the current status of local energy consumption. Furthermore, direct emission from industrial activity and evaporation from urban soil and road dust might also contribute PAHs to the urban atmosphere. The results of risk assessment showed that residents in Quanzhou were more likely to be affected by cancer than those in Xiamen. This study revealed the need for better efforts to protect public health against the effects of air pollution caused by the imbalance between economic development and environmental policies.

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