



Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of Xiamen, China

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ARTICLE INFO

Article history:

Received 20 January 2010

Received in revised form 23 July 2011

Accepted 9 August 2011

Available online 22 September 2011

Keywords:

PAHs

Concentration distribution

Diagnostic ratio

Source

BaP_{eq}

Xiamen

ABSTRACT

An intensive sampling program was conducted from October 2008 to September 2009 at the five different environmental sites in Xiamen, Fujian Province, to study the spatial and temporal characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in the gaseous and particulate phase, respectively. The PAHs concentrations at different sites were quite distinct during four seasons. The average concentrations of PAHs in winter were about 8.4 times higher than those in spring, and the concentrations of background were 0.56 times lower than those of industrial area. In addition, the higher temperature in summer affected the particle/gas partitioning of PAHs and led to the higher concentrations of gaseous PAHs. Diagnostic ratios of PAHs, which were employed to indicate the primary sources of PAHs in Xiamen, showed that the traffic vehicle exhaust was the largest contributor and the primary source for PAHs in Xiamen, especially in urban area; while the stationary combustion processes, such as petrochemical factories and power plants, were mainly responsible for PAHs sources in the industrial areas. The health risk of PAHs in the particulate phase was higher than those of the gaseous phase at the five sampling sites. The average toxic equivalent (BaP_{eq}) of the benzo[a]pyrene values for PAHs were 0.14, 0.32, 1.38 and 3.59 ng m⁻³ in spring, summer, autumn and winter, respectively. Furthermore, the results of average BaP_{eq} in all four seasons indicated that the health risks of particulate PAHs were higher than those of the gaseous PAHs at different sampling sites.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), mainly originated from incomplete combustion of organic matter, are persistent organic pollutants existing in the environment extensively, and have a highlight of air pollution research due to their mutagenic and carcinogenic properties (Dong and Lee, 2009).

Sources of PAHs contaminations include domestic and industrial coal combustion, biomass combustions, and vehicle emissions (Wan et al., 2006; Heywood et al., 2006; Shen et al., 2010; Tian et al., 2009). Stationary combustion emission and automobile exhausts have been recognized as the major PAHs contributors (Li et al., 2003; Wan et al., 2006). For example, the previous studies demonstrated that PAHs originated from the coal-related sources made a 70–87% contribution to the total sources in Dalian (Wan et al., 2006). Furthermore, it was estimated that approximately 10.7% of the PAHs emissions in China in 2004 were from the residential coal combustions (Shen et al., 2010). For the vehicle related sources, it was reported that the motor vehicles accounted for as much as 90% of the particle-

phase PAH masses in the air in downtown of Copenhagen and the PAHs levels varied both temporally and spatially, depending on the traffic patterns (Nielsen, 1996). The reports of Harrison et al. (1996) confirmed the similar conclusion that primary vehicular emissions accounted for 44–93% of the concentrations of individual PAHs in the air borne particles in Birmingham (UK). There are many researches regarding particle-phase PAHs. However, the concentrations of PAHs in the gaseous phase and distributions of PAHs between particulate and vapor phases were not considered.

Xiamen, a subtropical and coastal city in the southeastern China, has a warm weather without heating episode and high relative humidity throughout the year (air temperature ranged from 4 to 38 °C with 20.9 °C mean during 2008–2009). The prevailing wind directions in autumn and winter are North and Northeast in Xiamen. This could bring cold and dry air masses from northern China. On the other hand, the warm and wet air masses carried by Southeaster from sea dominate in summer. In 2008, Xiamen has a population of 2.5 million with 1565 km² area, being a main economic and culture center of Fujian Province. With the rapid development of economy, like many cities in China, Xiamen is increasingly facing some air pollution problems. Specifically, the rising number of motor vehicles has been regarded as one of main reasons for the deterioration of air quality in the urban area, number of which increases from 190,432 in

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2000 to 508,522 in 2008 as shown in Ding et al. (2001) and Ge et al. (2009). The concentrations of total suspended particles (TSP) in the atmosphere also increase from 2000 to 2009 (Ding et al., 2001; Ge et al., 2009). The high levels of TSP often contain carcinogenic and mutagenic organic matter, including PAHs (Ayrault et al., 2010; Bi et al., 2003). Therefore, the risks associated with human exposure to atmospheric PAHs become higher and higher in the urban areas.

Despite the fact that PAHs in Xiamen had been reported by some literatures (Ye et al., 2006), no intensive research had been conducted on spatial and temporal distributions for the PAHs in the atmosphere of Xiamen, especially, the distributions of PAHs in the gaseous phase. The objectives of this paper are: (1) to measure the concentrations of ambient PAHs in gaseous and particulate phases and study spatial and temporal characteristics of the PAHs in the atmosphere, (2) to identify possible sources of PAHs, and (3) to assess the health risk of PAHs in the atmosphere of this coastal city.

2. Experiment

2.1. Sites and sampling

Air samples were collected at five sites in Xiamen: Tingxi reservoir (TX), Institute of Urban Environment, CAS (IUE), Lulian hotel (LL), Xianyue residential area (XY), Xiamen University (XU) (Fig. 1).

The TX site, as a background site, is located in a forestry reserve with a medium-sized reservoir which is the source of drinking water for Tong'an district of Xiamen. The samplers were placed on

the rooftop of the reservoir office, and approximately 6 m above the ground. This site is close to reservoir and far from traffic road. The IUE site, as a suburban sampling site, is located in Jimei District with rapid urbanization and is surrounded by highways, schools, residential buildings and Xinglin Bay. The samplers were installed on the rooftop of the laboratory building, and about 30 m above the ground. The LL site, as an industrial sampling site, is located in Haicang District, which is a main base of petrochemical and power sources in Xiamen. The samplers were mounted on the rooftop of a four-story hotel, and about 15 m above the ground.

The XY and XU sites, as the urban sampling sites, were selected in Siming District to represent commercial and educational area, respectively. The samplers at these two sites were placed on the rooftop of the residential building and classroom building, respectively, and were about 15 m and 18 m above the ground, respectively.

The 24-h air samples were obtained from October 2008 to September 2009, about 20 samples were collected at five sites for every season. The air samples were collected with the middle-volume air samplers (PS-1, Thermo Fisher Scientific, USA), at a flow rate of 160 L min^{-1} . Suspended particles were retained on a Whatman glass microfiber filter (GFF) (grade GF/A, diameter 10.16 cm), and vapor-phase species were absorbed on a polyurethane foam plug (PUF) (length 8.0 cm, diameter 6.25 cm). Considering the regular weather change of seasons in Xiamen and the shortage of samplers, these samples although not collected simultaneously at the five sites, the standard deviations of the three measurements for different samples of compounds are less than 10%, and therefore, we believe

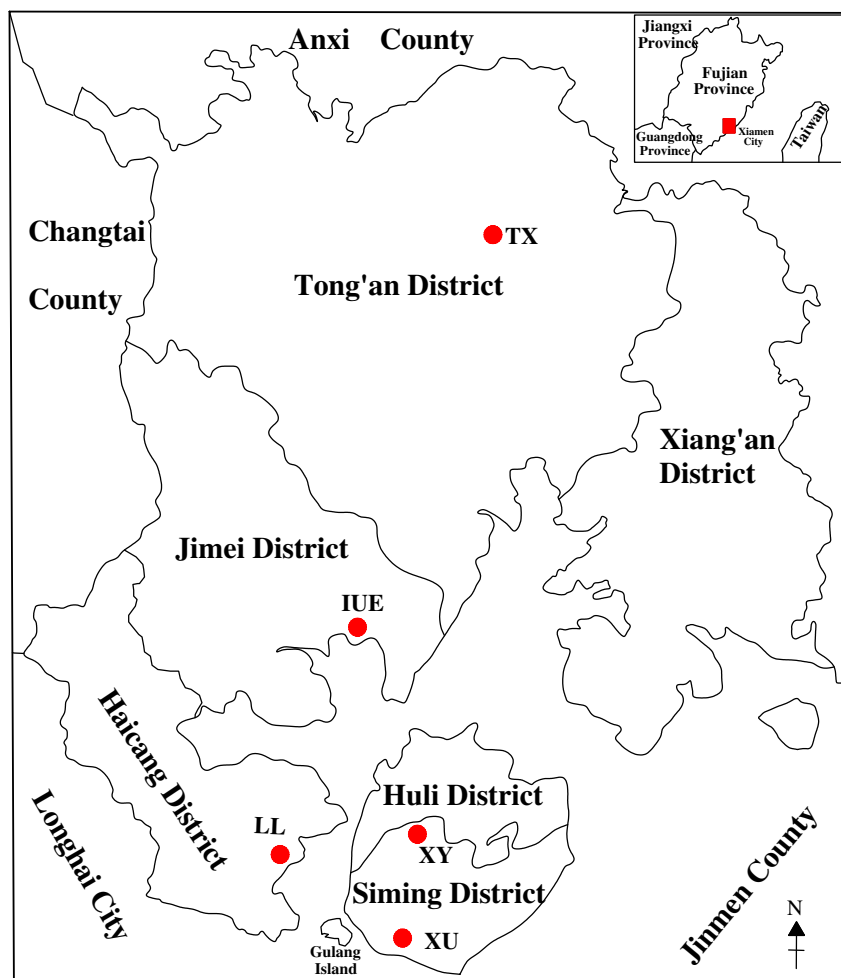


Fig. 1. Location of the five sampling sites in Xiamen shown as large red dots.

that data reported here are representative for each season and each site to explain Xiamen air pollution.

The GFFs were previously annealed for 5 h at 450 °C in a furnace to remove organic matter and PUFs were pre-cleaned by dichloromethane (DCM) in Soxhlet for 72 h, after processed, these sampling materials were stored in a baked aluminum foil within sealed polyethylene plastic bags before use. After sampling, loaded GFFs were wrapped with prebaked aluminum foils and sealed with double layers of polyethylene bags, and PUFs were placed in solvent rinsed glass jars with aluminum foil-lined lids, and then stored at $-20\text{ }^{\circ}\text{C}$ until extraction. After stabilizing under constant temperature ($25 \pm 1\text{ }^{\circ}\text{C}$) and humidity ($50 \pm 1\%$), particles mass loadings were obtained gravimetrically by an analytical balance (Sartorius 0.01 mg, Germany), and determined by weight after sampling minus that before sampling. Typical uncertainty for gravimetric measurements is $\pm 20\text{ }\mu\text{g}$, which represents less than $\pm 5\%$ of total aerosol mass of field samples.

During the sampling period, the meteorological parameters, including ambient temperature, relative humidity, and wind direction, were also recorded. Table 1 lists the meteorological parameters and TSP concentrations during the sampling periods.

2.2. Analytical procedure

Standards of 16 PAHs in a mixture (as specified in US EPA Method 610) and a surrogate of acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} and perylene- d_{12} were obtained from Ultra Scientific Inc. (North Kingstown, RI, USA). An internal standard of pyrene- d_{10} was obtained as liquid of 99.5% purity (Labor Dr. Ehrenstorfer-Schöfers, Germany). All reagents including n-hexane (95.0% purity) and DCM (99.5% purity) were chromatogram grade and purchased from Tedia, USA.

PUF samples were Soxhlet extracted with DCM for 72 h, while GFFs were extracted with DCM by ultrasonic bath (Model KQ320DE) for 30 min and this process was repeated three times. The extracts were concentrated by a rotary evaporator (Model RE-52AA). Then the concentrated extracts were purified by the activated silica-alumina (2:1, V/V) column and the targeted solution was re-concentrated to about 2 mL by the rotary evaporator. The eluent was reduced to 1 mL under a gentle stream of ultra-pure nitrogen gas, and stored in refrigerator at $-20\text{ }^{\circ}\text{C}$ until analyzed. The 10 μL internal standard solution was added just before analysis.

The samples were analyzed by gas chromatography (HP7890A, Agilent Co., USA) equipped with mass spectroscopy detector (HP 5975, Agilent Co., USA) with helium (1.4 mL min^{-1}) as carry gas. The capillary column (HP-5MS UI, Agilent Co., USA) was 30 m in

length with an internal diameter of 0.25 mm and a film thickness of 0.25 μm . 1 μL sample was injected in a splitless mode. The column temperature was initially held at 50 °C for 1 min, increased to 200 °C at $10\text{ }^{\circ}\text{C min}^{-1}$, then increased to 280 °C at $5\text{ }^{\circ}\text{C min}^{-1}$ and finally held for 12 min. Data acquisition and processing were controlled by a HP Chem-Station data system and the selected-ion monitoring (SIM) mode was chosen.

The PAHs determined in this study were aphenanthrene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), chrysene (CHR), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DahA), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP) and benzo[ghi]perylene (BghiP).

2.3. Quality assurance and quality control (QA/QC)

Field blanks were employed to determine any potential contamination during the transportation and storage of sample, and the experiments of method blanks (solvent) and spiked blanks (standards spiked into solvent) were also conducted. Surrogate standards were added to all samples (including those for QA) to supervise procedures and matrix effects. The blank levels were less than 6% of the mass during the test. PAHs levels in the solvent blanks ($n = 5$) were lower than those in the field blanks. The relative deviation duplicate samples for all the individual PAHs were less than 10%.

During the GC–MS analysis, the response factors for individual PAHs relative to the internal standard were determined by the analysis of the calibration solution containing 16 PAHs, 4 deuterated PAHs and one internal standard. The recovery efficiencies of acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} and perylene- d_{12} were 48.45–66.57%, 43.60–64.12%, 55.61–101.76% and 59.90–116.05%, respectively. The concentrations reported in this paper were calibrated by the blank levels but not by the surrogate recovery efficiencies. The limit of detection (LOD) was defined as mean blank mass plus three standard deviations. The LOD values for PAHs ranged from 1.47×10^{-3} – $1.13 \times 10^{-2}\text{ ng m}^{-3}$.

3. Results and discussion

3.1. Seasonal variability of PAHs concentrations

Fig. 2 describes the average concentrations of the particulate and gaseous PAHs at the five sampling sites. The average total (particulate and gaseous phases) PAHs concentrations varied from 2.03 (IUE) to

Table 1
The meteorological parameters and TSP concentrations during sampling period.

Sampling site	Sampling period	Ambient temperature (°C)	Relative humidity (%)	Predominant wind direction	TSP($\mu\text{g m}^{-3}$)
TX	17–19 April 2009(spring)	18–26	40–75	NE	12.36 ± 4.75
	6–8 July 2009(summer)	26–34	60–90	S	19.26 ± 3.42
	30–31 October 2008(autumn)	21–27	37–73	NE, NE–E	65.10 ± 4.87
	24–26 December 2008(winter)	8–18	55–85	NE	96.18 ± 5.33
IUE	28 April–1 May 2009(spring)	19–25	40–70	NE	37.81 ± 1.20
	15–18 July 2009(summer)	25–34	65–90	S	29.72 ± 9.82
	27–29 October 2008(autumn)	21–30	54–94	NE, SE–E	196.71 ± 9.59
	27–30 December 2008(winter)	13–20	45–80	NE	213.90 ± 6.25
XU	20–23 April 2009(spring)	20–27	40–90	NE	39.70 ± 5.51
	1–4 July 2009(summer)	26–33	60–85	S, SW–S	27.06 ± 4.75
	23–26 October 2008(autumn)	23–30	54–89	NE, SE–E	72.14 ± 7.88
	31 December 2008–1–4 January 2009 (winter)	9–15	50–90	NE	142.56 ± 23.54
XY	20–23 April 2009(spring)	20–28	30–70	NE, S	34.27 ± 3.90
	23–26 June 2009(summer)	24–32	60–95	SW–S	21.03 ± 6.58
	23–26 October 2008(autumn)	22–27	61–89	NE, SE–E	127.60 ± 16.53
	1–5 January 2009(winter)	12–19	55–85	NE, NE–E	144.72 ± 19.21
LL	24–27 April 2009(spring)	16–24	50–90	NE	69.36 ± 23.46
	2–5 July 2009(summer)	26–34	55–90	S	34.54 ± 11.32
	27–30 October 2008(autumn)	22–28	58–89	NE, SE–E	145.00 ± 11.42
	24–27 December 2008(winter)	11–17	50–85	NE	169.72 ± 33.62

8.60 (XY) ng m^{-3} in spring, 7.90 (XU) to 21.30 (IUE) ng m^{-3} in summer, 5.54 (TX) to 76.55 (LL) ng m^{-3} in autumn and 35.95 (XU) to 62.44 (LL) ng m^{-3} in winter, with a mean of $21.89 \pm 20.09 \text{ ng m}^{-3}$. Coleman et al. (1997) found that the concentrations of PAHs at Manchester were in the range of 20–164 ng m^{-3} . Gardner et al. (1995) reported that the average PAHs concentration in Castleshwa, London, was 22 ng m^{-3} . The results in Xiamen were similar to those of these studies. However, compared with the investigation of Bi et al. (2003), the concentrations of PAHs (134.4–298.5 ng m^{-3}) in Guangzhou were much higher than those of in Xiamen.

Spring and summer had lower PAHs concentrations, while autumn and winter had higher PAHs concentrations. The temperature and meteorological conditions might be mostly responsible for the seasonal behaviors of PAHs (Tian et al., 2009). In autumn and winter, there were relative low levels of photochemical reactions and frequent formations of an inversion layer in the atmosphere in this subtropical city (Li et al., 2006). These conditions limited the dispersion and decomposition of PAHs, and resulted in high PAHs concentrations in the atmosphere. On the other hand, in spring and summer, there were intensive sunlight, also frequent monsoon and rainfall, which were in favor of dilution, dispersion and decomposition of PAHs, resulting in the low PAHs concentrations in the atmosphere.

In order to confirm the above reasons, the relationship among PAHs concentrations and several meteorological parameters (temperature, relative humidity, wind direction, see Table 1) were studied. Fig. 3 displays the relationship between the partitioning of total PAHs and temperature. As can be seen, atmospheric temperature significantly affected the partitioning of PAHs between particulate and gaseous phases. The higher temperature increased the partitioning of PAHs from the particulate phase into the gaseous phase, resulting in lower particulate PAHs concentrations. These results were similar to what had been reported by other researchers (Gigliotti et al., 2000; Bi et al., 2003).

Fig. 4 shows backward trajectories of the air masses to Xiamen during the sampling period. In this study, we used the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (<http://www.arl.noaa.gov/raedy/hysplit4.html>) model to determine the back trajectory. In all cases, the results showed that, in autumn and winter, the higher concentrations occurred when winds were from North and Northeast. This is because of the pollutants carried by the air

masses from the North China in these seasons. Although North wind would happen in spring too, the concentration of PAHs was low due to high air pressure and frequent rainy days in this season. In summer, the prevailing wind direction is Southeast and South brings with relatively clean air masses from sea. The higher temperature led to higher concentrations of PAHs in the gaseous phase, and therefore the lowest concentrations of total PAHs in summer did not occur.

3.2. Spatial variation of PAH concentrations at the different sites

Besides meteorological parameters, the environmental locations of the sampling sites were also considered as an important contributor to the concentrations of PAHs. The LL site, as an industrial sampling site, is located in the Haicang District, where the stationary exhausts (including coal-fired power plants and petrochemical plant) and vehicle emissions were the main sources of the atmospheric PAHs. The annual average concentration of PAHs was $25.83 \pm 22.10 \text{ ng m}^{-3}$, which was the highest concentration of PAHs among the five sampling sites. The XY sampling site is located in the urban area with a mixed residential, traffic, and commercial environment. The dual impacts of the vehicle exhausts and daily cooking emissions may also lead to the high concentration of PAHs. The XU site is located in an educational and tourism area with the vehicle emission as the primary source for PAHs and nearby ship emissions as the secondary. The IUE sampling site is located at the suburban with biomass combustions and infrastructure construction activities as sources for PAHs. The TX sampling site is located in a forest area near a reservoir with no local source. Therefore, the lowest annual average concentrations of PAHs with $14.14 \pm 13.64 \text{ ng m}^{-3}$ were reported at this sampling site. Generally, the concentrations of PAHs in the industrial areas were the highest, following by residential, suburban, and educational areas.

3.3. Comparison of particulate and gaseous PAHs

Fig. 5 displays the correlation of the particulate and gaseous PAHs concentrations with the concentrations of TSP. The high correlation ($R^2 = 0.63$) between the particulate PAHs and TSP concentrations is clear. This indicates that the particulate PAHs were closely related to TSP, while there was no significant correlation ($R^2 = 0.17$) between gaseous PAHs and TSP concentrations, especially in autumn and winter.

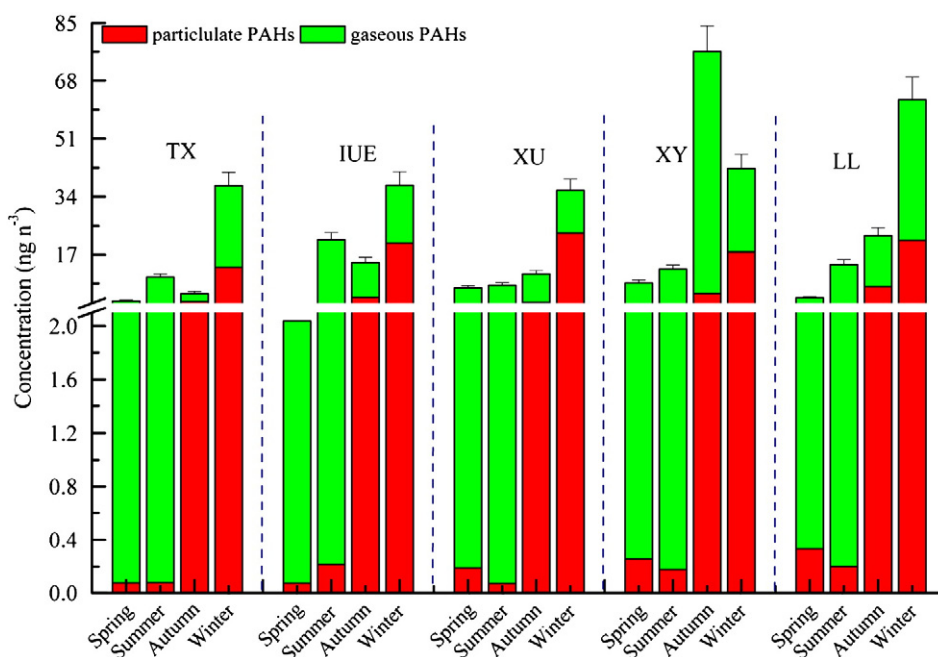


Fig. 2. Average concentrations of PAHs in the particulate and gaseous phases at the five sampling sites.

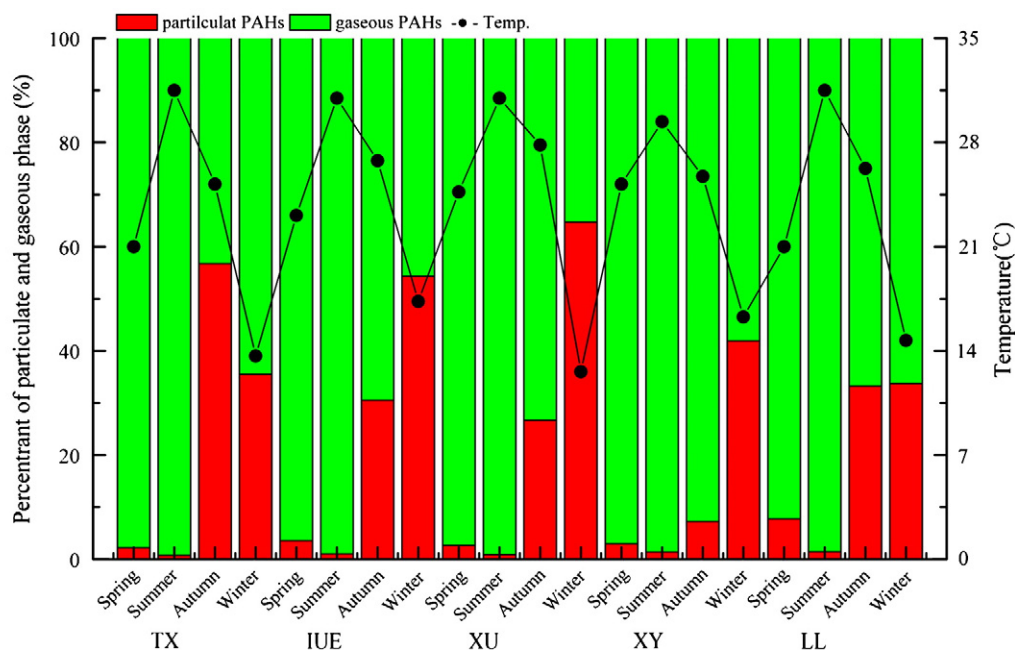


Fig. 3. Partitioning of total PAHs between the particulate/gaseous phase and temperature.

The apportionment of total PAHs between particulate and gaseous phase in Fig. 3 reveals that the percentages of the gaseous PAHs were 96.26% (LL)–97.82% (TX) in spring, 98.57% (LL)–99.27% (TX) in summer, 43.27% (TX)–92.73% (XY) in autumn and 35.26% (XU)–66.27% (LL) in winter, respectively. Although seasonal concentrations of PAHs took ascending trends from spring to winter, the percentages of the gaseous were high in spring and summer and gradually became low in autumn and winter (Fig. 3). The percentages of the particulate PAHs in all four seasons presented oppositional trends compared to gaseous PAHs. These results were consistent with the researches of other authors (Gigliotti et al., 2000; Bi et al., 2003; Papageorgopoulou et al., 1999; Dimashki et al., 2001).

Fig. 6 shows the distributions of 2–6 ring PAHs in the particulate and gaseous phases. It was found that the gaseous PAHs were dominated by the 3–4 ring (MW = 152–228) PAHs, including PHE, ANT, FLA and PYR. The percentages of these 3–4 ring PAHs in the total PAHs were 10.71% (IUE, spring)–63.33% (TX, spring), 1.74% (XU, winter)–36.74% (TX, winter), 2.92% (TX, autumn)–24.70% (IUE, summer) and 1.66% (TX, autumn)–16.32% (IUE, spring). The particulate PAHs were dominated by the 5–6 ring PAHs with higher molecular weight (MW = 252–278) and low vapor pressure, including BbF, BghiP, IcdP, BaP, and BkF. The 4-ring compounds (MW = 228), like BaA and CHR, had similar concentrations at some samples in both gaseous and particulate phases. The PAHs with different molecular weights had different particle/gas distribution coefficients (Offenberg and Baker, 2000; Esen et al., 2006) and the contributions to the gaseous concentrations generally decreased with increasing molecular weight from 99.2% to <0.01%. These results were consistent with other studies (Bi et al., 2003).

3.4. Preliminary results for source identification of PAHs at the five sampling sites

Atmospheric PAH profiles can be affected by meteorological variables such as solar radiation and temperature, and their sources mainly come from the incomplete combustion. Despite these facts, the ratios (also called diagnostic ratios) between some of these compounds were considered as the “fingerprint” of an emission source (Khalili et al., 1995; Dickhut et al., 2000), because they exhibited the characteristics of the specific source. FLA/(FLA + PYR), BaA/(BaA + CHR), InP/(InP + BghiP)

and ANT/(PHE + ANT) were the conventional diagnostic ratios to characterize the potential emission sources of PAHs. Rogge et al. (1993) reported that diagnostic ratio of FLA/(FLA + PYR) was 0.44 for the motor vehicle exhaust with catalytic converter. The IcdP/(IcdP + BghiP) ratios of particles from gasoline vehicle, diesel vehicle and coal-fired were 0.18, 0.37 and 0.56, respectively (Grimmer et al., 1983). These diagnostic ratios could be applied to identify possible emission sources of PAHs very well (Kavouras et al., 2001). A comparison between the various diagnostic ratios was obtained in the literature of U.S. EPA (2003), Yunker et al. (2002) and Pio et al. (2001).

Table 2 lists diagnostic ratios of PAHs attributed to specific sources. Table 3 exhibits the diagnostic ratios of PHE/(PHE + ANT), FLA/(PYR + FLA), BaA/(CHR + BaA) and IcdP/(IcdP + BghiP) in the atmosphere of Xiamen for the different seasons at the five sites. The results of Table 3 showed that there were only slight differences in the diagnostic ratios between sampling sites, except TX site, for the different seasons. This implied that the sources for PAHs were similar for these sites. The diagnostic ratio values of PHE/(PHE + ANT), FLA/(PYR + FLA), BaA/(CHR + BaA) and IcdP/(IcdP + BghiP) were 0.69–0.94, 0.44–0.76, 0.47–0.83 and 0.34–0.54, respectively. The values of FLA/(PYR + FLA) at the IUE site in summer and winter were 0.42 and 0.44, respectively, closed to what had been reported by Rogge et al. (1993).

The IcdP/(IcdP + BghiP) ratio was about 0.42 in background (TX), suburban (IUE) and educational area (XU), close to the value of biomass combustion (wood or vegetation) shown in Table 2. This implies that biomass emission sources affected these sampling sites. The IcdP/(IcdP + BghiP) ratios ranged from 0.35 to 0.52 and 0.44 to 0.52 at the XY and LL sites, respectively, indicating the effects from vehicle emissions and coal combustion (about 0.32 and 0.48 for vehicle and coal combustion) (Yunker et al., 2002; U.S. EPA, 2003). The value (0.35) of IcdP/(IcdP + BghiP) at the XY site further indicated the emission from the natural gas combustion (see Table 2).

The values of BaA/(CHR + BaA) were higher at the TX site with 0.70–0.86 indicating that the biomass affected the TX site. These are associated with the main energy source (wood and straw combustion) for local farmers, who lived 10 km away from the TX. The values of BaA/(CHR + BaA) at the other four sampling sites were ranged from 0.51 to 0.83, similar to those (0.50–0.93) of the vehicle exhausts (see Table 2). This indicated that vehicle emissions were a big contributor at these urban sites. Fig. 7 shows the relationship between

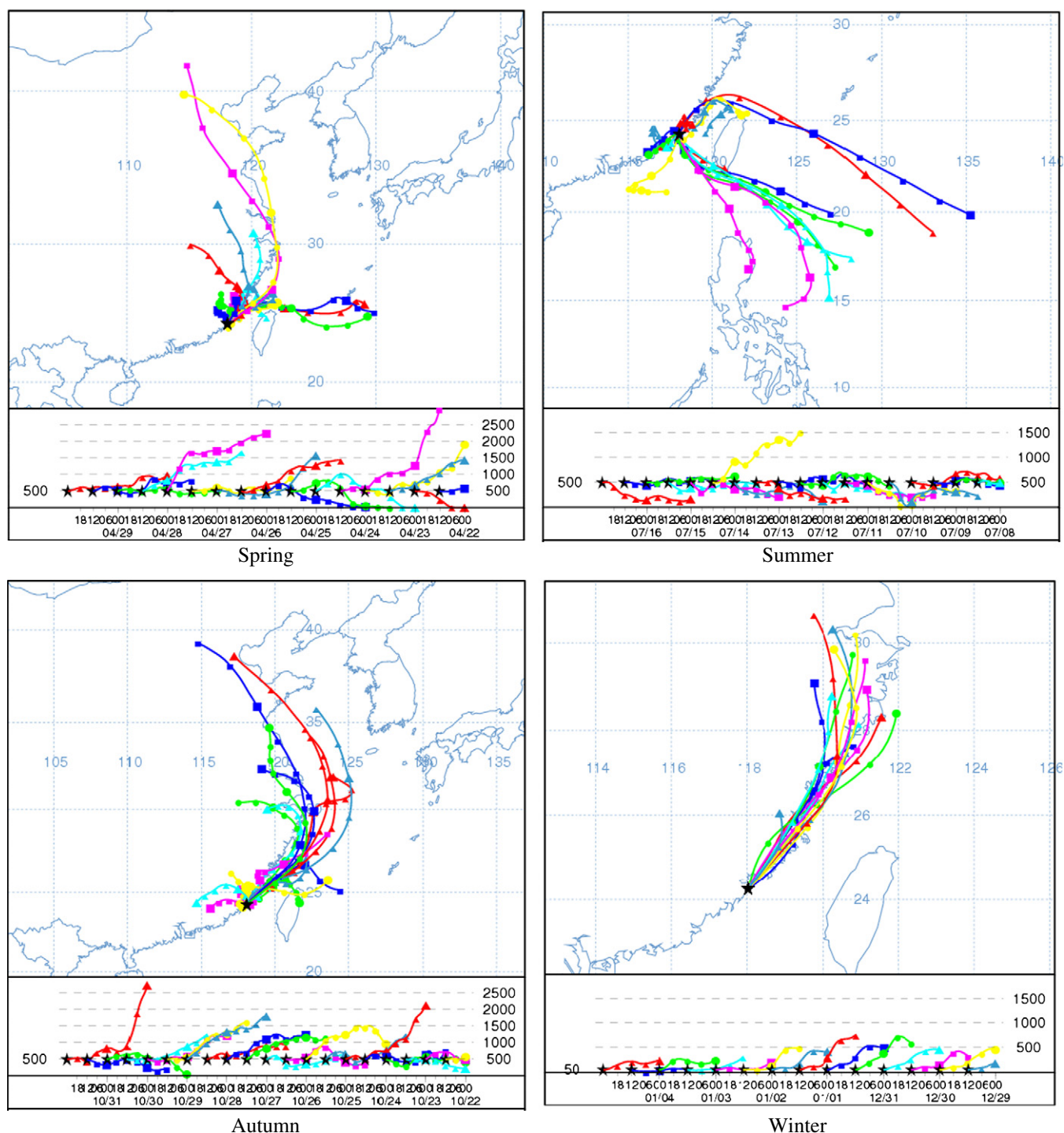


Fig. 4. Backward trajectories of the air masses for Xiamen during the sampling period.

the ratios of FLA/(FLA + PYR) and PHE/(PHE + ANT). As can be seen, the LL, XU, XY and IUE sites had similar sources of PAHs to some degree, such as diesel or gasoline vehicles and coal combustion. Therefore, multiple sources affected the PAHs pollution in the urban, suburban and industrial areas of Xiamen. This is in agreement with the results reported by Ye et al. (2006) for Xiamen.

3.5. Health-risk assessment

One approach to estimate the health-risk related to exposure to a targeted PAH species is to calculate BaP equivalent concentration

(BaP_{eq}) which is based on its PAH carcinogenic potency relative to BaP. The carcinogenic potency of the PAHs exposures could then be estimated as the sum of each individual BaP_{eq}. To calculate the BaP_{eq} for each individual PAH species, the toxic equivalency factors (TEFs) of the individual PAH relative to BaP carcinogenic potency are required. Up to date, only a few proposals for TEFs are available (Robert et al., 1999; Nisbet and LaGoy, 1992). The data of TEFs from Robert et al. (1999) were used in this study.

Table 4 summarizes the BaP_{eq} exposure levels for the particulate and gaseous PAHs in the atmosphere. The gaseous BaP_{eq} levels (4.77×10^{-2} – 56.6×10^{-2} ng m⁻³) in spring and summer were higher

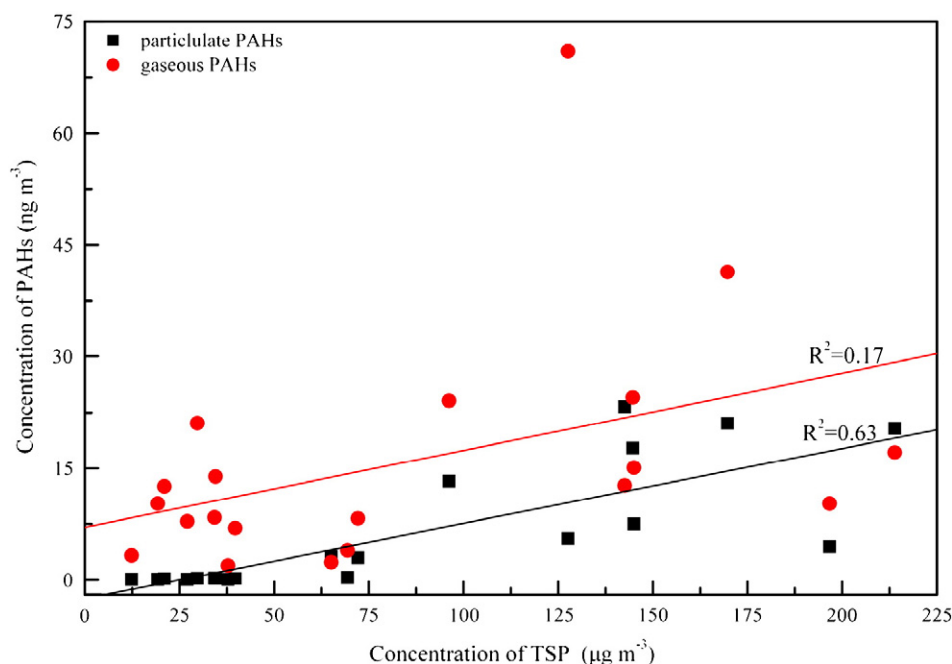


Fig. 5. Correlations of the particulate and gaseous PAHs and TSP.

than the corresponding particulate BaP_{eq} levels (1.18×10^{-2} – $4.34 \times 10^{-2} \text{ ng m}^{-3}$). The result is not so surprising, since the high temperature conditions in spring and summer caused the PAH primarily existed in the gaseous phase. The particulate PAHs were dominated by high molecular weight PAHs. The BaP_{eq} values for the particulate PAHs (45.8×10^{-2} – $355 \times 10^{-2} \text{ ng m}^{-3}$) in autumn and winter were significantly higher than the corresponding BaP_{eq} values for the gaseous PAHs (2.90×10^{-2} – $190 \times 10^{-2} \text{ ng m}^{-3}$). Here, the highest exposure level was found for particulate PAHs ($355 \times 10^{-2} \text{ ng m}^{-3}$) at the LL site in winter time. The health risk of particulate PAHs was higher than the gaseous phase at the five sampling sites. The average BaP_{eq} value in the atmosphere of Xiamen was 1.36 ng m^{-3} in 2008–2009,

which was lower than other urban areas, such as Fuji (1.91 ng m^{-3}) (Takeshi et al., 2004), Guangzhou (4.10 ng m^{-3}) (Li et al., 2004), but higher than Birmingham (0.99 ng m^{-3}) (Smith and Harrison, 1996).

The confined concentrations of BaP, as an indicator for the control of PAHs in the atmosphere, are 10 ng m^{-3} and 1 ng m^{-3} based on the Chinese standard (GB3095-1996) and EU standard (2005/69/EC), respectively. The concentrations of BaP were 0.01 – 2.60 ng m^{-3} and ND – 0.35 ng m^{-3} in particulate and gaseous phase, respectively. This implies that the atmospheric PAHs pollution in Xiamen was not serious under Chinese standard. However, the BaP values in winter exceeded the EU standard. Although the average BaP_{eq} values in Xiamen were not high compared to the other coastal cities in China (Li et al., 2004;

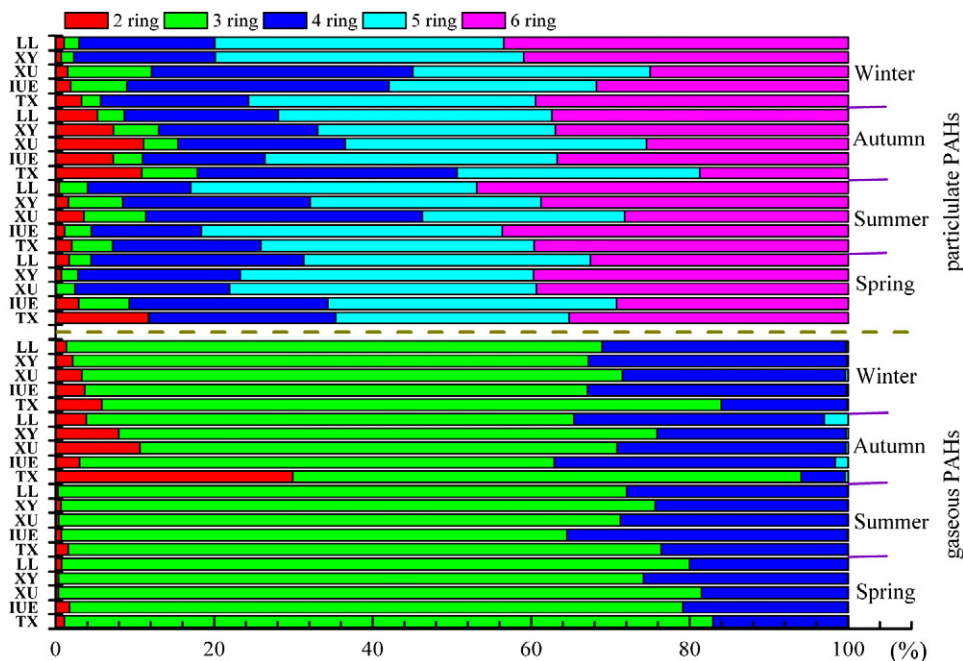


Fig. 6. Distributions of 2-, 3-, 4-, 5-, and 6-ring PAHs in the particulate and gaseous phases.

Table 2

Diagnostic ratios of PAHs attributed to specific sources compiled from U.S. EPA (2003).

Ratio	Source type						
	Diesel vehicle	Gasoline vehicle	Natural gas combustion	Oil combustion	Coal combustion	Vegetation combustion	Wood combustion
PHE/(PHE + ANT)	0.73 ± 0.18	0.77 ± 0.10	0.88 ± 0.13	0.89 ± 0.12	0.85 ± 0.11	NA	0.84 ± 0.16
FLA/(FLA + PYR)	0.40 ± 0.05	0.52 ± 0.13	0.49 ± 0.18	0.52 ± 0.20	0.57 ± 0.21	0.49 ± 0.07	0.51 ± 0.16
BaA/(BaA + CHR)	0.65 ± 0.28	0.50 ± 0.10	0.39 ± 0.15	0.50 ± 0.22	0.46 ± 0.19	NA	0.59 ± 0.25
IcdP/(IcdP + BghiP)	0.19 ± 0.13	0.32 ± 0.11	0.32 ± 0.17	0.36 ± 0.14	0.48 ± 0.29	0.35 ± 0.04	0.42 ± 0.18

Table 3

Diagnostic ratios of PAHs in the atmosphere of Xiamen.

Seasons	Sampling sites	Diagnostic ration			
		PHE/(PHE + ANT)	FLA/(PYR + FLA)	BaA/(CHR + BaA)	IcdP/(IcdP + BghiP)
Spring	TX	0.87	0.72	0.86	0.43
	IUE	0.86	0.74	0.77	0.42
	XU	0.82	0.72	0.76	0.42
	XY	0.80	0.55	0.83	0.39
	LL	0.91	0.76	0.74	0.44
Summer	TX	0.75	0.52	0.65	0.42
	IUE	0.75	0.42	0.47	0.40
	XU	0.69	0.54	0.60	0.34
	XY	0.76	0.52	0.56	0.35
	LL	0.75	0.48	0.51	0.38
Autumn	TX	0.89	0.67	0.70	0.50
	IUE	0.94	0.32	0.76	0.48
	XU	0.93	0.36	0.77	0.47
	XY	0.84	0.37	0.68	0.44
	LL	0.94	0.32	0.72	0.44
Winter	TX	0.42	0.64	0.71	0.50
	IUE	0.95	0.44	0.70	0.54
	XU	0.84	0.54	0.68	0.53
	XY	0.94	0.50	0.62	0.52
	LL	0.92	0.50	0.62	0.52

Tsai et al., 2001), the high values of BaP in winter should be paid much attention. Therefore, how to directly decrease the BaP_{eq} levels in four seasons in a feasible way, especially during winter time, and control individual PAHs, especially for BaP, should be the goal of further investigation for the environmental department.

4. Conclusions

In this study, the spatial and temporal characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in the gaseous and particulate phases were studied from October 2008 to September 2009 at the five

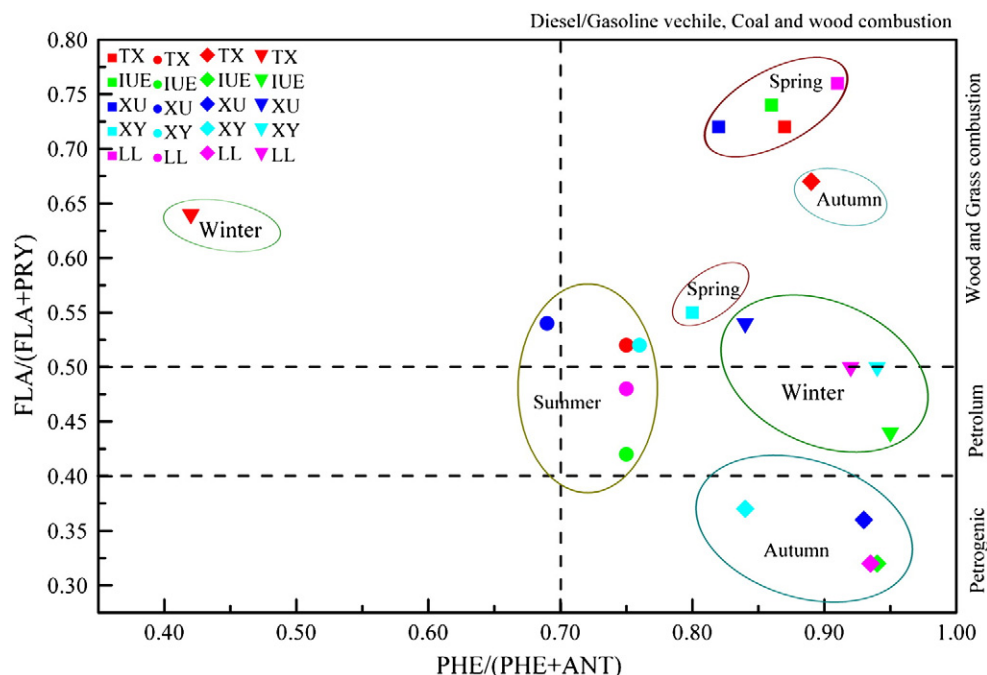
**Fig. 7.** Diagnostic ratios between FLA/(FLA + PYR) and PHE/(PHE + ANT).

Table 4BaP_{eq} exposure levels for the particulate (P) and gaseous (G) PAHs in Xiamen City ($\times 10^{-2}$ ng m⁻³).

Compounds		BaP		BbF		BaA		CHR		PYR		FLA		ANT		PHE		Σ8PAHs
TEF(%)		100		15		12		25		4.6		3.3		0.2		2.8		BaP _{eq}
Season	Sampling sites	P	G	P	G	P	G	P	G	P	G	P	G	P	G	P	G	P+G
Spring	TX	1.00	–	0.150	–	0.120	0.120	–	–	–	0.460	0.0300	1.52	–	0.0600	–	5.85	9.31
	IUE	1.00	–	0.150	0.150	0.120	–	–	1.75	–	1.47	–	0.59	–	0.220	–	0.588	6.04
	XU	2.00	–	0.450	–	0.120	0.240	0.250	–	0.0500	1.52	0.0300	3.07	–	0.170	–	10.7	18.6
	XY	2.00	–	0.450	–	0.240	0.600	0.250	0.250	0.0500	2.76	0.0700	4.95	–	0.200	–	12.0	23.8
	LL	3.00	–	0.600	–	0.240	–	0.250	0.500	0.0900	–	0.130	0.460	–	0.040	0.0300	6.46	11.8
Summer	TX	1.00	–	0.150	–	–	0.240	–	0.250	–	2.71	0.0300	5.91	–	0.340	–	14.6	25.2
	IUE	2.00	–	0.450	0.150	0.120	1.32	0.250	3.00	0.0500	9.34	0.0300	17.2	–	0.590	–	25.0	59.5
	XU	1.00	–	0.150	–	0.120	0.120	–	0.250	0.0500	2.90	0.0300	5.31	–	0.230	–	9.16	19.3
	XY	1.00	–	0.300	–	0.120	0.240	0.250	0.500	0.0500	4.05	0.0300	7.03	–	0.390	0.0300	18.0	32.0
	LL	2.00	–	0.300	0.150	0.120	0.840	0.250	1.50	–	4.97	0.0300	8.78	–	0.430	0.0300	18.6	38.0
Autumn	TX	35.0	–	4.80	0.150	3.36	0.120	2.75	0.500	1.33	0.180	1.19	0.230	0.00200	0.0200	0.450	1.70	51.8
	IUE	49.0	–	9.15	0.600	3.00	3.84	2.25	2.25	0.780	5.43	0.590	6.70	0.00200	0.0600	0.310	14.3	98.3
	XU	33.0	–	6.30	0.150	2.52	2.16	2.50	0.500	0.740	3.59	0.560	4.59	0.00200	0.0600	0.250	11.3	68.3
	XY	59.0	4.00	14.0	1.20	4.68	10.6	4.50	10.5	1.10	26.7	1.02	32.4	0.00600	1.38	0.560	103	275
	LL	86.0	35.0	13.5	0.900	5.64	5.04	6.00	2.75	1.61	7.22	1.29	8.75	0.00400	0.0900	0.500	21.6	196
Winter	TX	141	–	26.8	0.150	10.3	2.88	10.0	1.00	0.276	5.34	2.05	7.89	0.00400	1.77	0.670	17.5	230
	IUE	243	–	3.60	0.300	21.8	5.40	23.8	1.00	7.50	8.42	7.72	10.8	0.0100	0.0700	3.44	20.8	358
	XU	225	–	31.0	0.150	25.0	2.76	23.0	4.50	8.51	4.42	93.2	7.26	0.180	0.0400	3.89	13.5	359
	XY	220	–	36.6	0.150	16.6	4.56	23.5	3.75	1.75	13.6	1.49	14.8	0.00600	0.140	0.590	30.9	369
	LL	260	1.00	48.2	0.450	18.1	9.96	23.5	11.5	2.48	21.2	2.05	22.9	0.00600	0.320	0.810	56.4	479

different sites in Xiamen, Fujian Province. It was found that PAHs concentrations were high in autumn and winter at the five sites. The PAHs concentrations in the ambient air of Xiamen ranged from 2.03 (IUE) to 8.60 (XY) ng m⁻³ in spring, 7.90(XU) to 14.07(LL) ng m⁻³ in summer, 5.54(TX) to 76.55(LL) ng m⁻³ in autumn and 11.23(XU) to 62.44(LL) ng m⁻³ in winter, respectively. Generally, the concentrations of PAHs in the industrial areas were the highest, following by residential, suburban, and educational areas. There was a good correlation between the particulate PAHs and the TSP, but almost no correlation between gaseous PAHs and TSP. It was found that the PAHs concentrations were high in autumn and winter seasons when Xiamen was influenced by the air masses from North and Northeast.

The results of diagnostic ratios indicated that vehicle exhaust including diesel and gasoline fuel exhaust was a primary source for atmospheric PAHs in the different functional areas of Xiamen. The coal combustion was another main source for atmospheric PAHs, especially in industrial areas.

The average BaP_{eq} values of PAHs in spring, summer, autumn and winter in Xiamen were 0.14, 0.32, 1.38 and 3.59 ng m⁻³, respectively. The results of average BaP_{eq} for all four seasons indicated that the health risks of particulate PAHs were higher than those in the gaseous at the five sampling sites, although there were some slight differences for particulate and gaseous BaP_{eq} in the four seasons.

Acknowledgments

This research was financially supported by Commonwealth Program of Environment Protection Department of China (No: 201009004), the National Natural Science Foundation of China (No. 41005082), and the Knowledge Innovation Program of the Chinese Academy of Sciences (No: KZCX2-YW-JS404 and KZCX2-EW-408). The authors would like to thank Dr. Shaocai Yu for assistance of grammar revision and Dr. Youwei Hong for technical assistance and GC–MS data acquisition. Anonymous reviewers are thanked for their comments.

References

Ayrault S, Senhou A, Moskura M, Gaudry A. Atmospheric trace element concentrations in total suspended particles near Paris, France. *Atmos Environ* 2010;44(30): 3700–7.

- Bi XH, Sheng GY, Peng PA, Chen YJ, Zhang ZQ, Fu JM. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos Environ* 2003;37(2):289–98.
- Coleman PJ, Lee RGM, Alcock RE, Jones KC. Observations on PAH, PCB, and PCDD/F Trends in U.K. Urban Air, 1991–1995. *Environ Sci Technol* 1997;31(7):2120–4.
- Dickhut RM, Canuel EA, Gustafson KE, Liu K, Arzayus KM, Walker SE, et al. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. *Environ Sci Technol* 2000;34(17): 4635–40.
- Dimashki M, Lim LH, Harrison RM, Harrad S. Temporal trends, temperature dependence, and relative reactivity of atmospheric polycyclic aromatic hydrocarbons. *Environ Sci Technol* 2001;35(11):2264–7.
- Ding GY, Cai SG, Yu QP, Zheng SJ, Chen JB, Wang HP, et al. Yearbook of Xiamen special economic zone. China Statistics Press; 2001.
- Dong TT, Lee BK. Characteristics, toxicity, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea. *Chemosphere* 2009;74(9):1245–53.
- Esen F, Cindoruk SS, Tasdemir Y. Ambient concentrations and gas/particle partitioning of polycyclic aromatic hydrocarbons in an urban site in Turkey. *Environ Forensics* 2006;7(4):303–12.
- Gardner B, Hewitt CN, Jones KC. PAHs in air adjacent to two inland water bodies. *Environ Sci Technol* 1995;29(9):2405–13.
- Ge XY, Sheng LM, Qiu YL, Han Z, Ye SM, Li QY, et al. Yearbook of Xiamen special economic zone. China Statistics Press; 2009.
- Gigliotti CL, Dachs J, Nelson ED, Brunciak PA, Eisenreich SJ. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. *Environ Sci Technol* 2000;34(17): 3547–54.
- Grimmer G, Jacob J, Naujack KW. Profile of the polycyclic aromatic compounds from crude oils Part3. Inventory by GC–MS–PAH in environmental materials. *Frese-nius J Anal Chem* 1983;314(1):29–36.
- Harrison RM, Smith DJT, Luhana L. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ Sci Technol* 1996;30(3):825–32.
- Heywood E, Wright J, Wienburg CL, Black HJ, Long SM, Osborn D, et al. Factors influencing the national distribution of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in British soils. *Environ Sci Technol* 2006;40(24): 7629–35.
- Kavouras IG, Koutrakis P, Tspakis M, Lagoudaki E, Stephanou EG, Von Baer D, et al. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environ Sci Technol* 2001;35(11): 2288–94.
- Khalili NR, Scheff PA, Holsen TM. PAH source fingerprints for coke oven, diesel and gasoline engines, highway tunnels and wood combustion emission. *Atmos Environ* 1995;19(3):533–42.
- Li A, Jang JK, Scheff PA. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ Sci Technol* 2003;37(13): 2958–65.
- Li J, Zhang G, Qi SH, Liu GQ. Source analysis and apportionment of particulate phase polycyclic aromatic hydrocarbons(PAHs) in Guangzhou City. *Acta Sci Circumst* 2004;24(4):661–6.
- Li J, Zhang G, Li XD, Qi SH, Liu GQ, Peng XZ. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Sci Total Environ* 2006;355(1–3):145–55.

- Nielsen T. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmos Environ* 1996;30(20):3481–90.
- Nisbet C, LaGoy P. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 1992;16(3):290–300.
- Offenberg JH, Baker JE. Aerosol size distributions of elemental and organic carbon in urban and over water atmospheres. *Atmos Environ* 2000;34(10):1509–17.
- Papageorgopoulou A, Manoli E, Touloumi E, Samara C. Polycyclic aromatic hydrocarbons in the ambient air of Greek towns in relation to other atmospheric pollutants. *Chemosphere* 1999;39(13):2183–99.
- Pio CA, Alves CA, Duarte AC. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmos Environ* 2001;35(8):1365–75.
- Robert EAM, Brian GB, Josephy PD, Nigel JB. Comparison of the Ames Salmonella Assay and Mutatox Genotoxicity Assay for Assessing the Mutagenicity of Polycyclic Aromatic Compounds in Porewater from Athabasca Oil Sands Mature Fine Tailings. *Environ Sci Technol* 1999;33(15):2510–6.
- Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol: 2. Non-catalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environ Sci Technol* 1993;27(4):636–51.
- Shen GF, Wang W, Yang YF, Zhu C, Min YJ, Xue M, et al. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmos Environ* 2010;44(39):5237–43.
- Smith DJT, Harrison RM. Concentrations, trends and vehicle source profile of polycyclic aromatic hydrocarbons in the U.K. atmosphere. *Atmos Environ* 1996;30(14):2513–25.
- Takeshi O, Takashi A, Masahiro F, Hidetsuru M. Spatial distributions and profiles of atmospheric aromatic hydrocarbons in two industrial cities in Japan. *Environ Sci Technol* 2004;38(1):49–55.
- Tian FL, Chen JW, Qiao XL, Wang Z, Yang P, Wang DG, et al. Sources and seasonal variation of atmospheric polycyclic aromatic hydrocarbons in Dalian, China: factor analysis with non-negative constraints combined with local source fingerprints. *Atmos Environ* 2009;43(17):2747–53.
- Tsai PJ, Shieh HY, Lee WJ, Lai SO. Health-risk assessment for workers exposed to polycyclic aromatic hydrocarbons (PAHs) in a carbon black manufacturing industry. *Sci Total Environ* 2001;278(1–3):137–50.
- U.S. EPA. 1999 National Emissions Inventory. Washington, DC: US EPA; 2003 <ftp://ftp.epa.gov/EmisInventory/finalnei99ver3/haps/>.
- Wan XL, Chen JW, Tian FL, Sun WJ, Yang FL, Saiki K. Source apportionment of PAHs in atmospheric particulates of Dalian: factor analysis with nonnegative constraints and emission inventory analysis. *Atmos Environ* 2006;40(34):6666–75.
- Ye CX, Wang XH, Yin HL, Yuan WM, Hong HS. Characteristics of PAHs in PM₁₀ aerosols collected from different districts in Xiamen. *Acta Sci Circumst* 2006;26(9):1532–8.
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell HR, Goyette D, Sylvestre S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 2002;33(4):489–515.