



Characterization of polycyclic aromatic hydrocarbons and gas/particle partitioning in a coastal city, Xiamen, Southeast China

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Abstract

An intensive sampling program had been undertaken in autumn (October, 2008) and winter (December, 2008 and January, 2009) at urban (Xiamen University and Xianyu residential area), suburban (Institute of Urban Environment), industrial area (Lulian Hotel) and background (Tingxi Reservoir) in Xiamen, Fujian Province, to characterize the atmospheric concentration and gas-particle phase partitioning of PAHs. The average concentration of total PAHs in winter was almost 1.7 times higher than those in autumn. The log scale plot of K_p versus sub-cooled liquid vapor pressure (P_L^0) for all the data of autumn and winter season samples gave significantly different slopes. The slope for the winter samples (−0.72) was steeper than that for the autumn samples (−0.58). The partitioning results indicated that slope values varied depending on characteristics of specific site, source region and meteorological conditions which play important roles in the partitioning of PAHs. In addition, local emission sources had a stronger effect on partitioning results than long-transported polluted plume. The sources of PAHs in five sampling sites in Xiamen also have been discussed initially. Diagnostic ratios showed that the primary source of PAHs in urban, suburban and industrial area was from vehicle exhausts. While emission from petrochemical factory and power plant was another main contributor to industrial area.

Key words: PAHs; gaseous/particulate partitioning; diagnostic ratio; Xiamen

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds composed of at least two aromatic rings fused together. These compounds are persistent organic pollutants exist in environment extensively. Some PAHs are considered to be mutagenic and/or carcinogenic compounds and are linked to health problems, such as cataracts, kidney and liver damage. Thus, they have attracted a significant amount of attention in recent years (Dong and Lee, 2009).

PAHs are formed during incomplete combustion of organic materials from sources, such as residential heating, vehicle exhausts, industrial power generation, and production of coal tar. Among various anthropogenic sources of PAHs, the traffic source has been known to be the greatest contributor in many countries (Benner et al., 1989; Ye et al., 2006). However, up to now no quantitative source apportionment has been made for atmospheric PAHs in Xiamen, Fujian, China and the seasonality of the potential sources remains unknown.

Gaseous/particulate portioning for semi-volatility and persistence of PAHs has an important significantly in pro-

cess of environmental cycling (Lammel, 2009; Simcik et al., 1998), which is the key to understand the distribution, transport pathways and environmental fate of atmospheric PAHs. Although gaseous/particulate distribution of PAHs has been well documented (Vardar et al., 2004; Lammel, 2009), the process of PAHs in gaseous/particulate partitioning is still not understood completely (Galarneau et al., 2006). It is therefore essential to analysis semi-volatile PAHs behavior in air, especially for Xiamen where no literature has reported partitioning of PAHs in gas- and particle-phase.

Xiamen, a subtropical city in southeastern China, has warm weather and high relative humidity throughout the year (temperature is in the range of 4–38°C; with 20.9°C on annual average in 2008). The prevailing wind direction is northeast in autumn and winter, which can bring air masses to move across northern cities. Xiamen administrative area, with an area of 1565 km² and population about 2.5 million in 2008, is a main economic and culture center of Fujian Province. Previous studies indicated that the atmospheric environment in Xiamen was favorable for human health (Ye et al., 2006). However, with the rapid urbanization and industrialization, especially the increase of motor vehicles, environment pollutions may contain large amount of carcinogenic and mutagenic

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organic matter, of which PAHs in total suspended particles (TSP) were included. Therefore, the inhabitants experience a considerable increase of adverse health effect, which interested people's concern.

Although PAHs in Xiamen have been reported in some publications (Ye et al., 2006), no intensive research has been conducted in Xiamen on PAHs level in the atmosphere, especially for the distribution of PAHs in gas- and particle-phases. There is a lack of information about PAHs occurrence in the atmosphere in Xiamen. Therefore, the objectives of this article were: (1) to provide ambient PAHs concentration in gaseous and particulate phases, as well as to describe the gaseous/particulate partitioning in atmospheric aerosols during autumn and winter; and (2) to identify possible sources of PAHs in this coastal city.

1 Experiment

1.1 Sampling

Air samples were collected from 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).

TX is a background and located in forestry mountainous area with a medium-sized reservoir. The sampling site was taken on the rooftop of the reservoir office, approximately 6 m above the ground. IUE as a suburban sampling site is surrounded by highway, schools, residential buildings and Xinglin sea bay. The sampler was placed on rooftop of laboratory building, about 35 m above the ground. LL is chosen in an industrial area. The sampler was sited on the rooftop of a four-story hotel, about 12 m above the ground. This sampling site is close to industrial base where

petrochemical factory and power plant are located. XY and XU as the urban sampling sites are represent different functional areas. The former represents commercial area where traffic road and residential buildings are surrounded, while the later represents educational area which is near seaside, street and temple of Nanputuo. The sampling sites were placed on the rooftop of residential building and teaching building, about 15 and 18 m above the ground, respectively.

The air samples were collected simultaneously from every two sites during 23–31 October, 2008 (represent autumn) and 24 December 2008 to 5 January 2009 (represent winter). Air samples were collected every 24 hr. An Andersen high-volume sampler model PS-1 (Thermo Fisher Scientific, USA) with flow rate of 160 L/min was used for collecting suspended particles onto a filter, while a backflow adsorbent trap retained the gas fraction of PAHs. Particles were collected by passing air through Whatman glass fiber filters (GFF, 10.16 cm diameter). The adsorbent cartridge used was polyurethane foam (PUF, length 8.0 cm, diameter 6.25 cm) to collect PAHs in gas-phase. The GFFs were previously annealed for 5 hr at 450°C in a furnace to remove organic matter and PUFs were pre-cleaned by dichloromethane (DCM) in Soxhlet for 72 hr, after processed, these sampling materials were stored in 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 transported to the laboratory and stored at -20°C until extraction. All of those filters were weighted before and after sampling with an analytical balance (Sartorius T-114, Germany) after stabilizing under constant temperature (25 ± 1 °C and humidity (50 ± 1 %) to get mass concentration of particulate matter.

1.2 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., USA. An internal standard of pyrene- d_{10} was obtained as liquid of 99.5% purity (Labor Dr. Ehrenstorfer-Schäfers, Germany). All reagents including *n*-hexane and DCM were chromatogram grade and purchased from Tedia, USA, which are 95% and 99.5% purity, respectively.

PUF samples were Soxhlet extracted with DCM for 72 hr, while GFFs were extracted with DCM by ultrasonic agitation (KQ300DE, Kunshan Ultrasonic Instrument Co., Ltd., China). The procedure repeated three times, and each for 30 min. These extracts were concentrated and the solvent was removed using rotary evaporator (RE-52AA, Shanghai Yarong Biochemistry Instrument Co., Ltd., China). Mixed compounds were separated by activated silica-alumina (2:1, V/V) column and the target solution was concentrated by rotary evaporation until approximately 1–2 mL. Then, the final volume was adjusted to 1 mL by nitrogen blowdown and stored in refrigerator at

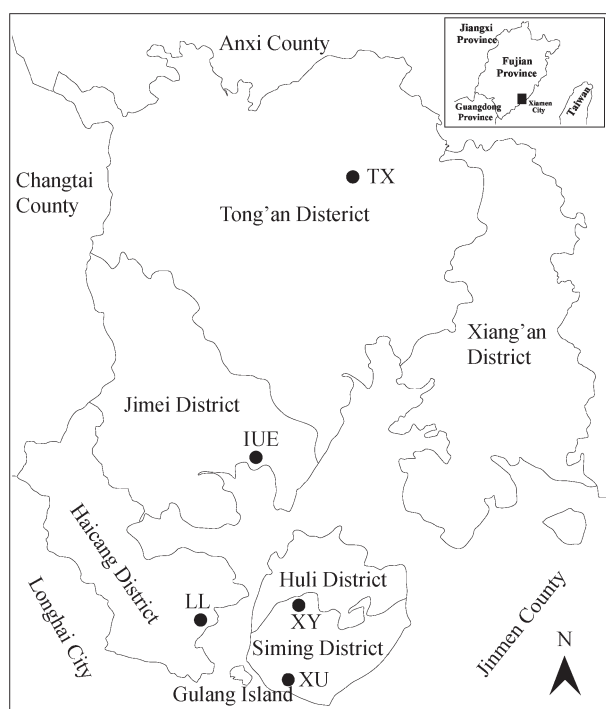


Fig. 1 Location of the five sampling sites (TX, IUE, LL, XY, XU) in Xiamen.

–20°C until analysis.

The samples were analyzed with a gas chromatography-mass spectrometry (GC-MS) system consisting of an Agilent model 7890A GC and an Agilent model 5975 mass selective detector (MSD) (USA). The MSD operated in electron impact mode with electron energies of 70 eV. A capillary column (HP-5MS UI, 30 m × 0.25 mm × 0.25 µm, length × ID × film thickness) was used. Splitless mode was applied at the GC inlet for the introduction of 1 µL sample. The GC temperature was held at 50°C for 1 min and raised to 200°C at 10°C/min, then to 280°C at 5°C/min and held for 12 min. The MSD was run in selected ion monitoring mode for optimum sensitivity. Data acquisition and processing were controlled by a HP Chem-Station data system. Identification of individual PAHs was based on the retention times of target ion peaks (within ± 0.05 min of the retention of the calibration standard).

The PAHs determined in this study are abbreviated as follows: naphthalene (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).

1.3 Quality assurance and quality control

Field blanks that accompanied the samples from the sampling sites were used to determine any potential background contamination during sampling, transport, and storage. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were also used. Surrogate standards were added to all samples (including those for quality assurance) to monitor procedures and matrix effects. The blank levels were less than 6% of the mass in the samples. PAHs level in solvent blanks ($n = 5$) were lower than those in the field blanks. The relative difference for individual PAHs congener identified in paired duplicate samples were all < 13%.

During GC-MS analysis, response factors for individual PAHs relative to the internal standard were determined from the analysis of the calibration solution containing 16 PAHs, 4 deuterated PAHs and one internal standard. No any targeted PAHs was detected in standards or blanks. Analytical recoveries of the surrogate PAHs in samples were 48.45%–66.57% for acenaphthene- d_{10} ; 43.60%–64.12% for phenanthrene- d_{10} ; 55.61%–101.76% for chrysene- d_{12} and 59.90%–116.05% for perylene- d_{12} . Reported concentrations were corrected for blank levels but not for surrogate recoveries.

2 Results and discussion

2.1 Ambient air PAH concentration and distribution

The average concentrations of PAHs in particle- and gas-phase at five sampling sites are shown in Table 1. The total (particle- and gas-phase) PAHs concentration in

ambient air was ranged from 5.54 (TX) to 76.55 ng/m³ (XY) in autumn, and 35.95 (XU) to 62.85 ng/m³ (LL) in winter. Table 1 shows that PHE, FLA and PYR were the dominant congeners among the total PAHs not only in particle-phase but also in gas-phase at five sampling sites. The total concentration of PHE, FLA and PYR ranged from 0.77 (TX) to 37.18 ng/m³ (XY), 0.43 (TX) to 10.14 ng/m³ (XY) and 0.32 (TX) to 6.05 ng/m³ (XY) in the autumn samples, respectively, the concentrations of which were higher in autumn than that in winter. Total PAHs concentration in TX autumn and winter samples were 5.54 and 37.37 ng/m³, which were lower than those in other sampling sites indicating the influence of pollution source from biomass combustion and temperature inversion.

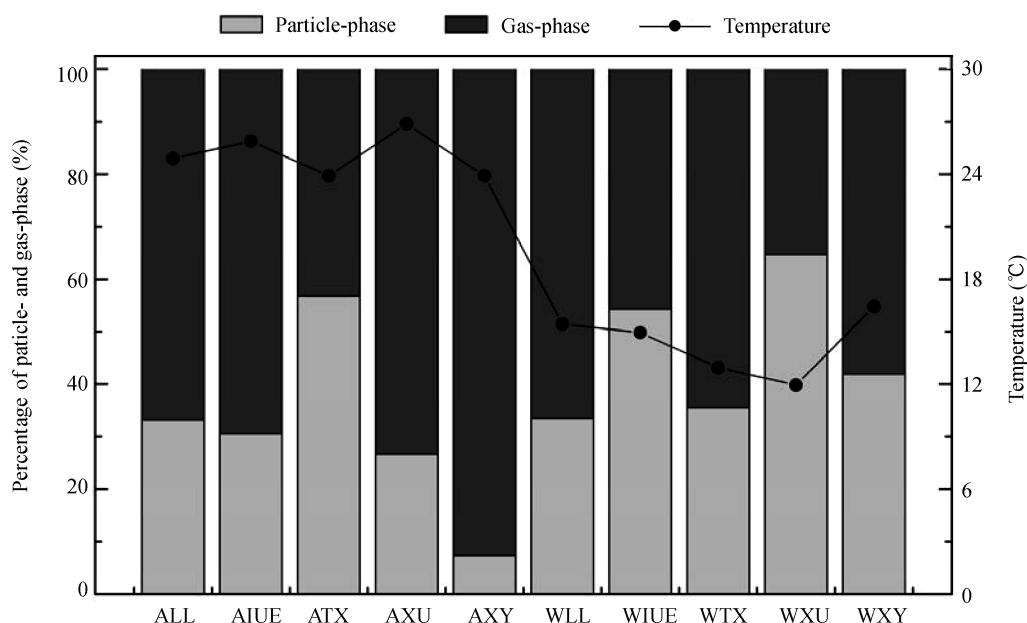
Table 1 also indicates that concentration of PAHs in winter were higher than that in autumn, and which were also higher in urban than that in suburban and background. Low levels of photochemical degradation and limited mixture layers or the frequent formation of a temperature inversion layer in the atmosphere in Xiamen during winter would aggravate the occurrence of high PAHs concentration in the samples. High levels of photochemical degradation and of mixture layers in the atmosphere and frequent monsoon and rainfall during autumn would lead to low concentrations of PAHs in the samples. The different concentrations of PAHs in five sampling sites mainly relate with surrounding environment. XY was located in residential areas, which was a commercial area with a busy transportation. The dual impacts of vehicle exhaust and cooking emission may result the highest level concentration in autumn. LL was placed in industrial district, exhaust from petrochemical factory and power plant was the main source of PAHs, and led to the high concentration of PAHs. Infrastructure construction and agricultural activity were the main factors which would influence PAHs concentration in IUE. XU was an education and tourist area, vehicular emission and the exhaust gas from ships were sources for PAHs. TX sampling site was surrounding by forest and a reservoir. There was almost no pollution source excluding occasional biomass combustion, which would cause a low concentration of PAHs.

The total particle-phase PAHs in the atmosphere ranged from 3.14 (TX) to 7.49 ng/m³ (LL) in autumn samples and 13.26 (TX) to 23.27 ng/m³ (XU) in winter samples, which accounted for 7.27% (XY)–56.73% (TX) and 33.51% (LL)–64.74% (XU) in the total PAHs, respectively (Fig. 2). Whereas, the total gas-phase PAHs has a higher percent in total PAHs during autumn (43.27% (TX)–92.73% (XY)) than that during winter (35.26% (XU)–66.49% (LL)). The relationship of distribution of particle-/gas-phase PAHs and temperature can be found in Fig. 2 clearly, where the relative concentration of gas-phase PAHs in autumn were higher than that in winter. This can be interpreted as the gas-particle distribution of semi-volatile PAHs, which was dependent on temperature; therefore, PAHs distributions tend to shift toward the particle-phase in winter (Gigliotti et al., 2000; Bi et al., 2003).

Figure 3 shows the variations of total PAHs in particle-/gas-phase and concentration of TSP in five sampling sites.

Table 1 Average concentration of particle- and gas-phase PAHs at five sampling sites (ng/m³)

Sampling site	Autumn					Winter				
	LL (n = 4)	IUE (n = 3)	TX (n = 2)	XU (n = 4)	XY (n = 4)	LL (n = 5)	IUE (n = 4)	TX (n = 3)	XU (n = 4)	XY (n = 5)
Particle-phase										
NAP	0.39 ± 0.05	0.33 ± 0.02	0.34 ± 0.03	0.33 ± 0.01	0.41 ± 0.06	0.23 ± 0.02	0.39 ± 0.07	0.43 ± 0.02	0.36 ± 0.09	0.12 ± 0.09
ACY	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.05 ± 0.01	0.02 ± 0.00	0.06 ± 0.01	0.02 ± 0.01
ACE	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.00	0.01 ± 0.00	0.03 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.00
FLO	0.03 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.01 ± 0.00	0.04 ± 0.01	0.03 ± 0.00	0.09 ± 0.00	0.02 ± 0.00	0.10 ± 0.01	0.02 ± 0.01
PHE	0.18 ± 0.03	0.11 ± 0.01	0.16 ± 0.03	0.09 ± 0.01	0.20 ± 0.01	0.29 ± 0.03	1.23 ± 0.12	0.24 ± 0.06	1.39 ± 0.17	0.21 ± 0.12
ANT	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.01	0.01 ± 0.00	0.03 ± 0.00	0.03 ± 0.01	0.05 ± 0.00	0.02 ± 0.00	0.90 ± 0.83	0.03 ± 0.02
FLA	0.39 ± 0.10	0.18 ± 0.03	0.36 ± 0.10	0.17 ± 0.02	0.31 ± 0.10	0.62 ± 0.05	2.34 ± 0.06	0.62 ± 0.12	2.82 ± 0.53	0.45 ± 0.30
PYR	0.35 ± 0.02	0.17 ± 0.03	0.29 ± 0.08	0.16 ± 0.01	0.24 ± 0.03	0.54 ± 0.06	1.63 ± 0.11	0.60 ± 0.09	1.85 ± 0.46	0.38 ± 0.27
CHR	0.24 ± 0.08	0.09 ± 0.00	0.11 ± 0.02	0.10 ± 0.02	0.18 ± 0.04	0.94 ± 0.04	0.95 ± 0.07	0.40 ± 0.11	0.92 ± 0.32	0.94 ± 0.70
BaA	0.47 ± 0.12	0.25 ± 0.11	0.28 ± 0.09	0.21 ± 0.10	0.39 ± 0.21	1.51 ± 0.22	1.82 ± 0.13	0.86 ± 0.48	2.09 ± 0.50	1.39 ± 1.12
BbF	0.90 ± 0.18	0.61 ± 0.08	0.32 ± 0.11	0.42 ± 0.08	0.93 ± 0.16	3.21 ± 0.14	0.24 ± 0.00	1.79 ± 0.23	2.07 ± 1.93	2.44 ± 1.78
BkF	0.72 ± 0.05	0.49 ± 0.16	0.26 ± 0.07	0.34 ± 0.16	0.05 ± 0.01	1.52 ± 1.17	2.42 ± 1.65	1.44 ± 0.12	2.45 ± 0.76	1.96 ± 0.06
BaP	0.86 ± 0.21	0.49 ± 0.18	0.35 ± 0.20	0.33 ± 0.06	0.59 ± 0.19	2.60 ± 0.03	2.43 ± 0.50	1.41 ± 0.11	2.25 ± 0.78	2.20 ± 1.56
IcdP	1.24 ± 0.33	0.79 ± 0.24	0.30 ± 0.07	0.36 ± 0.14	0.91 ± 0.23	4.82 ± 0.09	3.48 ± 1.23	2.63 ± 1.01	3.11 ± 1.21	3.79 ± 2.24
DahA	0.11 ± 0.01	0.07 ± 0.02	0.03 ± 0.00	0.04 ± 0.00	0.09 ± 0.02	0.35 ± 0.02	0.24 ± 0.03	0.17 ± 0.05	0.20 ± 0.06	0.29 ± 0.17
BghiP	1.56 ± 0.04	0.86 ± 0.31	0.29 ± 0.06	0.40 ± 0.11	1.15 ± 0.13	4.33 ± 0.04	2.99 ± 1.03	2.61 ± 1.56	2.71 ± 1.04	3.47 ± 2.12
Total particle-phase PAHs	7.49 ± 1.71	4.49 ± 1.47	3.14 ± 0.89	3.00 ± 1.03	5.56 ± 0.06	21.06 ± 1.45	20.36 ± 2.53	13.26 ± 1.87	23.27 ± 6.05	17.72 ± 8.79
Gas-phase										
NAP	0.58 ± 0.03	0.31 ± 0.11	0.72 ± 0.09	0.88 ± 0.14	5.66 ± 2.13	0.57 ± 0.00	0.63 ± 0.02	1.41 ± 0.06	0.42 ± 0.11	0.53 ± 0.25
ACY	0.07 ± 0.03	0.04 ± 0.00	0.08 ± 0.04	0.03 ± 0.01	0.38 ± 0.11	1.09 ± 0.81	0.24 ± 0.07	0.34 ± 0.10	0.08 ± 0.00	0.77 ± 0.05
ACE	0.13 ± 0.06	0.04 ± 0.02	0.13 ± 0.05	0.06 ± 0.03	0.39 ± 0.09	0.33 ± 0.02	0.24 ± 0.06	0.25 ± 0.07	0.23 ± 0.00	0.17 ± 0.03
FLO	0.90 ± 0.21	0.64 ± 0.02	0.64 ± 0.17	0.52 ± 0.21	3.55 ± 1.14	5.10 ± 0.17	2.62 ± 1.03	3.14 ± 1.24	3.29 ± 0.21	3.29 ± 0.05
PHE	7.72 ± 1.10	5.11 ± 1.50	0.61 ± 0.11	4.05 ± 1.32	36.98 ± 12.10	20.14 ± 2.15	7.43 ± 0.13	6.25 ± 1.15	4.83 ± 0.82	11.04 ± 0.06
ANT	0.44 ± 0.12	0.29 ± 0.20	0.08 ± 0.00	0.30 ± 0.01	6.90 ± 3.21	1.58 ± 0.30	0.33 ± 0.13	8.86 ± 2.10	0.22 ± 0.03	0.69 ± 0.08
FLA	2.65 ± 1.10	2.03 ± 1.21	0.07 ± 0.02	1.39 ± 1.10	9.83 ± 2.57	6.94 ± 0.19	3.28 ± 1.22	2.39 ± 1.08	2.20 ± 0.36	4.51 ± 0.08
PYR	1.57 ± 0.05	1.18 ± 0.81	0.04 ± 0.01	0.78 ± 0.23	5.81 ± 2.61	4.62 ± 0.37	1.83 ± 0.71	1.16 ± 0.06	0.96 ± 0.22	2.97 ± 0.05
CHR	0.11 ± 0.06	0.09 ± 0.00	0.02 ± 0.00	0.02 ± 0.01	0.42 ± 0.17	0.46 ± 0.16	0.04 ± 0.02	0.04 ± 0.01	0.18 ± 0.16	0.15 ± 0.01
BaA	0.42 ± 0.12	0.32 ± 0.15	0.01 ± 0.01	0.18 ± 0.05	0.88 ± 0.23	0.83 ± 0.12	0.45 ± 0.17	0.24 ± 0.11	0.23 ± 0.04	0.38 ± 0.04
BbF	0.06 ± 0.00	0.04 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.08 ± 0.03	0.03 ± 0.03	0.02 ± 0.00	0.01 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
BkF	0.05 ± 0.02	0.03 ± 0.01	ND	0.01 ± 0.00	0.06 ± 0.03	0.02 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
BaP	0.35 ± 0.11	ND	ND	ND	0.04 ± 0.01	0.01 ± 0.01	ND	ND	ND	ND
IcdP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DahA	ND	0.09 ± 0.03	ND	ND	ND	0.04 ± 0.03	ND	ND	0.03 ± 0.01	0.01 ± 0.01
BghiP	ND	ND	ND	ND	ND	0.02 ± 0.02	ND	ND	ND	0.01 ± 0.00
Total gas										
-phase PAHs	15.06 ± 3.12	10.22 ± 1.84	2.40 ± 0.32	8.24 ± 1.45	70.99 ± 7.13	41.79 ± 2.38	17.13 ± 2.32	24.11 ± 1.43	12.68 ± 1.36	24.54 ± 0.06
ANT/(PHE+ANT) ^a	0.06	0.05	0.10	0.07	0.16	0.07	0.04	0.58	0.15	0.06
FLA/(FLA+PYR)	0.61	0.62	0.57	0.62	0.63	0.59	0.62	0.63	0.64	0.60
BaA/(BaA+CHR)	0.72	0.76	0.71	0.77	0.68	0.63	0.70	0.71	0.68	0.62
IcdP/(IcdP+BghiP)	0.44	0.48	0.51	0.47	0.44	0.53	0.54	0.50	0.53	0.52

Data are expressed as average ± SD. ^a Ratio was obtained by the total concentration of every compounds. ND: not detected.**Fig. 2** Relationship of distribution of total particle-/gas-phase PAHs and temperature. A: autumn; W: winter.

It is obviously that the variation trend of concentration for PAHs in particle-phase and TSP was coincident in different sampling sites, whereas it was not coincident variation

trend between PAHs in gas-phase and TSP, especially that in winter samples. Therefore, there was no significant relationship can be found between the concentrations of

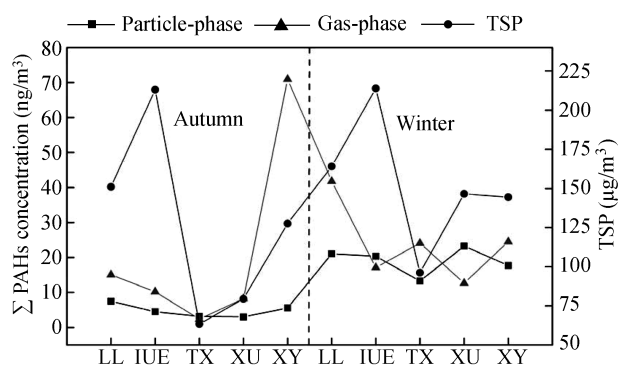


Fig. 3 Variations of particle-/gas-phase PAHs and total suspended particles (TSP) in five sampling sites.

PAHs in gaseous phase and TSP. Seasonal trend was apparent for PAHs concentration in gaseous phase. The relative percent of concentration levels in autumn was high and gradually decreased in winter. Gustafson and Dickhut (1997) suggested that gaseous PAHs (PHE, ANT, FLA, and PYR) have an exponential increase under high ambient temperature. For particulate PAHs, the variation trend of relative percent concentration was observed in the opposite direction, with lower relative percent concentration levels in autumn and higher levels in winter. That was not paradoxical because low levels of photochemical degradation and frequent formation of a temperature inversion layer in the atmosphere during winter would deteriorate pollution of PAHs, and the temperature would affect different relative percents of particle-/gas-phase PAHs, which also can be proved by Fig. 2.

Figure 4 shows the distribution of 2–6 ring PAHs in particle- and gas-phase. The predominant PAHs in the gas-phase were two- to four-ring compounds, including PHE (25.27% (TX)–52.09% (XY) in autumn and 25.92% (TX)–48.18% (LL) in winter), FLA (2.88% (TX)–19.86% (IUE) in autumn and 9.92% (TX)–19.18% (IUE) in winter), FLO

(4.99% (XY)–26.64% (TX) in autumn and 12.20% (LL)–25.93% (XU) in winter), and PYR (1.49% (TX)–11.54% (IUE) in autumn and 4.83% (TX)–12.09% (XY) in winter), and five- to six-ring PAH compounds (MW 250–300) with low vapor pressure were predominant in the particulate PAHs, including BbF, BghiP, IcdP, BaP, and BkF. Four-ring compounds (MW 228) like BaA and CHR had similar concentrations at some samples in the gaseous and particulate phases. PAHs with different molecular weights have different particulate/gaseous distribution coefficients, the gaseous phase contribution generally decreased with increasing molecular weight from 99.2% to < 0.01%. Two- and three-ring PAHs were associated primarily with the gaseous phase, 5- and 6-ring PAHs were associated mainly with particulate phase (Fig. 4). These results were consistent with other studies (Bi et al., 2003). In addition, Fig. 4 also shows the relative composition of PAHs in sampling site, excluding background (TX) sampling sites, has a good consistency, which suggested the PAHs in different functional areas have the same or similar sources of pollutant. Using concentration of 16 class PAHs that have been detected in suburban sampling sites (IUE) and other sampling sites (LL, XU, XY and TX) to analysis correlation (Fig. 5), there was a significant correlation ($P < 0.01$), excluding TX samples, which further indicated that there were similar sources of PAHs in different functional areas.

2.2 Comparison of PAHs concentrations

Table 2 displays the PAHs concentration of North America, Europe, and Asia. From Tables 1 and 2, we can observe that the average total PAHs concentration in winter was about 1.7 times higher than those in autumn. This different might be explained by the fact of meteorological factor, such as frequent temperature inversion would aggrandize PAHs pollution in winter. The average total PAHs concentration in autumn was similar with that in Houston

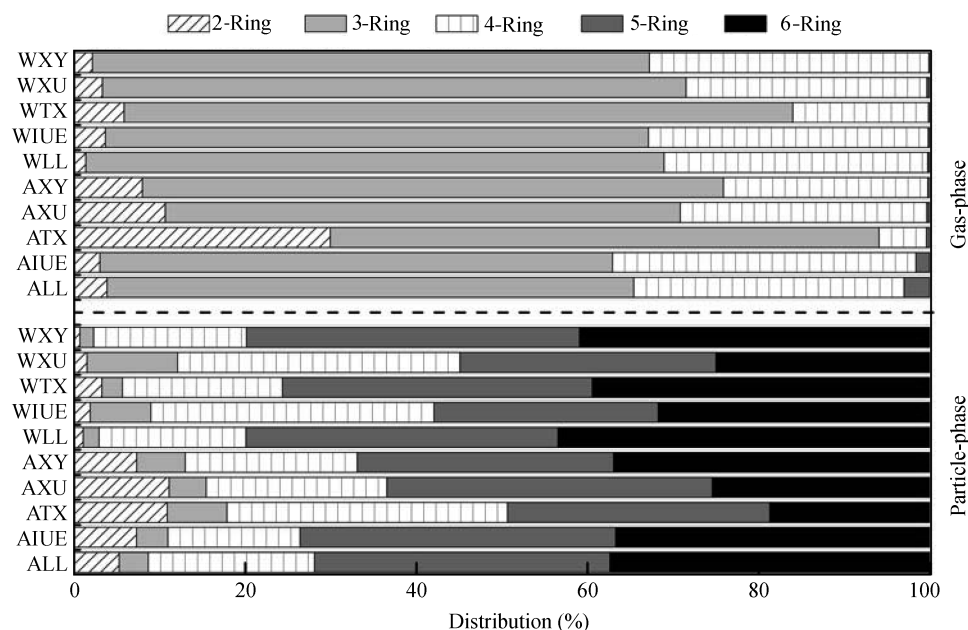


Fig. 4 Distribution of 2-, 3-, 4-, 5-, 6-ring PAHs in particulate and gaseous phases. A: autumn; W: winter.

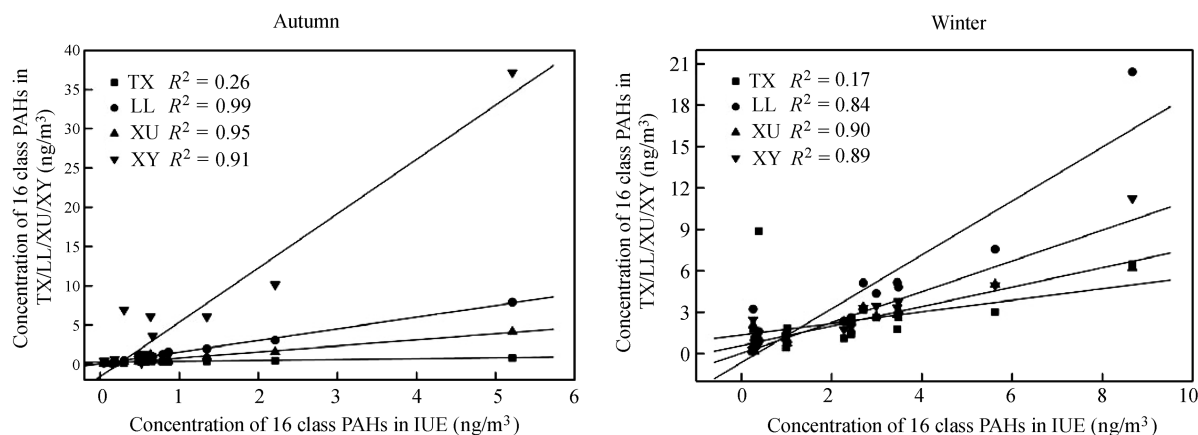


Fig. 5 Correlation of the concentration of individual PAHs in IUE and LL/XU/XY/TX.

Table 2 Comparison of total PAHs concentration between the present study and previous publications

Location	Date	Conc. (ng/m ³)	Reference
London, UK	1991	166	Halsall et al., 1994
London, UK	1997	39	Dimashki et al., 2001
Chicago, USA	1994–1995	164	Simicik et al., 1997
Chicago, USA	2004	70	Sun et al., 2006
Houston, USA	1999–2000	26	Naumova et al., 2002
Elizabeth, USA	1999–2000	35	Naumova et al., 2002
Birmingham, UK	1999	45	Harrad and Laurie, 2005
Heraklion, Mediterranean	2000–2002	79	Tsapakis and Stephanou, 2005
Teplice, Czech	1993–1994	127	Pinto et al., 1998
Kozani, Greece	2000–2001	27	Terzi and Samara, 2004
Toronto, Canada	2000–2001	< 50	Motelay-Massei et al., 2005
Hong Kong, China	1999–2000	91	Lee et al., 2001
Seoul, Korea	1999	89	Park et al., 2002
Bursa, Turkey	2004–2005	258	Esen et al., 2006
Qingdao, China	2001–2002	87.5	Guo et al., 2003
Guangzhou, China	2001–2002	337	Li et al., 2006
WaLiguan, China	2005	19	Cheng et al., 2006
Xiamen, China	Oct 2008	26.1	This study
	Dec 2008–Jan 2009	44.6	

(Naumova et al., 2002) and Kozani (Terzi and Samara, 2004), in winter was similar with that in Birmingham, UK (Harrad and Laurie, 2005) and lower than Chicago (Simick et al., 1997; Sun et al., 2006), Teplice (Pinto et al., 1998). Compare with the coastal city in China, we found that the pollution of total PAHs in Xiamen was lower than other coastal city from north (Qingdao) to southeast (Xiamen), and then to south (Guangzhou and Hong Kong). PAHs pollution in Guangzhou was serious in these coastal cities, where the PAHs concentration was approximately 10 times higher than that in Xiamen. In addition, it was obvious that PAHs concentrations in Xiamen during autumn and winter were higher than that in WaLiguan which is a typical background site and only has 19 ng/m³ in ambient atmosphere (Cheng et al., 2006). However, the average value of PAHs in background (TX, 21.4 ng/m³) was slightly higher than that in WaLiguan. In a word, the average PAHs concentration in Xiamen was low compared with other coastal cities among China, North America and Europe. Nevertheless, it is worth of, for administrative department, paying attention to atmospheric pollution, in order to keep a better environment of this tourism-city.

2.3 Gas-particle partitioning of PAHs

Gas-particle partitioning of PAHs is subjected to seasonal variation not only because of changes in emission profiles but also in meteorological conditions and particle characteristics. In many studies, using Eq. (1), the gas-particle partitioning of PAHs (K_p) has been examined as a function of sub-cooled liquid vapor pressure (P_L^0) of the compounds (Fernandez et al., 2002; Esen et al., 2008).

$$\log K_p = m_r \log P_L^0 + b_r \quad (1)$$

Focusing on a single sampling period reduces the effect of fluctuations in atmospheric conditions and particle characteristics. Liang et al. (1996) suggested that under equilibrium conditions and for the same compound class, the slope (m_r) should be -1 regardless of whether absorption or surface adsorption dominates the partitioning process. However, in more recent studies it was concluded that m_r may deviate significantly from -1 for equilibrium partitioning (Vardar et al., 2008; Bi et al., 2004). The deviations from the equilibrium value of -1 have commonly been attributed to sampling artifacts, non-exchangeability, new pollutants input during sampling and a lack of constancy in activity coefficients (Terzi and Samara, 2004; Vardar et al., 2004; Goss and Schwarzenbach, 1998; Simcik et al., 1998). The effects of non-exchangeable PAHs on the measured $\log K_p$ values are small for low volatility PAHs, whereas for most volatile compounds, this effect is significantly large due to the facts that they are mainly in the gaseous phase (Pankow and Bidleman, 1992). In a word, if the activity coefficient of the chemical in the organic matter is not constant, it is also possible to get slopes not equal to -1 .

Figure 6 shows that the slope for the autumn samples was -0.58 , whereas it was -0.72 for the winter samples, which indicated that the winter samples to be closer to equilibrium value of -1 than the autumn samples. Gas-particle partitioning results of autumn and winter samples in this study were consistent with the results obtained from urban samples taken in the Guangzhou City by Bi et al. (2004), in Houston by Naumova et al. (2003) and in Turkey by Esen et al. (2008). For an urban area, similar

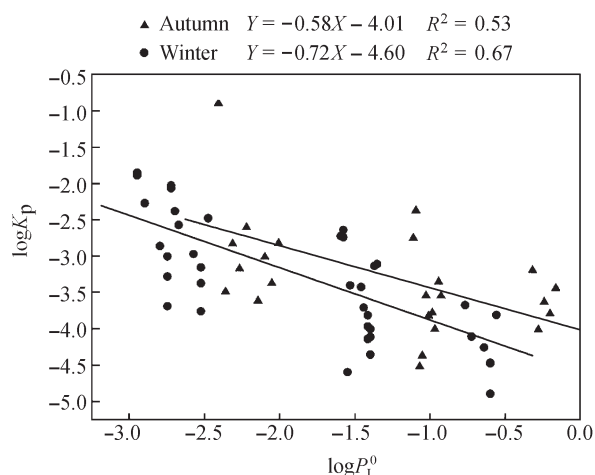


Fig. 6 Plots of $\log K_p$ versus $\log P_L^0$ for all the samples collected in Xiamen. Data source of $\log P_L^0$ is from Offenberger and Baker (1999).

results have been reported (Esen et al., 2008; Terzi and Samara, 2004; Lohmann et al., 2000). Lohmann et al. (2000) observed steeper slope (-0.77) for coldest event and shallowest slope (-0.67) during warmest event in the northwest England atmosphere. On the other hand, in some studies opposite seasonal pattern was observed, slopes in winter period were shallower than those in summer period (Galarneau et al., 2006). It is worthy to note that not all of the studies showed same kind of seasonal trend in slopes.

It has been reported that partitioning of PAHs showed different characteristics depending on air mass trajectories (Vardar et al., 2004, 2008). Figure 7 shows backward trajectories of air masses coming from northeast areas to sampling site in Xiamen, and also indicates that the influence of wind direction in autumn and winter is almost same. However, it was possible that the pollution contributed to Xiamen would be different during autumn and winter, and carried much more organic matter by air mass from the Yangtze River Delta in winter which may

affect partitioning coefficient of PAHs. Characterization of the organic matter associated with gaseous/particulate partitioning of PAHs must be done to support this interpretation (Offenberg and Baker, 2000). Of course, detailed influencing factors at each site need to be studied deeply to explain the differences on those partitioning results.

Based on these observations, it can be concluded that specific characteristics of sampling sites and meteorological conditions play important roles in the gas-particle partitioning of PAHs in Xiamen.

2.4 Primary research on sources of PAHs in five sampling sites

Atmospheric PAHs profiles can be affected by meteorological variables such as sunlight radiation and temperature, and its sources mainly come from incomplete combustion. Despite these facts, the ratios between some of these compounds were considered as “fingerprint” of an emission source (Khalili et al., 1995; Dickhut et al., 2000), and this ratio was diagnostic parameters (diagnostic ratios). These diagnostic ratios between PAHs were used to characterize potential emission sources and distinguish PAHs sources (Kavouras et al., 2001).

Table 1 provides information on diagnostic ratios for PAHs, such as FLA/(FLA+PYR), BaA/(BaA+CHR), BaA/(BaA+CHR) and IcdP/(IcdP+BghiP), which can be used to investigate their origin or as an indication of the aging of air samples (Lohmann et al., 2000). A comparison between the various diagnostic ratios by US EPA (2003), Yunker et al. (2002) and Pio et al. (2001) was conducted. Analysis of the ratios could be associated to various sources. Because only TSP may result in a significant underestimation of the contribution of anthropogenic emission, these ratios were determined by the total concentration including the gaseous and particulate phases. In particular, the FLA/(FLA+PYR) values were determined to be 0.57 and 0.63 in ATX and WTX, which

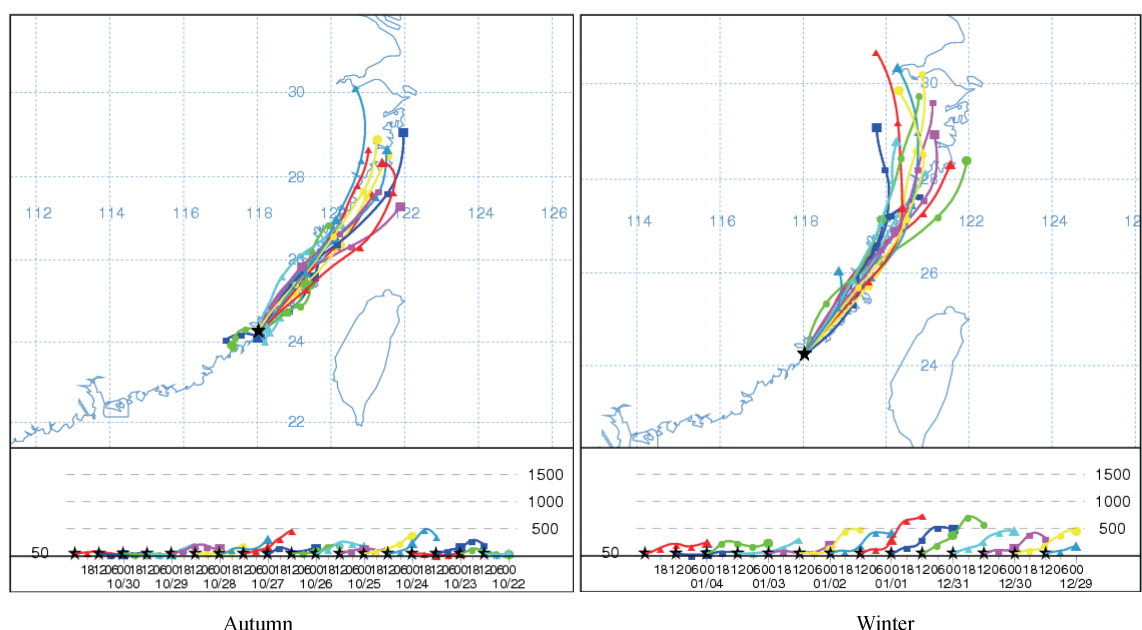


Fig. 7 Backward trajectories of air mass from northeast to Xiamen during sampling times.

are comparable to the values reported for biomass (wood or vegetation) combustion (0.51 ± 0.16) (Yunker et al. 2002; Pio et al., 2001; US EPA, 2003). The source of biomass combustion for TX can be further assessed from IcdP/(IcdP+BghiP) ratios (0.42 ± 0.18) by Yunker et al. (2002), which was coincident with results of this study (0.51 in ATX and 0.50 in WTX). The literature reported values for IcdP/(IcdP + BghiP) are 0.36 ± 0.14 and 0.48 ± 0.29 for oil and coal combustion, respectively (Yunker et al., 2002; US EPA, 2003). The mean ratio in this study was 0.44 – 0.48 in urban and industrial area, respectively, which is comparable to that for vehicle emissions and exhausts from petrochemical factory and power plant. The BaA/(BaA+CHR) ratio in WXU and AXY was 0.68 , indicating that diesel vehicle was a great contributor in these areas and also can be assessed by PHE/(PHE+ANT) that was 0.73 ± 0.18 in literature (Yunker et al., 2002; US EPA, 2003). The parameters were compared with those reported previously (Yunker et al., 2002; Pio et al., 2001; US EPA, 2003). Figure 5 also approves indirectly there have similar sources in these sampling sites.

Overall, our results suggest that the major source of organic compounds in the air of urban and industrial area in Xiamen was fossil fuel combustion from automobiles. The ratios of FLU/(FLU+PYR) was determined by Rogge et al. (1993) for non-catalyst (0.41), and catalyst-equipped (0.51) automobiles. The ratio was calculated to be 0.60 – 0.63 in this study, which is close to the value for catalyst-equipped automobiles. In Xiamen City, in order to keep favorable place for living, most of automobiles are equipped with the converters after 2000. In addition, emission from coal combustion in power plant was another main source for industrial area.

3 Conclusions

The total particle-phase PAHs in the Xiamen atmosphere ranged from 3.14 (TX) to 7.49 ng/m³ (LL) in autumn and 13.26 (TX) to 23.27 ng/m³ (XU) in winter, and the total gas-phase PAHs in the air between 2.40 (TX) and 71.00 ng/m³ (XY) in autumn and 12.68 (XU) and 24.54 ng/m³ (XY) in winter. PHE, FLA and PYR were the predominant compounds in Xiamen. Measured atmospheric PAHs concentration showed that the relative concentration of particle-phase was significantly lower in autumn samples than that in winter samples, which was opposite result for gas-phase PAHs. There were obvious differences of total PAHs in different functional areas, which has the highest concentration in industrial area (LL) and commercial area (XY), followed by suburban (IUE), and TX as background sampling sites has the lowest concentration of PAHs.

Gaseous/particle partitioning of PAHs showed more shallow slopes ($m_r = -0.58$) and steeper slope ($m_r = -0.72$) were observed in autumn and winter sampling time, respectively. The m_r varied depending on specific characteristics of sampling site and meteorological conditions.

The correlation of the concentration for individual PAHs at five sampling sites and diagnostic ratio analysis results

indicated that vehicle exhausts were a primary source for PAHs in different functional areas of Xiamen. In addition, coal combustion was another main source in industrial area. Therefore, it can be proposed that some effective control measures should be taken to reduce the urban atmospheric pollution and keep the reputation of best environment for Xiamen City, China.

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