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Particle size distributions of polycyclic aromatic hydrocarbons in rural and urban atmosphere of Tianjin, China

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Abstract

The size distributions of 16 polycyclic aromatic hydrocarbons (PAHs) and particle mass less than 10 μm in aerodynamic diameter (D_p) were measured using a nine-stage low-volume cascade impactor at rural and urban sites in Tianjin, China in the winter of 2003–2004. The particles exhibited the trimodal distribution with the major peaks occurring at 0.43–2.1 and 9.0–10.0 μm for both urban and rural sites. The concentrations of the total PAH (sum of 16 PAH compound) at rural site were generally less than those of urban site. Mean fraction of 76.5% and 63.9% of the total PAH were associated with particles of 0.43–2.1 μm at rural and urban sites, respectively. Precipitation, temperature, wind speed and direction were the important meteorological factors influencing the concentration of PAHs in rural and urban sites. The distributions of PAHs concentration with respect to particle size were similar for rural and urban samples. The PAHs concentrations at the height of 40 m were higher than both of 20 and 60 m at urban site, but the mass median diameter (MMD) of total PAH increased with the increasing height. The mid–high molecular weight ($278 \geq \text{MW} \geq 202$) PAHs were mainly associated with fine particles ($D_p \leq 2.1 \mu\text{m}$), whereas low molecular weight ($128 \geq \text{MW} \geq 178$) PAHs were distributed in both of fine and coarse particle. The fraction of PAHs associated with coarse particles ($D_p > 2.1 \mu\text{m}$) decreased with increasing molecular weight. The relatively consistent distribution of PAHs seemed to indicate the similar combustion source of PAHs at both of rural and urban sites. The fine differences of concentration and distribution of PAHs at different levels at urban site suggested that the different source and transportation path of particulate PAHs.

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Keywords: PAHs; Size distribution; Different height

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous harmful semivolatile organic compounds formed

by incomplete combustion of organic materials, especially those from human activities (Baek et al., 1991; Harrison et al., 1996). Particular interest has been focused on PAHs because some of them are known to be mutagenic or carcinogenic (IARC, 1984, 1991). The atmospheric pollution is the primary pathway of people exposure to PAHs in the polluted atmosphere, such as direct respiration or indirect ingestion from the polluted

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vegetables and corns by deposited PAHs. Tianjin is a big city in northern China and large amount of fossil fuel (coal and petroleum) have been consumed for the economic development. Additionally, large numbers of boiler chimneys with the height of 45 m in urban area for domestic heating in winter emit large quantities of smoke and dust into the atmosphere. As a result, PAHs produced due to the coal incomplete combustion emit into the urban atmosphere and severely impact human health. It also cannot be ignored that the influence of PAHs from coal combustion for cooking and heating in village because of the low quality and poor efficiency of honeycomb briquets, which are ubiquitously and largely used in Chinese villages.

The concentrations of pollutants in atmosphere are controlled by a balance between those factors which lead to pollutant accumulation and those which lead to pollutant dispersion. And the meteorological factors have both of the characteristics mentioned above. Rocha et al. (1999) reported the highest values of concentrations of PAHs in airborne particulate matter occurred in winter of decreasing temperatures and when minimum values of precipitation/humidity were attained at both of Oporto and Vienna. Many other researchers have found that the concentrations of particulate PAHs were lower in rural than those of urban in the same season and lower in summer and spring than those of winter at the same sites (Allen et al., 1996; Smith and Harrison, 1996; Bae et al., 2002; Omar et al., 2002). There are several studies related to vertical concentration gradients for CO, NO_x, and aerosol particles in urban air (Bauman et al., 1982; Qin and Kot, 1993; Zoumakis, 1995). However, there is very little information available for particulate PAHs vertical gradients in urban areas.

The freshly generated PAHs, emitted into the atmosphere in the form of gas phase and ultrafine particles (Richter and Howard, 2000), usually transport to the surface of coarse particle through volatilization, condensation, and collision (Strommen and Kamens, 1999; Venkataraman et al., 1999; Schnelle-Kreis et al., 2001). The partition of PAHs between different sizes of particles depends upon the ambient temperature, the relative humidity, the particle surface available for sorption and the compound properties (Venkataraman et al., 1994; Allen et al., 1996). The particle behaviors such as transport in the air, dry or wet deposition from the atmosphere to natural surfaces, and deposition in the human lungs are mainly influenced by particle size distributions (Hinds, 1982; Baek et al., 1991). Therefore, information on the particle size distribution of PAHs is essential to estimate their inputs into ecosystems and human respiration system. Additionally, airborne particles with different sizes have different sources. Fine particles ($D_p < 2 \mu\text{m}$) are produced predominantly from gas to particle conversion and from incomplete combustion whereas coarse particles ($D_p > 2 \mu\text{m}$) originate mostly

from mechanical processes, such as grinding, wind, or erosion (Whitby, 1978). Therefore, study of the size distributions of particle-bound PAHs can give important information about their origin and atmospheric behavior. Moreover, accurate risk assessment about human PAHs exposure can be made with the help of information on the atmospheric size distribution of PAHs because particles smaller than $3.0 \mu\text{m}$ are easily transported through the upper respiratory tract into the bronchioles and alveoli of the lungs, and larger particles will be retarded at the upper respiratory tract and then expectorated out of respiratory tract. Many studies have been made on the distribution of PAHs with respect to particle size. Urban PAHs size distributions were typically multimodal, and most PAHs were found to be predominately associated with fine particles in most cases, especially the higher molecular weight PAH compounds (Venkataraman and Friedlander, 1994; Venkataraman et al., 1994, 1999; Allen et al., 1996; Offenberg and Baker, 1999; Kaupp and McLachlan, 2000; Cancio et al., 2004).

The purposes of this work were to (1) compare the differences of the size distributions and concentrations of particle-bound PAHs between rural and urban site, (2) investigate the differences of concentration and size distribution of PAHs at different height in urban atmosphere and the variability of total PAH along with sampling time at both rural and urban sites. The results of this study are important to evaluate the risk of particle-bound PAHs exposure and develop the dry deposition model of particulate PAHs from atmosphere to natural surfaces.

2. Experiments

2.1. Description of sampling sites

Size-segregated aerosol samples were collected from a rural and an urban sites in Tianjin during the winter of 2003–2004, located at the cornfield of Chenlou county in Wuqing district and the meteorological tower in the South of urban center, respectively (Fig. 1). The rural sampling height was 1.5 m above the ground. The nearest highroad was roughly 1 km West away and the village was about 150 m to the South. The cornfield was smooth and the height of wheat plant was about 10 cm. The atmospheric contaminants at rural site from urban area were relative less with respect to urban site. The possible sources include vehicle exhausts, emissions from small-scale combustors used for cooking and heating (wood and coal) and long-range transport from urban area.

At urban site, three samplers were installed at the height of 20, 40 and 60 m of the meteorological tower (250 m) of the Meteorological Bureau of Tianjin lying

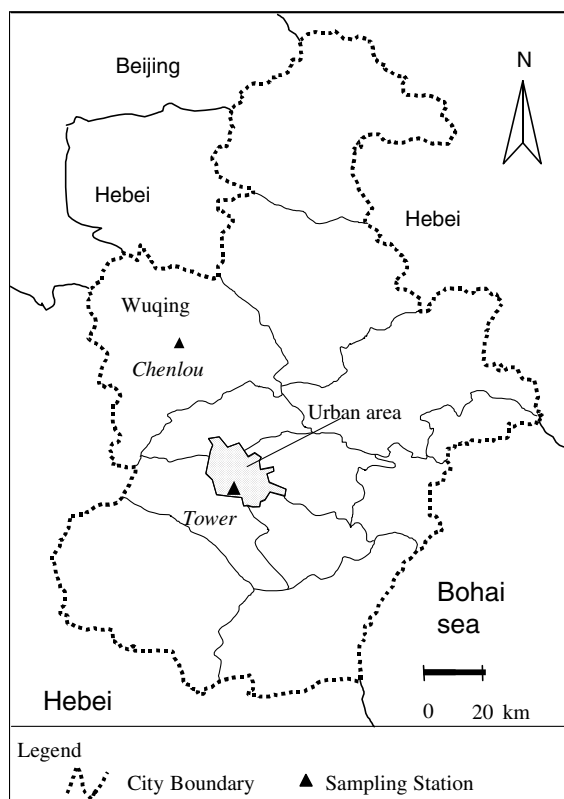


Fig. 1. Location map of the sampling stations in Tianjin.

in the center of a crossroads, surrounded by large residential areas. Temperature, wind speed and direction were on-line monitored at 15 different levels (5, 10, 20, 30, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 250 m) during the sampling period. The meteorological tower was at a distance of about 1 km to a chimney of coal burning boiler using in winter for heating and the average height of buildings within a radius of 300 m was about 20 m. The height of the boiler chimney was about 45 m according the coal combustion power. Therefore, the possible sources of PAH in the urban atmosphere include motor vehicles, coal- or oil-burning boilers, residential cooking and re-suspended soil dust.

2.2. Sample collection

Airborne particles were collected using a home made nine-stage low-pressure cascade impactor at a flow rate of 28.31 min^{-1} (FA-3, similar to Andersen MARK II). Each stage on the FA-3 consists of an impaction plate above and a nozzle plate below. The use of micro-orifice nozzle can collect airborne particles according to individual particle aerodynamic behavior without creating an excessive pressure drop across the impactor stage. The prepared glass fiber filters (\varnothing 80 mm) were used as

the surrogate surface and placed on each impaction plate to collect the impacted particles of different size. The glass fiber filters must be flat in order to collect the particles designed by the cascade impactor. The available particles were separated into the following size ranges: <0.43 (back up filter), 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and 9.0–10.0 μm in aerodynamic diameter (D_p). The glass fiber filters were baked at 500°C for 8 h to volatilize any organic contaminants before sampling. Much long-term sampling was necessary in order to collect sufficient particles to monitor PAHs due to the lower pump flow rate (28.31 min^{-1}). Size-separate samples were taken over periods of 70–95 h and the total sampling volume was about $120\text{--}160 \text{ m}^3$. PAHs may desorb/volatile from the impacted particles due to the much long sampling time, especially for those low molecular weight PAHs. The amount of desorption from sampled particles will not significantly affect the measurements because the average air temperature during all the sampling time is below 10°C (Venkataraman et al., 1999). The glass fiber filters were weighted before and after sampling to determine the amount of particles collected. The glass fiber filter was equilibrated for 24 h in a desiccator with allochroic silicel before weighing on a micro-balance (Model BP110S, Sartorius) accurate to 0.1 mg. After sampling, the glass fiber filter was removed from the pump, folded with the adsorbed particulate matter on the inner side, wrapped in an aluminium foil, transported from the field to lab on a filter box. After weighing, all filters were stored at -18°C and analyzed within 15 days from collection. Samples were collected on 9 days between November 18 and 27, 2003 and 9 days between December 31, 2003 and January 8, 2004 for rural and urban sampling, respectively. During the sampling intervals domestic heating began in both of rural and urban area.

The particle samplings conditions are presented in Table 1. There were two rain events during the rural sampling period. The first rainfall was about 15 mm and the second was no more than 5 mm. Parallel to sampling, the meteorological parameters such as temperature, relative humidity, wind direction and speed were monitored. The temperature ranged from 5 to 12°C and from -5 to 8°C during rural and urban sampling, respectively.

2.3. Analytical procedure

The extraction procedure for removing PAHs from the particulate matter used an accelerated solvent extractor (ASE 300, Dionex), equipped with 34 ml stainless-steel extraction cells. Filters were cut into strips and extracted with dichloromethane (DCM). The extraction and cleaning details have been detailed in previous paper (Wu et al., 2005). The elute of the PAH fraction was concentrated to 1 ml under a gentle stream of dry

Table 1
Environmental conditions for sampling of cascade particles

Sample	Site	Height (m)	Date	Volume (m ³)	Mean temp. (°C)	Mean RH (%)	Mean wind speed (m s ⁻¹)	Weather
A22, A23	Rural	1.5	11/8/2003–11/21/2003	120.3	9.9	64	2.21	Cloudy → rainy → sunny
A24, A25	Rural	1.5	11/21/2003–11/24/2003	122.1	10.1	58	2.09	Sunny → cloudy
A26, A27	Rural	1.5	11/24/2003–11/27/2003	110.9	7.8	66	1.25	Cloudy → rainy → cloudy
A28 ^a	Urban	20	12/31/2003–1/1/2004	35.7	0.92	63	1.76	Sunny
A29 ^a	Urban	40	12/31/2003–1/4/2004	165.4	2.49	–	2.39	Sunny
A30 ^a	Urban	60	12/31/2003–1/4/2004	164.4	3.14	–	3.11	Sunny
A31 ^b	Urban	20	1/4/2004–1/8/2004	159.6	1.04	56	1.16	Sunny
A32 ^b	Urban	40	1/4/2004–1/8/2004	159.6	0.91	–	1.68	Sunny
A33 ^b	Urban	60	1/4/2004–1/8/2004	159.7	1.67	–	2.16	Sunny

“–” No data.

^a The first urban sampling.

^b The second urban sampling.

nitrogen and transferred to 1.5 ml vials and preserved in a refrigerator at -18°C till gas chromatography–mass spectrometry (GC–MS) analysis.

The particle-bound PAHs were analyzed by Agilent GC 6890/5973 MSD system. A 30 m \times 0.25 mm i.d. HP-5MS (film thickness 0.25 μm) was used. The GC analyses were performed with an oven temperature program from 60 to 280 $^{\circ}\text{C}$ at the rate of 5 $^{\circ}\text{C min}^{-1}$, isothermal holding at 280 $^{\circ}\text{C}$ for 20 min using helium as the carrier gas; injector and transfer line temperature of 280 and 230 $^{\circ}\text{C}$, respectively. The injector volume was 1 μl in the splitless mode. The MS was operated using the electron impact (EI) ionization mode at 70 eV, scanning from 50 to 550 mass units at 0.82 s scan⁻¹. Compound identification was based on the MS database (NIST 98) and GC retaining time of authentic PAH standards containing naphthalene (NAP), acenaphthylene (ACPY), acenaphthene (ACP), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLUA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (INCDP), dibenz[*a,h*]anthracene (DBA) and benzo[*ghi*]perylene (BghiP) (PAH mixture 610/525/550 in methanol from Chem Service, US). The MSD was operated at selected ion monitoring (SIM) mode. The ions used for PAHs quantification were the molecular ions and the concentrations were quantified using the external standard method. The concentrations of individual PAH compounds were calculated by dividing their mass with the sampling volume, and expressed as ng m^{-3} .

Table 2
The recovery and limits of detection (LOD) of 16 PAH compounds

Compounds	NAP	ACPY	ACP	FLU	PHE	ANT	FLUA	PYR	BaA	CHR	BbF	BkF	BaP	INcdP	DBA	BghiP
Recovery (%)	92	66	68	82	88	96	100	104	99	101	104	93	77	91	97	103
LOD (ng)	1064	10.1	12.3	49.3	70.8	7.9	20.8	10.7	5.6	19.1	6.4	6.1	8.7	2.6	1.6	4.7

2.4. Quality control and quality assurance

The analytical recovery efficiencies of the 16 individual PAH were determined by processing a solution containing known PAH concentrations spiked onto the blank filters through the same experimental procedure used for the samples. The mean recoveries of the 16 PAHs ranged from 66% to 104% (SD = $\pm 12\%$) (Table 2) and were used to correct the amounts of the PAH compounds found the samples.

The limit of detection (LOD, ng) was defined as the mean blank mass plus three standard deviations (Hallsall et al., 1994; Cotham and Bidleman, 1995; Vardar et al., 2002). LODs for 16 PAHs ranged from 1.6 to 1064 ng (Table 2). The largest amounts found in the blanks were for naphthalene. In general, PAHs amounts in the particle samples were higher than LODs. Sample quantities exceeding the LOD were quantified and blank corrected by subtracting the mean blank amount from the sample amount. A 100-ml solvent (redistilled dichloromethane and hexane) was concentrated to a total volume of 0.5 ml and then analyzed with GC–MS in order to monitor the background.

2.5. Meteorological data collection

During rural (Chenlou) sampling period, temperature and relative humidity (WHM5, Tianjin Meteorological Instrument Plant), wind speed and direction (DEM6, Tianjin Meteorological Instrument Plant), monitored every two hours at the same height of particles sampling. Rainfall was measured with two scaled

buckets for each sampling time. Wind speed and direction at the 15 different levels were on-line measured with EC9-1 (Changchun Meteorological Instrumental Plant) every 10 s and saved in the computer. Temperature and humidity were measured with a homemade temperature–humidity instrument, but the humidity instrument was only installed at three levels (20, 120 and 250 m). Temperature and humid data were also collected every 10 s just like wind speed and direction. During the 9 days of urban sampling, about 1296 profiles of wind speed, temperature and humidity collected.

3. Results and discussion

3.1. Particle mass

The sum of segregated particle concentrations (eight stages plus after-filter) ranged from 182 to 238 $\mu\text{g m}^{-3}$ in the rural atmosphere (Chenlou village) and from 267 to 524 $\mu\text{g m}^{-3}$ in the urban atmosphere (meteorological tower) (Table 3). Comparison of impactor results between locations is not possible due to nonconcurrent sampling. However, for all samples collected during the winter intensive, the urban atmospheric particles concentration measured by the impactor was significantly elevated relative to the rural samples ($0.387 \pm 0.09 \text{ mg m}^{-3}$ urban, $n = 6$; $0.218 \pm 0.03 \text{ mg m}^{-3}$ rural, $n = 6$; average \pm standard error). The comparison showed that there were more particle sources in urban atmosphere, indicating that the particle pollution and respiration exposure risk in urban atmosphere was more severe. Offenbergl and Baker (1999) have reported the elevated particles concentrations in Chicago urban atmosphere (average 27.7 $\mu\text{g m}^{-3}$ for TSP) relative to over lake Michigan (average 17.4 $\mu\text{g m}^{-3}$ for TSP) and rural samples (average 20.8 $\mu\text{g m}^{-3}$ for TSP). In addition, these ranges are higher than 119–216 $\mu\text{g m}^{-3}$ obtained for Mumbai (urban) in winter by Venkata-

raman et al. (1999) and 72–278 $\mu\text{g m}^{-3}$ obtained for Taiwan (traffic site) in summer by Chang et al. (2001).

The particle concentration in Chenlou (Table 3) was not significantly influenced by two rain washouts (Table 1) due to the long period sampling. The particles washed by rain were counterbalanced by later accumulation and new input of particles under the stable atmosphere. Fine differences between MMD (mass median diameter) of Chenlou samples are found (Table 3). The particle concentration of sample A28 (at the height of 20 m) was much higher than A29 (40 m) and A30 (60 m) partly due to the short sampling time of A28 (only 21 h). It can be seen from Table 3 that the particle concentration at 40 m height was higher than that of 20 and 60 m except the first sampling at the height of 20 m (A28). The MMD of particle at 40 m height was also the greatest among the three levels samplings. The fact that the boiler chimneys near the sampling site can be the main reason for the concentration difference at different levels. Wu et al. (2003) collected PM₁₀, PM_{2.5} and PM_{1.0} at different height (79, 59, 30, 19, 8 and 2 m) of the buildings near the traffic road in Macao and found the particles concentrations decreased with the increasing of height, and coarse particles concentrations decreased more quickly than those of fine particles. The absence of elevated emission, such as the chimney of boiler, can be used to explain the differences between Wu et al. (2003) and our results. As also can be seen from Table 2, the particle concentration at 40 and 60 m during the first urban sampling was lower than the corresponding concentration of the second sampling. This can be partly explained by the temperature, wind speed and wind direction difference between two sampling periods (Table 1 and Figs. 2, 3). The mean wind speed and temperature profiles during the second sampling period were lower than those of the first sampling indicating that the potential dispersion abilities of particles under low wind speed decreased and more

Table 3
Concentrations (ng m^{-3}) and MMD (μm) of particles and total PAH in rural and urban sites of Tianjin in winter

Chenlou				Meteorological tower					
Sample no.	Particle		Total PAH		Sample no.	Particle		Total PAH	
	Conc. ^a	MMD ^b	Conc. ^c	MMD		Conc.	MMD	Conc.	MMD
A22	235	1.88	144	1.11	A28	524	1.78	265	0.80
A23					A29	337	2.06	333	0.93
A24	238	1.85	287	0.9	A30	267	1.82	239	0.94
A25					A31	376	1.81	409	0.89
A26	182	1.84	308	0.87	A32	449	1.98	537	1.15
A27					A33	368	1.90	359	1.18

^a Concentration of particles of 0–10 μm collected with an FA-3 cascade impactor.

^b Mass median diameter.

^c Sum of 16 PAH compounds in the particles collected.

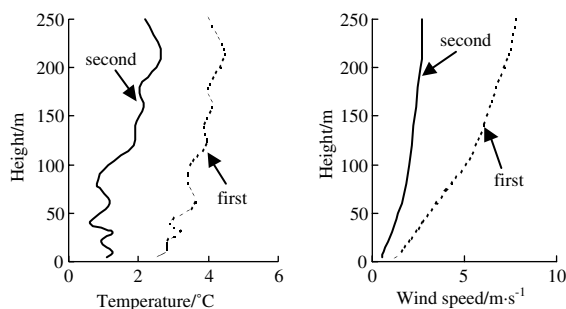


Fig. 2. Mean temperature and wind speed profiles during the two times of urban sampling.

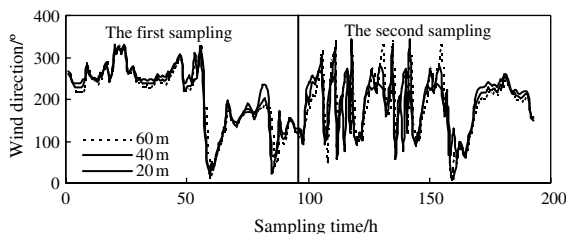


Fig. 3. Wind direction during the two times of urban sampling.

particles and soot would emit into the atmosphere followed more coal combustion for domestic heating. In addition, the wind directions during different sampling interval were different too (Fig. 3), and more particles might be transported to the station atmosphere during the second sampling interval for the wind directions were more fluctuant.

The average size distributions of particles collected from rural and urban atmosphere in Tianjin are shown in Fig. 4. The low limit of $0.1 \mu\text{m}$ was selected based on the results of urban aerosol studies involving size-fractionation partitioning devices of $0.0\text{--}0.1 \mu\text{m}$ resolution (Whitby et al., 1972). As can be seen from Fig. 4, particles exhibited a trimodal distribution at both locations,

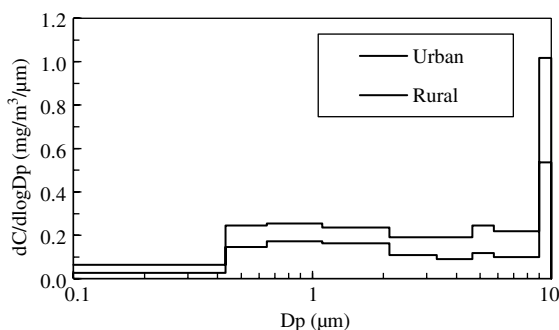


Fig. 4. Mean size distributions of particles collected at urban and rural site in Tianjin. dC = mass concentration of the certain particle-size interval, D_p = particle aerodynamic diameter.

with the major peaks occurred at $0.43\text{--}2.1$ and $9.0\text{--}10.0 \mu\text{m}$ for both urban and rural locations. This result indicated that the peak at a particle size $\leq 1.1 \mu\text{m}$ mainly came from young aerosol through gas-to-particle condensation processes, while the peak at $1.1\text{--}2.1 \mu\text{m}$ showed the occurrence of accumulation of aerosols (Lee et al., 1995). The size distribution also gives important information about the health affects of inhaled particles in rural and urban area of Tianjin. Particles with the diameter less than $3 \mu\text{m}$ will penetrate the upper respiration tract and settle at the site of bronchia and alveolus. From the data given in Table 3, almost all the MMDs of rural and urban particles were less than $2 \mu\text{m}$ suggesting that the particle pollution was severe. Fig. 4 also showed that the average concentrations of all particle-size intervals in rural atmosphere were lower than those in urban atmosphere. The similarity between urban and rural particle size distribution suggests that most airborne particles with aerodynamic diameter less than $10 \mu\text{m}$ come from similar sources (coal combustion, vehicular exhaust, and re-suspended particulate matter from paved roads and surfaces, and so on) and have attained a relative stable state under the local atmospheric environment conditions.

3.2. Total PAH concentrations

Total PAH (sum of 16 PAH compounds) concentrations associated with $D_p \leq 10 \mu\text{m}$ particles collected using FA-3 cascade impactor ranged from $144\text{--}308 \text{ ng m}^{-3}$ and $239\text{--}537 \text{ ng m}^{-3}$ for Chenlou and Meteorological tower sampling, respectively (Table 3). The total PAH at meteorological tower (urban) were about one or two order higher than those of Mumbai ($21\text{--}42 \text{ ng m}^{-3}$; Venkataraman et al., 1999) and Kuala Lumpur ($6.28 \pm 4.35 \text{ ng m}^{-3}$; Omar et al., 2002), and were close to the concentration of Inchon (410 ng m^{-3} ; Bae et al., 2002) in winter season. The average total PAH at Chenlou was also much higher than that of Yangsuri rural (119 ng m^{-3} ; Bae et al., 2002). The total PAH differences between Chenlou (rural) and meteorological tower (urban) were significant and similar results have been reported in Massachusetts (Allen et al., 1996), Kuala Lumpur (Omar et al., 2002), Birmingham (Smith and Harrison, 1996) and Korea (Bae et al., 2002) with the urban and rural total PAH were 49.5 , 6.28 , 4.37 , 410 and 1.94 , 1.3 , 1.13 , 119 ng m^{-3} , respectively.

Figs. 6 and 7 show the mean normalized size distribution ($dC/d\log D_p$ vs. $\log D_p$) of total PAH at rural and urban locations. As can be seen, total PAH exhibited analogously trimodal distributions for both sites with a major peak in $0.43\text{--}2.1 \mu\text{m}$ range, different from particle size distributions shown in Fig. 4. This finding is more consistent with Whitby's viewpoint that fine particles ($D_p < 2 \mu\text{m}$) were produced predominantly from gas to particle conversion and from incomplete combustion

whereas coarse particles ($D_p > 2 \mu\text{m}$) originate mostly from mechanical processes which were originally little contaminated (Whitby, 1978). The similar PAHs distributions have been reported in other studies (Sheu et al., 1997; Yang et al., 1999). The major peak contained on average 76.5% and 63.9% of $D_p \leq 10 \mu\text{m}$ particles for both rural and urban locations, respectively. The three peaks, in the range of 0.43–2.1, 4.7–5.8 and 9.0–10.0 μm , were almost consistent with the corresponding peaks of particle size distribution (Fig. 4), but significant differences of relative contribution were found in the range of 0.43–2.1 μm between particle and total PAH. This could result from the fact that the freshly produced particle-bound PAHs from combustion site had not reached equilibrium between particles of different size in the ambient air through short distance transport. PAHs were initially emitted in the gaseous and ultrafine particle phase and were primarily associated with fine particles. Then, PAHs can evaporate or desorb from fine particles and migrate to large particles with increasing time and distance. The size distribution differences between individual PAH compound will be discussed later.

As also can be seen from Fig. 5 and Table 3, the total PAH concentration of the first rural sampling was significant lower than those of next two samplings though their size distributions were very similar. The fraction of

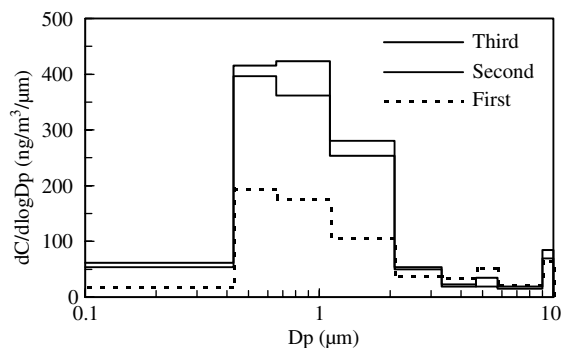


Fig. 5. Mean size distribution of total PAH in continuous three times rural (Chenlou) sampling.

total PAH contents in fine particles ($D_p \leq 2.1 \mu\text{m}$) to those of particles with $D_p \leq 10 \mu\text{m}$ was 69.8%, 86.5% and 84.5% for the three times of rural sampling, respectively. The high particle concentration did not correlate to high PAH concentration in three times sampling at Chenlou site (Table 3), which suggested that the collected airborne particles and particle-bound PAH came from different sources due to the variability of heating, cooking, rainwash, wind speed and direction during different sampling intervals.

Total PAH concentration at 40 m was higher than both of 20 and 60 m, indicating that there were more PAHs input to the atmosphere at the height of 40 m, such as from the boiler chimney emission, which were the main source of concomitants in airborne particles. The total PAH concentrations of the second urban sampling at different levels were all higher than those of the first sampling at the same height (Table 3). This can be partly explained from the differences of mean wind speed and temperature between two times of sampling (Table 1, Fig. 2). The PAH emission and accumulation in the urban atmosphere would increase followed by more domestic heating and less diffusion dilution. The correlation between particles and total PAH concentration was significant ($r^2 = 0.9698$, $n = 5$) for urban sampling at different levels excluding the sample A28 indicating that PAH-containing aerosols came from similar sources, such as soot, vehicle exhausts and re-suspension of fall-out (Rogge et al., 1993). Significant distribution differences between the different levels within the fine particle size range ($D_p \leq 2.1 \mu\text{m}$) have been detected indicating that the particulate PAH may have come from different sources or experienced different transportation route. The concentrations of total PAH associated with particles of $D_p \leq 1.1 \mu\text{m}$ decreased steadily with increasing height in two cases (Fig. 6). However, the MMD of total PAH monotonously increased with the increasing of height for both samplings (Table 3). The plausible explanation for the variation of concentration and MMD with height is that more fresh PAH-containing aerosols (such as vehicle exhausts) entered into 20 m high atmosphere, which was close to vehicle

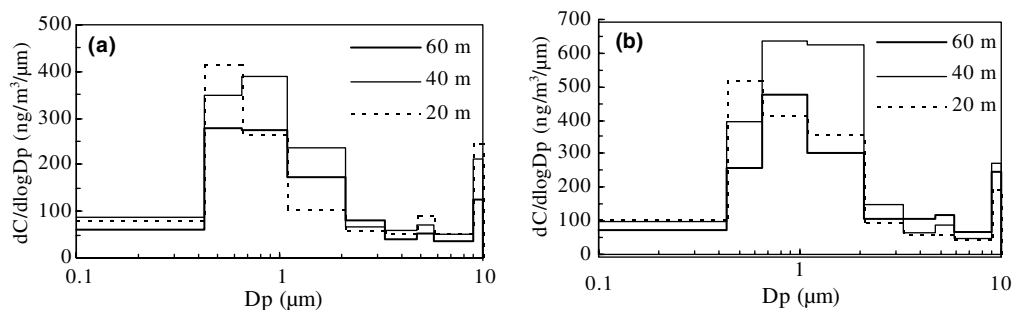


Fig. 6. Size distribution of total PAH at different levels in urban area: (a) the first urban sampling and (b) the second urban sampling.

sources mainly consisting of fine particles (Kerminen et al., 1997; Ristovski et al., 1998). The difference of PAH source and redistribution of PAH between gas phase and particle or different size particles determined the state of total PAH size distribution at the time of monitoring. Some researches have pointed out that the peak of particle size distribution of PAHs localized at a particles size $<1.0 \mu\text{m}$ essentially reflects the gas-to-particle condensation process in the young aerosols (Sheu et al., 1997; Yang et al., 1999).

3.3. Particle size distributions of individual PAHs

The distribution of PAHs concentrations on particles of different sizes are presented with normalized histogram approach ($dC/(Cd \log D_p)$ vs. $\log D_p$), which is a useful method for comparing the contributions of coarse and fine particles to pollutant concentrations (Vaeck and Cauwenberghe, 1985; Venkataraman et al., 1994, 1999; Allen et al., 1996; Oh et al., 2002). The mean normalized distributions of individual PAHs with particle size for rural and urban sites are presented in Figs. 7 and 8. There were no significant differences of particle size distribution between rural and urban samples for the same PAH compound. But distinct differences were observed for different PAH compounds for both rural and urban samples. Low molecular weight PAH (including NAP, ACPY, ACP, FLU, PHE, and ANT in this study) exhibit a multimode distribution, the major peaks are in the accumulation and coarse mode size range

($0.43\text{--}2.1$, $4.7\text{--}5.8$, and $9.0\text{--}10.0 \mu\text{m}$). The mid- and higher-molecular weight PAHs (include FLUA, PYR, BaA, CHR, BbF, BkF, BaP, INcdP, DBA, and BghiP in this study) are almost distributed in the accumulation mode size range ($0.43\text{--}2.1 \mu\text{m}$). Additional very minor peaks in the coarse mode at the size range of $9.0 \leq D_p \leq 10.0 \mu\text{m}$ are suggested by the data. As also can be seen from Figs. 7 and 8, PAH compounds with the same molecular weight have almost identical distributions with particle size (Venkataraman and Friedlander, 1994). The fact that higher molecular weight PAHs were adsorbed to the fine particles while more volatile PAHs were associated with larger particles have been reported by many studies (Venkataraman and Friedlander, 1994; Venkataraman et al., 1994, 1999; Allen et al., 1996; Offenberg and Baker, 1999; Kaupp and McLachlan, 2000).

There are several possible mechanisms to explain PAHs redistribution behavior. The distributions of lower molecular weight PAH in larger particles could result from differences in emission size distributions of these species or different gas-particles partitioning behavior (Venkataraman et al., 1999). PAH are mainly generated by combustion sources and emitted in the gas phase or associated with ultrafine particles, and then become associated with coarse particles by volatilization and condensation. Higher molecular weight PAHs, which have much lower subcooled liquid vapor pressures and Henry constant (US EPA, 1988), are expected to require much long times to partition to

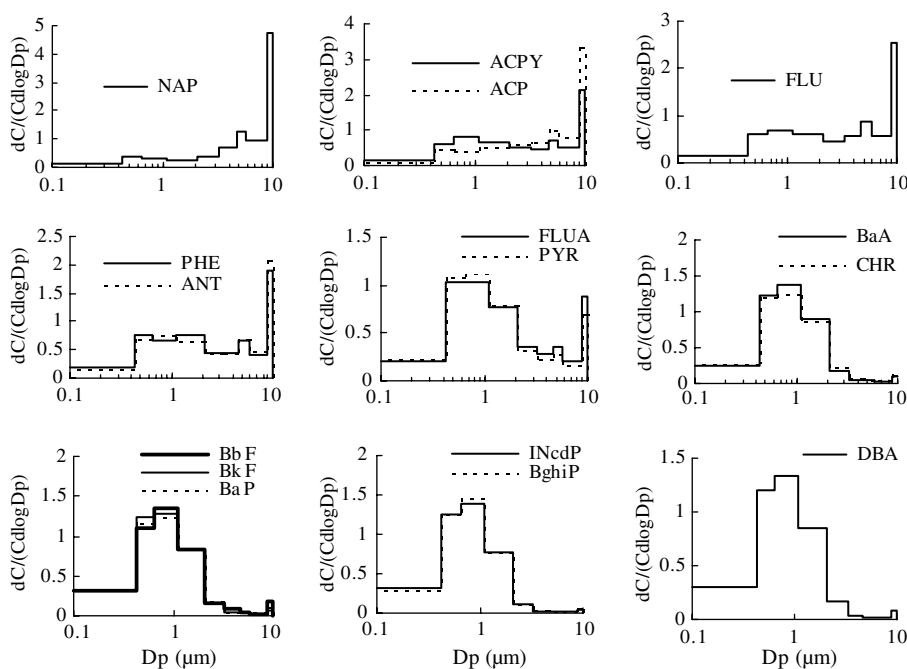


Fig. 7. Mean size distribution of individual PAHs in the meteorological tower samples.

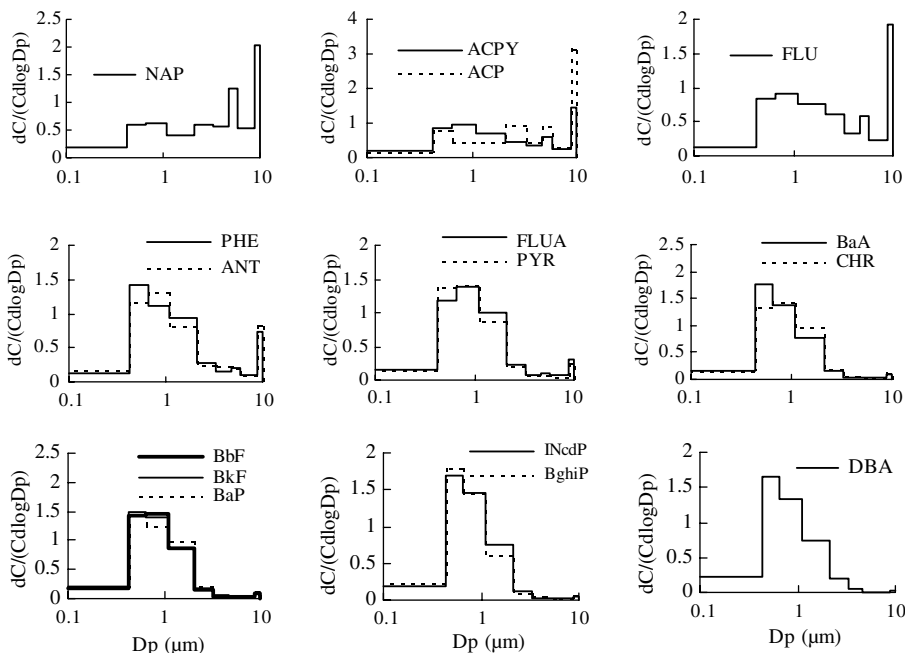


Fig. 8. Mean size distribution of individual PAH in the Chenlou samples.

coarse particles than lower molecular weight PAH and tend to remain in the fine particles (Allen et al., 1996). Allen (1997) calculated that the times to repartition between fine and coarse particles are on the order of months for very low vapor pressure PAH. As for coarse particles, the atmospheric residence times are short and, therefore, the time available for the equilibration with the atmospheric gas phase is limited. In addition, chemical affinities between PAHs and different size particles, different emission sources and different PAHs reactivity on photooxidation have also been used to explain the differences of PAH distribution with respect to particle size (Venkataraman and Friedlander, 1994; Allen et al., 1996; Venkataraman et al., 1999). Moreover, it should be mentioned that fine particles might coagulate each other and became into coarse particles. If the main mechanism for PAHs associated with coarse particles was only through coagula-

tion of particles, the PAHs profiles in fine and coarse particles would be similar. Allen et al. (1996) have explained that the hypothesis was not true. Similar results were found in this study. Fig. 9 demonstrates that the fraction of PAH associated with coarse particles ($D_p > 2.1 \mu\text{m}$) monotonically decrease as molecular weight increase from 128 to 278 for both rural and urban samples. The more volatile PAHs volatilized more rapidly from the fine particles and sorbed to the coarse particles than the involatile PAHs. The distribution differences indicated that higher molecular weight PAHs did not attain an equilibrium distribution among different particles we sampled. Particles would grow to the equilibrium size for a relative humidity (RH) of 99% (Slinn and Slinn, 1980). In this study, the data of mean RH are below 66% with a small variation (Table 3) and the effects of RH on the size distribution of PAHs would be ignored (Tsai et al., 2004).

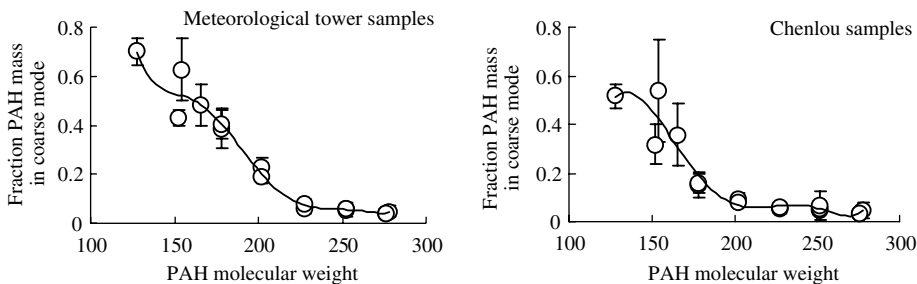


Fig. 9. Fraction of PAH associated with coarse particles ($D_p > 2.1 \mu\text{m}$) in the meteorological tower and Chenlou samples.

4. Summary

In this study, we find samples collected from the rural site had lower PAHs contents with respect to those collected from urban site in winter. Precipitation, wind speed, temperature were the major factors influenced the PAHs concentrations associated with particles. No significant differences of PAHs size distribution were observed between rural and urban samples indicating somewhat similar sources. But significant concentration differences of PAHs were found at different level in urban atmosphere due to the differences of sources and transportation path. The highest concentrations of PAHs at the height of 40 m indicate that emission from coal combustion boiler chimney contribute more PAHs in atmospheric particles. The MMD of total PAH increased with the increasing of height suggesting that vehicular emission contribute more fine particle-bound PAHs in low atmosphere than higher atmosphere. Different gas-particle partitioning behavior of lower and higher molecular weight PAHs could be the main factor that influences the distribution of PAHs with respect to different size particles.

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