Characterization and Source Identification of PM$_{10}$-bound Polycyclic Aromatic Hydrocarbons in Urban Air of Tianjin, China

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ABSTRACT

PM$_{10}$ samples were collected at six sampling sites in city center of Tianjin from April 2008 to January 2009. The concentrations of 17 selected polycyclic aromatic hydrocarbons (PAHs) in PM$_{10}$ were quantified. Spatial and seasonal variations of PAHs were characterized. The dominant PAHs in PM$_{10}$ samples were fluoranthene, pyrene, benz[a] anthracene, phenanthrene, chrysene, benzo[b]fluoranthene, anthracene, indeno[1,2,3-cd]pyrene and benzo[a]pyrene, accounting for above 85% of total PAHs. The total PAHs concentrations of the six sampling sites ranged from 23.4 to 513 ng/m^3. Spatial variations were predominantly due to the different strengths of source emission. The total PAHs concentrations at Dongli Monitoring Station (DL) site and Beichen Science and Technology Park (BC) site were higher than those at other four sites in heating period, while those at Meijiang community (MJ) site and Beichen Science and Technology Park (BC) site were higher in no-heating period. Higher PAHs concentrations during heating period and lower concentrations during no-heating period were observed at the six sampling sites, which may be caused by the stronger emissions from stationary combustion sources in heating period and the quicker air dispersion, washout effects, photo-degradation and higher percentage in the air in vapor phase in no-heating period. The PAHs concentrations in gaseous phase were predicted with gas/particle partition model, and the BaP and BaP equivalency results indicated that the health risk of gas and particle phase PAHs to human in Tianjin were higher than that in other cities. The contributions from potential sources to PAHs in PM$_{10}$ were estimated by the diagnostic ratios between PAHs and principal component analysis (PCA). In whole sampling period, coal combustion was found to the predominant contributor of PM$_{10}$-bound PAHs, followed by vehicles emission and wood combustion.

Keywords: PAHs; PM$_{10}$; Diagnostic ratios; PCA; Sources.

INTRODUCTION

PAHs are ubiquitous constituents on particulate matter that mainly originate from incomplete combustion of organic matter such as petroleum and coal (Khalili *et al.*, 1995; Guo *et al.*, 2003; Liu *et al.*, 2009). In urban ambient air, PAHs are almost entirely emitted from anthropogenic sources (Jones *et al.*, 1989; Caricchia *et al.*, 1999; Mantis *et al.*, 2005). PAHs are usually adsorbed on particulate matter (Chen *et al.*, 2005; Ravindra *et al.*, 2006; Zhang *et al.*, 2007; Liu *et al.*, 2009) and can be easily inhaled into the residents' lung as particular matter. Most PAH are carcinogenic and mutagenic to human and causes serious damage to human health. Although PAHs in ambient air

have been studied for a long time in other cities (Jones *et al.*, 1989; Furuuchi *et al.*, 2007; Wang *et al.*, 2007; Tekasakul *et al.*, 2008), few studies had been conducted in Tianjin city which is an important industrial city in China and about 30 millions tons of coal and petroleum were consumed annually. It was found that TSP bound PAHs mainly came from coal combustion in Tianjin in winter (Wu *et al.*, 2007). With the rapid urbanization, the consumption of petroleum and coal has grown considerably in Tianjin. The air pollution from particulate matter becomes gradually serious in Tianjin. Therefore, it is utmost necessary to investigate the abundance, speciation, distributions and potential sources of PAHs in aerosols to control the PAHs pollution in Tianjin.

In this study we present the spatial and temporal variation PM$_{10}$-bound PAHs in urban area of Tianjin. The possible sources of PM$_{10}$-bound PAH in Tianjin are also discussed based on the diagnostic ratios and the principal component analysis (PCA).

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MATERIALS AND METHODS

Sampling Sites

Tianjin is a typical metropolitan in of China with a population of approximately 10 million in 11,919 km². It is located in the north of China, on the lower reaches of the Haihe River and is adjacent to the Bohai Sea. It has distinct seasons with the annual mean temperature of 13.1°C, and the average rainfall of 500–700 mm. It is an important industrial center and a well-developed hub.

In Tianjin, winter includes the 4 months of 15 November to 15 March while summer is from 15 June to 15 August. Strong monsoon wind and dry/cold weather characterize winter seasons, whereas hot and humid climate with showers and thunderstorms represent summer seasons. Spring and autumn are warmly and windy.

Six sites were chosen as the sampling sites according to their different function in the city. The field descriptions were given as follows and the locations of the sites are shown in Fig. 1.

Beichen Science and Technology Park (BC) was chosen as a typical industrial/residential site. It is situated at about 8 m above ground level, and about 20 m away from a main road. Near this site, there are many cement, chemical and pharmaceutical industries. The site is adjacent to belt highway, which has a traffic volume of over 30,000 vehicles/day with a high proportion of diesel and heavy duty vehicles.

Daoxiangcun Community (DXC) was chosen as a typical commercial site: It is situated on the rooftop of the Teaching Building in Huiwen Campus, which is 25 m above the ground level. It is close to a downtown business center with many shops and restaurants. The traffic volume of the road is about 100,000 vehicles/day.

Hexi Monitoring Station (HX) was chosen as a residential site: No significant source of industry emission existed at this area. This site is close to the residential buildings.

Tianjin Monitoring Center (SZ) was chosen as a cultural site. It is situated on the rooftop of the office building in monitoring station, which is 25 m above the ground level, and about 100 m away from Nankai University. As HX site, there are not significant sources of industry emission at this area.

Meijiang Community (MJ) was chosen as a typical site in industrial/residential area: It is situated at about 6 m above ground level, and about 30 m away from the main road, Youyi Road. Many industries exist at this area.

Dongli Monitoring Station (DL) was chosen as a typical site in industrial area: A large of power plant, steel, chemical and printing industries are located in this area. They are far from the residential buildings and most of the vehicles are heavy duty ones. DL site is situated on the rooftop of the office building in Dongli Monitoring Station, which is 20 m above the ground level.

In winter, there are large amount of coal combustion boilers for domestic heating around all the six sites.

Sampling Processes

Ambient PM_{10} samples of 20 days were collected from April 2008 to January 2009. To study the seasonal variation, the samples of 5 days were collected for each season. Samples were collected simultaneously at five sites for 24 h everyday from 9:00 a.m. to next day 9:00 a.m. During the sampling period, a standard medium-volume PM_{10} samplers was employed at a flow rate of 100 L/min. Airborne particles were collected on 90 mm-diameter quartz-fiber filters (Pall Life Sciences, USA), which had been annealed at 450°C for 4.5 h to remove any organic materials. The filters were stored in a desiccator at 25°C and 45% relative humidity for 24 h before and after sampling, then weighted and stored in a freezer at –15°C packed in aluminum foil till extraction and analysis. All filters were extracted within 2 weeks after sampling. Table 1 lists the detailed sampling time and weather conditions at the six sampling sites.
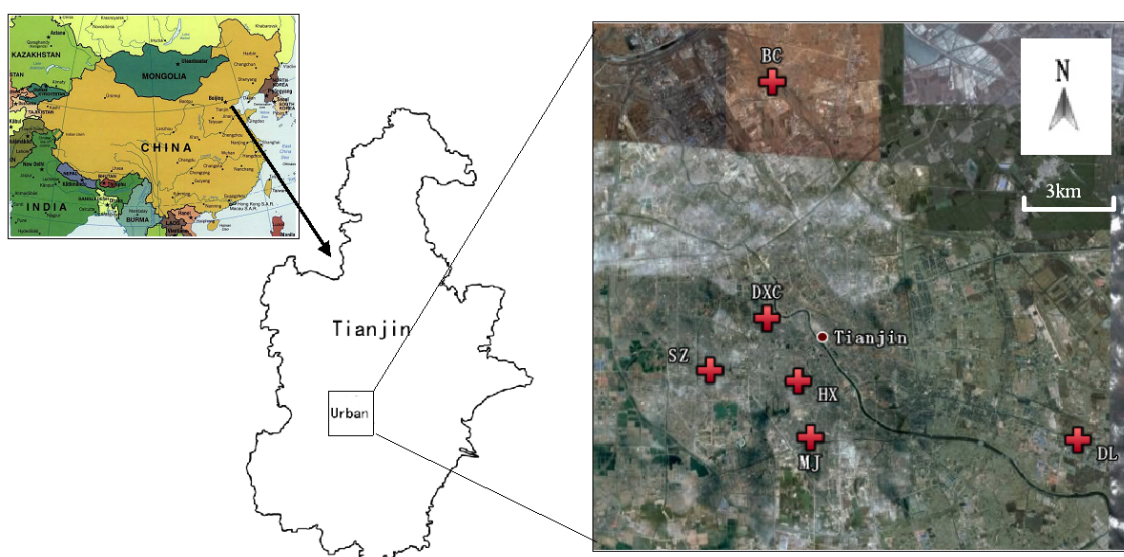

Fig. 1. Location map of the sampling sites in Tianjin.

Table 1. Sampling time and weather conditions at six sampling sites in Tianjin.

Season	Sampling time	Sampling sites						Weather	Wind direction	Mean air temp (°C)
		DXC	HX	BC	SZ	MJ	DL			
Spring	4/25/2008−4/26/2008, (24h)	Y	Y	Y	Y	Y	N	Light rain	SW, Windy	14.7
	4/26/2008−4/27/2008, (24h)	Y	Y	Y	Y	Y	N	Clear	W, Windy	15.3
	4/27/2008−4/28/2008, (24h)	Y	Y	Y	Y	Y	N	Clear	SW, Windy	15.6
	4/28/2008−4/29/2008, (24h)	Y	Y	Y	Y	Y	N	Clear	SW, Windy	15.8
	4/29/2008−4/30/2008, (24h)	Y	Y	Y	Y	Y	N	Clear	SW, Windy	15.4
Summer	7/21/2008−7/22/2008, (24h)	Y	N	Y	Y	Y	Y	Light rain	Calm	28.5
	7/22/2008−7/23/2008, (24h)	Y	N	Y	Y	Y	Y	Clear	Breezy	29.8
	7/23/2008−7/24/2008, (24h)	Y	N	Y	Y	Y	Y	Clear	Breezy	29.2
	7/24/2008−7/25/2008, (24h)	Y	N	Y	Y	Y	Y	Cloudy	NE, Windy	27.7
	7/25/2008−7/26/2008, (24h)	Y	N	Y	Y	Y	Y	Cloudy	NE, Windy	27.2
Autumn	10/9/2008−10/10/2008, (24h)	Y	N	Y	Y	Y	Y	Clear	Breezy	17.1
	10/10/2008−10/11/2008, (24h)	Y	N	Y	Y	Y	Y	Clear	N, Windy	18.3
	10/11/2008−10/12/2008, (24h)	Y	N	Y	Y	Y	Y	Cloudy	Breezy	17.4
	10/12/2008−10/13/2008, (24h)	Y	N	Y	Y	Y	Y	Clear	Breezy	17.6
	10/13/2008−10/14/2008, (24h)	Y	N	Y	Y	Y	Y	Cloudy	Breezy	17.4
Winter	1/7/2009−1/8/2009, (24h)	Y	Y	Y	Y	N	Y	Cloudy	Breezy	−1.50
	1/8/2009−1/9/2009, (24h)	Y	Y	Y	Y	N	Y	Clear	N, Windy	−4.0
	1/9/2009−1/10/2009, (24h)	Y	Y	Y	Y	N	Y	Clear	N, Windy	−4.0
	1/10/2009−1/11/2009, (24h)	Y	Y	Y	Y	N	Y	Clear	NW, Windy	−3.4
	1/11/2009−1/12/2009, (24h)	Y	Y	Y	Y	N	Y	Clear	NW, Windy	−4.0

Y: Sampling; N: No sampling

PAHs Analysis

The sampled filters were extracted ultrasonically with dichloromethane, concentrated by a rotary evaporator, purified with a silica gel cleanup technique, re-concentrated using rotary evaporator and finally condensed to exact 1 mL by a gentle nitrogen stream in 60°C water bath. The extracts were transferred into two ampoule bottles and stored in refrigerator until GC/MS analysis. The method of GC/MS analysis was according to the Method TO-13A (USEPA, 1999). For each sample, the procedures of sampling, pretreatment, and analysis had been completed within one month.

A gas chromatography coupled to mass spectrometry (trace 2000 GC–MS, Thermo Finnigan, USA) was used for determining PAHs with selected ion monitoring (SIM). A fused-silica DB-5MS capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). Helium was used as the carrier gas at a constant flow of 1.0 mL/min. A 1μl of solution was injected by applying a hot splitless injection technique at 280°C. The temperature program of the oven was started at 70°C (held for 2 min) and increased at a rate of 10 °C/min to 260°C (held for 8 min) and then increased at a rate of 5 °C/min to 300°C (held for 5 min). The mass spectrometry was operated in the electronic impact (EI) mode with an ion source temperature of 250°C and the electron impact energy was set at 70 eV.

Identification of the PAHs compounds using GC-MS was based on a combination of retention times and relative abundances of selected ions. Quantification of individual compounds was based on the comparison of peak areas with those of the internal standards (Cao *et al.*, 2005). In this study the 17 PAHs were analyzed including naphthalene (NaP), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (FLu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DBA), benzo[ghi]perylene (BghiP) and Coronene (COR).

Quality Control

Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were analyzed. PAHs were not detectable. Other contaminants did not interfere with the recognition or quantification of the compounds of interest. The average recoveries of the 17 PAHs from the standard mixture varied from 77% to 109% for PM_{10} samples. The other quality control descriptions on this study are in publications by Han *et al.* (2009).

RESULTS AND DISCUSSION

Concentration Level of PM_{10}-bound PAHs

Concentrations of PM_{10}-bound PAHs for six sampling sites are presented in Table 2. The total PAHs concentration of the six sampling sites ranged from 23.4 to 513 ng/m³, and was relatively higher in autumn and winter. The dominant PAHs in PM_{10} were FL, Pyr, BaA, PA, CHR, BbF, Ant, IND and BaP, accounting for above 85% of total PAHs. The highest concentration of total PAHs in PM_{10}

Table 2. Mean PAH concentrations (ng/m^3) in PM$_{10}$ at six sampling sites in Tianjin city during 2008–2009 (n = 5).

PAHs	Spring (April)					Summer (July)					Autumn (October)					Winter (January)				
	DXC	HX	BC	SZ	MJ	DXC	DL	BC	SZ	MJ	DXC	DL	BC	SZ	MJ	DXC	DL	BC	SZ	HX
Nap	0.42	0.29	0.57	0.29	0.16	0.11	N.D	N.D	0.16	N.D	0.07	0.11	0.15	0.08	0.10	0.49	0.30	0.50	0.70	0.79
AcPy	N.D	N.D	N.D	N.D	0.10	0.03	N.D	N.D	N.D	N.D	N.D	N.D	0.07	0.08	N.D	1.66	2.97	2.97	1.56	1.36
Acp	N.D	N.D	N.D	N.D	0.09	0.03	N.D	N.D	N.D	N.D	N.D	N.D	0.08	N.D	N.D	0.96	1.45	1.72	0.86	0.90
Flu	0.33	0.28	0.29	0.35	0.20	0.14	N.D	0.04	0.16	0.23	0.06	0.05	0.08	0.13	0.22	2.26	4.55	4.08	2.10	2.24
PA	2.64	2.09	2.37	2.33	1.84	1.39	1.20	1.27	1.13	1.48	1.06	0.93	1.34	1.29	2.00	28.8	59.0	56.3	27.1	28.5
Ant	2.92	2.44	2.72	2.57	3.23	1.74	1.34	1.32	1.26	1.67	1.26	1.14	1.86	1.66	2.79	29.9	27.1	22.8	24.9	29.2
FL	3.14	2.66	3.42	2.93	3.77	1.91	1.33	1.82	1.37	1.53	2.13	2.08	3.02	3.54	5.65	49.0	109	98.7	43.2	42.8
Pyr	2.31	2.04	2.71	1.48	3.68	1.60	1.28	1.58	1.09	1.24	1.77	1.90	2.76	3.21	4.80	40.0	102	86.1	34.4	34.3
BaA	7.62	4.41	5.88	4.69	6.15	3.83	4.81	7.27	4.15	2.64	5.51	3.67	4.24	9.76	15.4	20.0	42.7	33.8	17.4	20.3
CHR	3.41	3.11	2.78	2.36	3.64	2.16	2.06	3.18	2.09	1.76	4.07	3.75	5.69	5.39	8.65	20.0	42.6	33.7	17.5	20.2
BbF	3.12	5.38	4.12	3.46	12.7	9.68	6.55	10.9	7.31	4.50	9.79	8.22	13.1	6.84	17.1	7.14	11.0	12.3	6.62	6.54
BkF	3.09	2.88	2.82	2.06	5.83	4.45	4.21	6.01	3.72	2.70	4.74	3.97	5.76	3.14	4.60	4.75	7.40	8.2	4.48	4.40
BaP	2.24	1.76	2.22	1.60	4.02	3.26	3.24	3.53	2.83	1.81	2.62	3.09	4.99	4.23	6.52	14.03	32.4	27.8	13.1	13.3
IND	2.63	1.58	4.65	2.45	2.39	3.15	3.86	5.13	2.99	2.38	6.09	5.35	11.82	5.62	13.5	10.76	27.9	19.3	12.0	16.1
DBA	N.D	0.06	0.13	0.04	1.72	0.36	N.D	0.28	0.11	N.D	0.36	0.29	0.37	0.52	0.69	1.79	5.34	3.33	1.96	1.83
BghiP	1.81	1.52	2.17	1.09	1.45	1.92	3.25	3.95	1.52	0.84	3.14	3.25	5.02	3.99	5.89	11.8	25.9	20.9	11.8	12.1
COR	0.82	0.43	0.29	0.32	2.33	0.78	1.22	1.38	0.22	0.65	1.46	1.54	2.34	2.40	2.76	4.68	11.7	8.95	5.54	4.97
∑PAH	36.5	30.9	37.1	28.0	53.3	36.5	34.4	47.6	30.1	23.4	44.1	39.3	62.6	51.9	90.6	248	513	441	225	240

N.D: non-detectable

was found at DL site in winter. DL site is located in a heavy industries area and surrounded by Jing Tang Highway and belt highway of Tianjin. The high emission from the industrial and heating coal-fired boilers in winter and vehicular exhaust from highway may be responsible for the highest level of PAHs in DL site. The lowest concentration detected was at SZ site in summer, which is located in culture area without significant source strength. Average concentration of individual PAHs in the whole sampling time varied from 0.26 (NaP) to 19.2 (Fl) ng/m^3 (Table 3), and as tracers for coal combustion (Khalili *et al.*, 1995), the concentrations of FL, Pyr, BaA and CHR are significant high, which indicates coal combustion is an important source of PAHs emission in Tianjin.

Compared with the published data in other cities (Table 3), the most PAHs concentrations in Tianjin are lower than those in Tangshan city with dense steel and coke industries, are comparable to those reported in Beijing and Nanjing, but are significantly higher than those in Hong Kong, Naples and Athens. The higher PAHs levels in Tianjin are likely attributed to the combination of huge coal consumption and dense heavy traffic.

Distribution of PAHs in Different Rings

Examined PAHs could be classified according to their number of aromatic rings as follows: 2-ring including Nap; 3-ring including Acpy, Acp, Flu, PA and Ant; 4-ring including FL, Pyr, BaA and CHR; 5-ring including BbF, BkF and BaP, 6-rings including IND, DBA, and BghiP; 7-rings including COR. They can be further classified into lower molecular weight (LMW, 2- and 3-rings PAHs), middle molecular weight (MMW, 4-rings PAHs), and higher molecular weight (HMW, 5-, 6- and 7-rings PAHs).

LMW PAHs can be tracers for wood combustion (Khalili *et al.*, 1995) or industrial combustion of oil (Park *et al.*, 2002). MMW PAHs such as FL, Pyr, BaA and CHR are usually associated with coal combustion and can be identified from this source (Khalili *et al.*, 1995). HMW PAHs such as BbF, BkF, BghiP, IND, and COR may be associated with vehicles emission, and can be regards as tracers for this source (Miguel and Pereira, 1989; Li and Kamens, 1993; Venkataraman and Friedlander, 1994; Marr *et al.*, 1999).

Fig. 2 shows ring number distribution of PAHs for PM$_{10}$ in Tianjin in spring, summer, autumn, and winter. The concentration proportion of LMW, MMW and HMW PAHs were 1:5:2 in spring, 1:5:5 in summer, 1:10:10 in autumn and 1:3.3:1 in winter, respectively. HMW PAHs were found to be abundant in summer and autumn, reflecting the strong contribution from vehicles emission, while MMW PAHs in PM$_{10}$ had higher concentrations in winter than other seasons, owing to the higher emission from coal combustion sources. Additionally, MMW PAHs are semi-volatile organic compounds and distribute higher in particle phase when air temperature is low. LMW PAHs were the relatively abundant in winter, which may be caused by wood combustion for domestic cooking or heating. Therefore, the concentration proportion variation of LMW, MMW and HMW PAHs in different seasons can be used to reflect the variation in the categories of PAHs sources in these seasons.
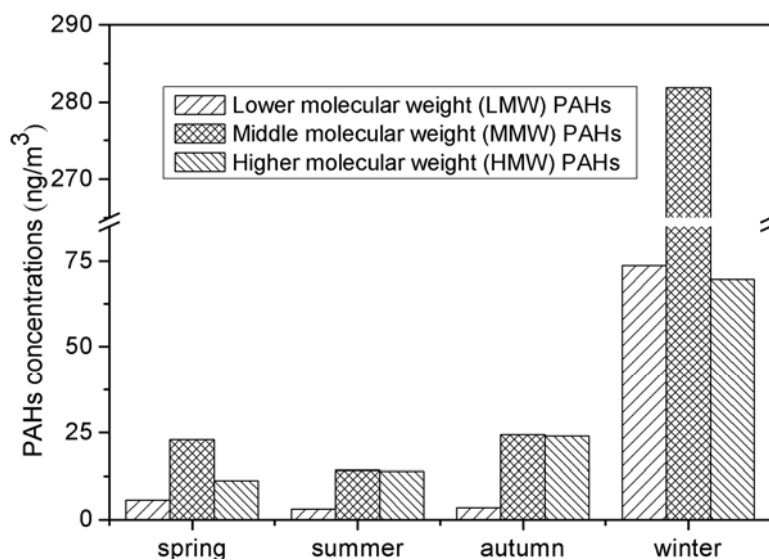
Seasonal and Spatial Variations of PAHs in PM$_{10}$

The year was divided in two periods, heating period (H, 15 November–31 March) and no-heating period (NH, 1 April–14 November). In Tianjin, there is very significant

Table 3. Comparison of average PAH concentrations in PM_{10} with other cities (ng/m^3).

	Tianjin (this study)	Tangshan (Shi *et al.*, 2009)	Beijing (Okuda, 2006)	Nanjing (Wang *et al.*, 2006)	Hong Kong (Guo *et al.*, 2003)	Naples (Caricchia *et al.*, 1999)	Athens (Mantis *et al.*, 2005)
Nap	0.26	N.A	N.A	N.A	N.A	N.A	N.A
AcPy	0.54	N.A	N.A	3.05	N.A	N.A	N.A
Acp	0.30	N.A	N.A	2.12	N.A	N.A	N.A
Flu	0.89	N.A	N.A	1.79	0.19	N.A	N.A
PA	11.20	28.7	6.20	4.99	0.53	0.93	0.16
Ant	8.19	N.A	1.10	0.52	0.14	0.17	0.14
FL	19.2	14.0	28.1	8.11	4.50	2.18	0.16
Pyr	16.5	11.45	20.5	6.26	4.16	1.44	0.21
BaA	11.2	8.10	15.5	3.76	0.83	1.57	0.15
CHR	9.41	20.6	21.5	9.09	2.68	2.47	0.23
BbF	8.32	53.9[A]	25.0	11.4	1.72	5.68	0.55
BkF	4.46		6.7	8.20	8.08	N.A	0.22
BaP	7.43	15.0	10.9	5.75	0.35	2.21	0.37
IND	7.98	14.9	8.5	8.23	2.03	2.93	0.64
DBA	0.96	21.2	N.A	2.19	3.42	4.21	0.13
BghiP	6.17	22.2	11.9	10.5	5.61	5.78	0.99
COR	2.74	10.8	4.0	N.A	N.A	4.38	N.A
∑PAH	116	244	160	86.0	34.2	27.8	3.95

N.A: not available; A: BbF + BkF

Fig. 2. Ring number distribution of PAHs for PM_{10} in Tianjin.

seasonal variation in PAHs concentrations. The higher PAHs in winter were mainly due to the high emission from the coal combustion. Additionally, in winter the prevailing wind in Tianjin is northeasterly which brings highly polluted air masses from the mainland such as Beijing and Tangshan to the sampling sites. On the contrary, in summer, the Asian monsoon brings clean oceanic air to Tianjin. Thus, lower PAHs levels in summer were likely attributed to the combining effect of quick atmospheric dispersion of pollutants, wash-out effect of rain, more photo degradation and higher percentage in the air in vapor phase (Guo *et al.*, 2003).

Fig. 3 shows the mean PAH profiles (percent contribution of each PAH compound to ∑PAH) for the six sampling sites in Tianjin. During no-heating period IND, BkF, BbF, CHR and BaA were the most abundant compounds at all sampling sites, while during heating period Pyr, FL, PA, Ant and CHR were the most abundant compounds. This phenomenon revealed the importance of vehicular emissions as PAH sources in no-heating period and coal combustion as PAH sources in heating period, because the compounds IND, BkF, BbF, CHR and BaA were identified as vehicles emission and the compounds Pyr, FL, PA, Ant and CHR were abundant in coal combustion emission (Khalili *et al.*, 1995).
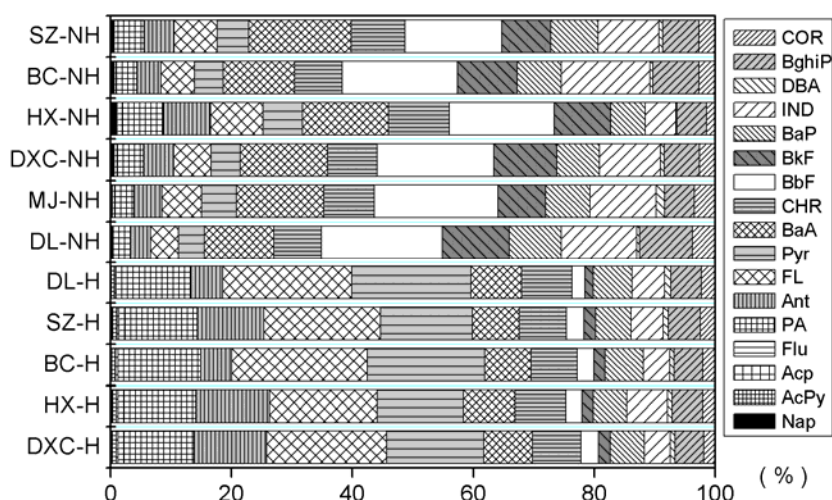
Fig. 3. Mean PAH profiles of ambient PM_{10} in the central urban of Tianjin.

A significant similarity was existed in the PAH profiles in both heating and no-heating period, which reveals the sources of PAHs around these sampling sites were extremely similar.

The seasonal and spatial variations of PAHs in PM_{10} in Tianjin are presented in Fig. 4. Higher PAHs concentrations in heating period and lower concentrations in no-heating period were observed at the six sampling sites. The ratio of heating period to no-heating period total PAHs was 5.0 at MJ site, 6.1 at SZ site, 6.3 at DXC site, 9.0 at BC site, and 13.9 at DL site, respectively. That phenomenon confirms that the coal combustion emission was an important source to PAHs in heating period since so many coal combustion boilers were used for house heating in Tianjin.

The total PAHs concentration at MJ and BC sites was higher than that at other four sites in no-heating period, and it was higher at DL and BC sites in heating period. However, the total PAHs concentration at DXC, SZ and HX sites was lower in whole sampling campaign. The major cause was the different surrounding of sampling sites. The BC site is adjacent to a road with high traffic volume. Moreover, many metal, chemical and pharmaceutical industries are located at this area. The DL sit is also located at an industrial area with high traffic volume. A large of coal-burning boiler emission may cause high PAH levels at the area in heating period. The MJ site was a mixture of residential/industrial area. The major sources of PAHs were household cooking activities, industrial sources and vehicle emissions at this site. The source strength of PAHs at this site was significantly higher than that at the other sites, because the traffic volume was very high and the sampling site was near the ground level. Since no significant emission sources were observed at DXC, SZ or HX sites, the PAH levels at these sites were lower.

Predicting the PAHs Concentrations in Gaseous Phases

PAHs exist in both the gas phase and particulate phase in the natural atmosphere. The distribution of PAHs between the gas and particulate phase is usually defined using the gas/particle partition coefficient, K_p ($m^3/\mu g$)

(Harner and Bidleman, 1998):

$$K_p = C_p / TSP / C_g \qquad (1)$$

where C_p and C_g are the PAHs concentrations in the particulate and gaseous phases, respectively (ng/m^3), and *TSP* is the concentration of total suspended particles in the air (mg/m^3). There is thus an incentive to calculate K_p as a function of the properties of the PAHs and the nature of the particulate material. Experimental partition data have been conventionally and successfully correlated by an equation of the form (Pankow and Bidleman, 1992; Simcik *et al.* 1998):

$$LogK_p = mLogp_L^0 + b \qquad (2)$$

where *m* and *b* are constants (the regression parameters) and $Logp_L^0$ is the subcooled liquid vapor pressure. The PAHs concentrations in gaseous phases (values of C_g) can be predicted by the Eq. (1) and (2). In this study, the values of *m* and *b* were the average value of literature data (Simcik *et al.*, 1998; Mandalakis *et al.*, 2002; Yeo *et al.*, 2003; He and Balasubramanian, 2009), and the parameter of $Logp_L^0$ were obtained from these literatures (Lei *et al.*, 2002; Finizio *et al.*, 1997; Odabasi *et al.*, 2006). The PAHs concentrations in the particulate (values of C_p) were calculated by the ratios of particle-bound PAH content in the different particle size ranges (Mi *et al.*, 1996; Sheu *et al.*, 1996, 1997; Yang *et al.*, 1998 and 1999; Tsai *et al.*, 2001). TSP concentrations were obtained by using the ratios of PM_{10} to TSP in Tianjin (Qin *et al.*, 2002).

The predicted results of C_g are shown in Table 4. The predicted annual average Cg were very high in LMW (Nap, Acpy, Acp, Flu, PA and Ant) and MMW (FL, Pyr, BaA and CHR) PAHs and low in HMW (BbF, BkF, BaP, IND, DBA, BghiP and COR) PAHs. This was because that LMW and MMW PAHs primarily existed in form of gas phase, but HMW PAHs were in particulate phase. The predicted C_g in heating period (C_g-H) were higher than that in no-heating period (C_g-NH).
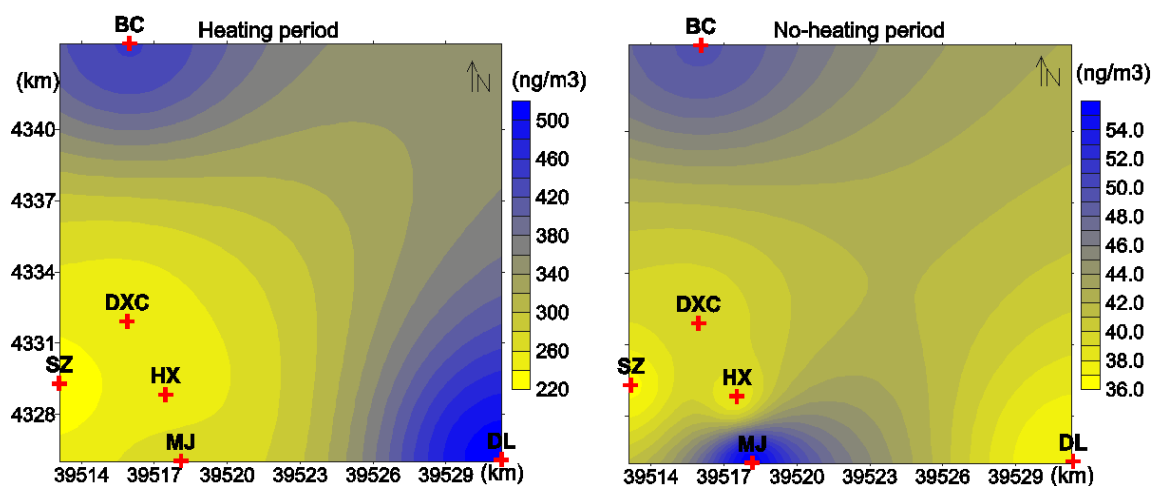
Fig. 4. Distribution of PAHs concentrations (ng/m³) in Tianjin.

Table 4. Parameters values of equations and predicted values of C_g.

PAHs	$LogP_L^0$	$LogK_p$	C_p-NH (ng/m³)	C_p-H (ng/m³)	Predicted C_g-NH (ng/m³)	Predicted C_g-H (ng/m³)	Predicted annual average C_g (ng/m³)
Nap	1.56	−5.26	0.20	0.62	94.7	296	196
AcPy	0.35	−4.56	0.04	2.68	3.69	254	129
Acp	0.17	−4.46	0.03	1.43	2.30	107	54.5
Flu	−0.31	−4.18	0.21	3.63	8.27	143	75.7
PA	−1.11	−3.72	1.85	44.9	25.0	606	315
Ant	−1.14	−3.70	2.43	32.5	31.3	419	225
FL	−2.21	−3.08	2.96	77.1	9.14	238	124
Pyr	−2.35	−3.00	2.36	64.3	6.07	165	85.7
BaA	−3.60	−2.27	6.47	30.3	3.14	14.7	8.92
CHR	−3.77	−2.17	4.23	32.3	1.63	12.5	7.06
BbF	−4.80	−1.58	8.80	9.81	0.86	0.96	0.91
BkF	−4.75	−1.61	4.56	6.87	0.48	0.72	0.60
BaP	−5.10	−1.40	3.55	23.5	0.23	1.55	0.89
IND	−5.97	−0.90	4.99	19.0	0.10	0.39	0.25
DBA	−6.14	−0.80	0.34	3.30	0.01	0.05	0.03
BghiP	−6.10	−0.82	3.26	20.6	0.06	0.35	0.21
COR	−7.61	0.05	1.48	9.01	0.00	0.02	0.01

Health Risk Assessment

In principle, the health risk assessment of PAHs can be assessed based on its BaP and BaP equivalent concentration (BaPeq). BaP is considered one of the most powerful mutagens and often used as a general indicator of PAHs and regarded by the World Health Organization (WHO) as a good index for whole PAH carcinogenicity. In this study, BaP was found in a majority of samples with the mean value of 3.04 ng/m³ in no-heating period and 20.1 ng/m³ in heating period which were extremely higher than those in Athens (0.37 ng/m³, Mantis *et al.*, 2005), Hong Kong (0.35 ng/m³, Guo *et al.*, 2003), Taiwan (2.16 ng/m³, Fang *et al.*, 2005) and Naples (2.21 ng/m³, Caricchia *et al.*, 1999). BaPeq represents the relative carcinogenic potency of the corresponding PAH, it can be calculated by multiplying its concentration with the corresponding toxic equivalent factor (Nisbet and LaGoy, 1992). In this study, to assess

the real health risk of PAHs for people in Tianjin, the sum of concentrations of gas and particle phase were calculated and applied. Both BaPeq and BaP results in Tianjin were shown in Fig. 5, it can be observed that they had shown the similar patterns of spatial distributions. In heating period, the highest BaPeq was found at DL sampling site with a value of 68.8 ng/m³, followed by BC, DXC, HX and SZ sites with values of 54.8, 32.4, 32.2 and 31.9 ng/m³, respectively. In no-heating period, the values of BaPeq were 10.9, 8.79, 7.19, 7.14, 7.06 and 4.92 ng/m³ for MJ, BC, SZ, DL, DXC and HX site, respectively. It was found that the levels of BaPeq were about 4.4–9.6 times higher in heating period than that in no-heating period. In addition, average concentration of BaPeq in the whole city during the sampling period was 7.67 ng/m³ in no-heating period and 44.0 ng/m³ in heating period, which was much higher than that in Taiwan (17.9 ng/m³, Fang, *et al.*, 2004),
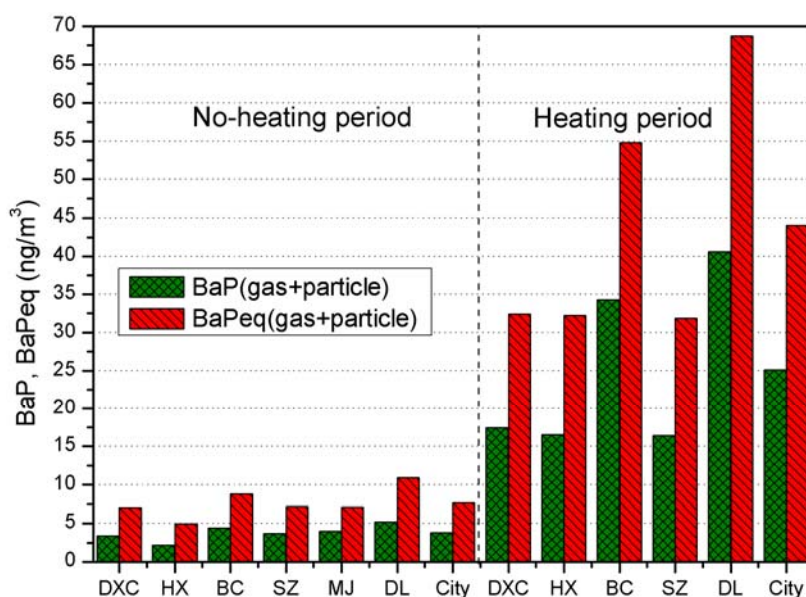
Fig. 5. BaP and BaPeq in the central urban of Tianjin , China.

Beijing (3.67 ng/m^3, Liu *et al*., 2007), London (1.83 ng/m^3, Baek *et al*., 1992) and Florence (0.92 ng/m^3, Lodovici *et al*., 2003).

The local population in Tianjin appears to be exposed to significantly higher cancer risk (exceeding 2.0 ng/m^3) as compared to the population in other cities. This suggests that atmospheric PAHs pollution has had a serious threat to the lives of people in Tianjin. The serious PAHs pollution in Tianjin may be attributed to dense heavy traffic and industries, especially large amount of domestic heating boilers without controlling exhausts in heating period. Additionally, the climatic conditions maybe not very favorable for PAH dispersion/dilution in Tianjin.

Potential Sources of PAHs

The ratio values of individual PAH species are frequently employed as diagnostic tools to identify the origin of PAHs in ambient air (Kavouras *et al*., 1999; Papageorgopoulou *et al*., 1999; Bi *et al*., 2003; Guo *et al*., 2003; Mantis *et al*., 2005). The diagnostic ratios calculated between PM$_{10}$-bound PAHs in this study (Table 5) suggest that all six sites are affected by combustion sources with variable seasonal contribution. The concentration ratio values of combustion PAHs to the total PAHs (CPAHs/∑PAH$_{17}$) were higher in heating period than those in no-heating period almost at all the sites. The above ratio are in accordance to those previously reported in other areas such as Athens (Mantis *et al*., 2005) and Eordea basin in Greece (Kalaitzoglou *et al*., 2004), where intensive coal was burned for power generation. It indicates that coal combustion was also the main contributor to PAHs in Tianjin.

The ratios of FL/Pyr, IND/IND + BghiP, BaP/BghiP and BaP/BaP + CHR can be used to identify the predominant sources for PAHs since the values are quite different to various sources such as gasoline emission, diesel emission, and coal combustion, respectively (Sawicki, 1962; Lee *et*

al., 1982; Khalili *et al*., 1995; Kavouras *et al*., 1999; Kavouras *et al*., 2001; Manoli *et al*., 2004; Chen *et al*., 2005; Mantis *et al*., 2005). In this study, the ratio FL/Pyr, IND/IND + BghiP, BaP/BghiP and BaP/BaP + CHR of the six sampling sites range from 0.94 (DL) to 1.27 (SZ), 0.48 (BC) to 0.54 (HX), 1.10 (HX) to 1.25 (BC) and 0.39 (DL) to 0.43 (DXC and BC) in heating period respectively (Table 5). The ratio FL/Pyr, IND/IND + BghiP and BaP/BghiP are approaching those reported in Tianjin and Seoul (Parka *et al*., 2002; Wu *et al*., 2007). The ratios FL/Pyr and BaP/BghiP indicate coal combustion may be the main source of PAHs at all sampling sites in heating period. The ratios BaP/BaP + CHR suggest that gasoline emissions or coal combustion were dominant in Tianjin in heating period. The ratios IND/IND + BghiP indicate diesel emission and coal combustion existed simultaneously. Although the extremely consistent contribution results of PAHs sources had not been obtained, we concluded that coal combustion was the main contributor to PM$_{10}$-bound PAHs in Tianjin in heating period.

In no-heating period, the ratios FL/Pyr, IND/IND + BghiP, BaP/BghiP and BaP/BaP + CHR of the six sites range from 1.06 (DL) to 1.41 (SZ), 0.51 (HX) to 0.68 (MJ), 0.97 (DL) to 1.37 (SZ) and 0.36 (HX) to 0.54 (DL), respectively (Table 4). Compared these ratios with that in heating period, the peak values are higher in no-heating period, but they are not significant differences. The ratios BaP/BaP + CHR tend to suggest that gasoline emissions were dominant PAHs source, while the ratios IND/IND + BghiP indicate a significant contribution of PAHs from diesel emission. According to the ratios of FL/Pyr and BaP/BghiP in no-heating period, coal combustion was a main contributor of PAHs emission. The ratio FL/Pyr, IND/IND + BghiP, BaP/BghiP and BaP/BaP + CHR had shown the inconsistent contribution results of PAHs sources. So the further exploration is needed to identify these sources in no-heating period.

Table 5. Diagnostic ratios of PAHs in PM_{10} in Tianjin and those of reported sources.

Site	CPAHs/∑PAH$_{17}$	FL/Pyr	IND/(IND + BghiP)	BaP/BghiP	BaP/(BaP + CHR)
DXC-NH	0.83	1.35	0.60	1.26	0.50
DXC-H	0.83	1.24	0.48	1.19	0.43
HX-NH	0.77	1.31	0.51	1.08	0.36
HX-H	0.80	1.26	0.54	1.10	0.40
BC-NH	0.85	1.18	0.61	1.02	0.47
BC-H	0.87	1.19	0.48	1.25	0.43
SZ-NH	0.82	1.41	0.60	1.37	0.50
SZ-H	0.84	1.27	0.50	1.11	0.42
DL-NH	0.86	1.06	0.60	0.97	0.54
DL-H	0.88	0.94	0.51	1.13	0.39
MJ-NH	0.83	1.16	0.68	1.33	0.52
Gasoline engine	0.73[a]	<1.0[b]	0.18[d]	0.30–0.44[e]	0.49[g]
Diesel engine	0.78[a]	<1.0[b]	0.35–0.70[f]	0.30–0.44[e]	0.73[g]
Coal combustion	0.87[c]	1.0–1.4[b]	0.56[d]	0.9-6.6[e]	0.07–0.24[h]

CPAH: FL + Pyr + BaA + CHR + BbF + BkF + BaP + IND + BghiP
[a] Manoli *et al.* (2004); [b] Lee *et al.* (1982); [c] Mantis *et al.* (2005); [d] Kavouras *et al.* (1999); [e] Sawicki (1962); [f] Kavouras *et al.* (2001); [g] Khalili *et al.* (1995); [h] Chen *et al.* (2005).

Principal Component Analysis (PCA)

PCA is an important method to identify the major sources of air pollutant emissions and to select statistically independent source tracers (Harrison *et al.*, 1996; Guo *et al.*, 2003; Shi *et al.*, 2009). We used PCA to further identify the emission sources of PAHs in no-heating period. The principle of PCA is to transform an original set of variables into a smaller set of linear combinations that account for most of the variance of the original set. The factor loadings which are obtained for each variable within the factors generated by the PCA, are a type of correlation coefficient, and higher values are therefore associated with greater significance.

Due to non-detectable or too low concentrations of NaP, AcPy, AcP and DBA in PM_{10}, only 13 PAH species measured in PM_{10} in no-heating period were subjected to PCA with varimax rotation. Table 6 provides the results of PCA for 13 PAHs in no-heating.

Factor 1: it explains 49.3% of the variance with a high load for FL,Pyr, BaA, CHR, BaP,IND and BghiP, and a lower load for BbF and COR, which are all the MMW and HMW PAHs. According to Marr *et al.* (2000), the compounds BaP, IND, BghiP and COR are characteristic of gasoline emissions. On the other hand, Khalili *et al.* (1995) identified ANT, PA, FL, BaA, Pyr and CHR as tracers for coal combustion. Additionally, vehicular emission has been known as an important source of PAHs in some urban of cities (Guo *et al.*, 2003; Bourette *et al.*, 2005; Kume *et al.*, 2007; Shi *et al.*, 2009), and coal combustion was identified as the main contributor of PAHs emission in Tianjin (Wu *et al.*, 2007). Based on the above analysis, we concluded that Factor 1 was a mixture source of the gasoline emissions and coal combustion. The conclusion is consistent with that obtained by diagnostic ratios in some aspects.

Factor 2: it explains 22.4% of the variance with a high load for Flu, PA and Ant. According to Khalili *et al.*

(1995), the presence of Flu, PA, Ant and Pyr indicates the dominance of wood combustion. Traditional biomass combustion for cooking and heating are still popular in the north of China. Thus, in this work this factor is associated with wood combustion.

Factor 3: it explains 16.1% of the variance with a high load for BkF, and a lower load for BbF. These compounds have been identified as coming from diesel emission sources (Li and Kamens, 1993; Harrison *et al.*, 1996). Tianjin is a well-developed hub with a sea–land–air transportation network, and own large amount of heavy diesel engines with large loads. So it can be confirmed that diesel emission was one of the major sources of PAHs in Tianjin in no-heating period.

Table 6. PCA analysis of PAHs in PM_{10} in central urban of Tianjin.

PAHs	Factor 1	Factor 2	Factor 3
Percent of variance (%)	49.3	22.4	16.1
Flu		0.92	
PA		0.94	
Ant		0.91	
FL	0.83		
Pyr	0.85		
BaA	0.88		
CHR	0.92		
BbF	0.59		0.73
BkF			0.90
BaP	0.82		
IND	0.89		
BghiP	0.91		
COR	0.74		

Extraction Method: Principal Component Analysis;
Rotation Method: Varimax with Kaiser Normalization;
Number of factors: 3; Factor loading ≥ 0.5 listed.

According to the PCA results, coal combustion, gasoline emissions, wood combustion and diesel emissions are the major sources of PAHs in Tianjin in no-heating period.

CONCLUSIONS

PAHs in PM_{10} in Tianjin had been determined at six sampling sites for one year. PAH levels were the highest at heavy industrial area in heating period and the lowest at an culture area in no-heating period. Obviously, the PAHs levels in PM_{10} were closely associated with source strength and meteorological conditions. Higher heating period PAHs concentrations and lower no-heating period concentrations were observed in all sampling sites. The concentrations observed in this study are higher than those reported in other countries. The local populations in Tianjin are exposed to significantly higher cancer risk, compared with the population in other cities. Based on the diagnostic ratios and PCA analysis, coal combustion and gasoline engine emissions were found to be the predominant source to PM_{10}-bound PAHs in Tianjin in no-heating period. Other sources such as emission from wood combustion and diesel engine emission also play an important role in PAHs production. In heating period, coal combustion was regards as the more predominant source to PM_{10}-bound PAHs than that in no-heating period. Additionally, meteorological conditions also promote the PAHs pollution in heating period, such as lower dispersion of air pollutants, less photo-degradation and higher percentage in the air in solid phase.

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