



## A seasonal study of polycyclic aromatic hydrocarbons in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> in five typical cities of Liaoning Province, China

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### ABSTRACT

Fourteen polycyclic aromatic hydrocarbons (PAHs) in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> samples collected in five cities (Shenyang, Anshan, Jinzhou, Fushun and Dalian), Liaoning Province, China in 2004 and 2005 were analyzed by using a HPLC equipped with fluorescence and UV detectors. Results showed total PAHs concentrations in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were in the range of 75.32–1900.89 ng m<sup>-3</sup> and 16.74–303.24 ng m<sup>-3</sup>, respectively. 90% of the total PAHs were in PM<sub>2.5</sub>. PAHs in PM<sub>2.5</sub> had a winter to summer ratio varying from 6.5 to 125.8 while PAHs in PM<sub>2.5-10</sub> had a ratio ranging from 1.7 to 37.6. Total PAHs concentrations were most abundant at residential/commercial sites and were fewest at an industrial site for both PM<sub>2.5</sub> and PM<sub>2.5-10</sub>. Urban background sites showed unexpected higher PAHs concentrations. Total BaP equivalent concentration (BaP<sub>eq</sub>) for PM<sub>2.5</sub> ranged from 7.80 to 88.42 ng m<sup>-3</sup> in different function zones. Similarities of PAHs profiles between sampling sites and between fine and coarse fractions were compared by coefficient of divergence which indicated that remarkable differences in PAHs compositions existed. Principal component analysis (PCA) associated with diagnostic ratios revealed coal combustion and vehicle emission were the major sources for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> associated PAHs.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been widely accepted as a class of ubiquitous and mutagenic environmental pollutants and attracted much attention in previous studies on air pollution recently [1,2]. PAHs are products of incomplete combustion and pyrolysis of fossil fuels such as petroleum and coal and other organic materials from natural and anthropogenic sources [3–13] including fossil fuels combustion [14], vehicle exhaust [15,16], open-fire straw burning [16,17], cigarette smoking [17], wood combustion [18], industrial production [19], including waste incineration [6], metal production [20], coke production [20], iron production [5,17], airplane production [17], etc. Results of previous studies had shown that the main sources of PAHs in urban area were traffic exhaust (diesel or gasoline) and certain industrial processes [20,21]. Zhang and Tao [17] pointed out that in China, the major emission sources for atmospheric PAHs were biofuel, coke production, domestic coal, traffic oil, open straw burning, petrol refinery and consumer products which contributed 66.4%, 14.4%, 10.7%, 2.0%, 2.0%, 1.0% and 0.9%, respectively. Tian et al. [22] concluded that in heating period, the main pollution sources were

coal-fired boiler emission (56%), residential coal combustion (33%) and traffic emissions (11%). As for non-heating period, the main sources were gasoline engine emission, traffic tunnel emission and coal-fired power plant, and the overall source contributions of traffic emission (gasoline engine in traffic tunnel) was 79% and of coal-fired power plant was 21% in Dalian, China.

An important property-particle size determined the PAHs size distribution, and furthermore, the inhalable and respirable PAHs fractions [3]. In general, average fine particulate PAHs concentrations were all higher than coarse particulate PAHs concentrations [23–25]. Schnelle-Kreis et al. [26] found that in most cases the amount of PAHs associated with coarse particles was less than 10% of the total. Baek et al. [27] reported that 95% of particulate PAHs sampled in London were in particles with diameter less than 3.3 μm.

Temporal variation of PAHs has been investigated in some studies and most results showed higher PAHs concentrations in winter than in summer [4,20,21,24,28,29]. Although several studies have been conducted to compare PAHs between urban sites and suburban sites [4,24,25,30], only a few measurements were conducted to compare the difference in different function zones in urban areas [31–32].

In particular, benzo[a]pyrene (BaP) had always been selected as an indicator of carcinogenic PAHs [24,32] and some countries and organizations had also set up standards for it. The guided level of

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BaP is 0.25 ng m<sup>-3</sup> in USA [8], 1.0 ng m<sup>-3</sup> in European Union [8,21], 0.25 ng m<sup>-3</sup> in UK [21,24], 1.0 ng m<sup>-3</sup> in Italy [24], 1.0 ng m<sup>-3</sup> in WHO [33] and 10 ng m<sup>-3</sup> in China [34]. While the environmental health risk associated with exposure to atmospheric particulate PAHs has yet not to be assessed for the cities of Liaoning Province.

PAHs are present in both aerosol phases. The PAHs of low molecular weight (2 and 3 aromatic rings) were found preferentially in the gas phase while the ones of larger molecular weight (4–6 aromatic rings) were found adsorbed on the surface of suspended particles [2,3,11,19,20,29,32]. Therefore, it is important to evaluate the amount, distribution and possible sources of PAHs in the atmospheric aerosols since their absorbed amount through breathing depends upon their atmospheric concentration [35].

In Liaoning Province, air quality monitoring networks have been constructed to monitor criteria air pollutants such as SO<sub>2</sub>, NO<sub>x</sub>, CO, O<sub>3</sub> and PM<sub>10</sub>. Less attention has been paid on monitoring PAHs that requires more elaborate sampling and analytical protocols. Studies related to PAHs have recently been conducted in some cities such as Shenyang [36] and Dalian [22]. The main objectives of these studies were to detect and quantify the PAHs compounds in PM. However, PAHs partition between PM<sub>2.5</sub> (particles with aerodynamic diameter less than 2.5 μm, fine fraction) and PM<sub>2.5-10</sub> (2.5 μm < aerodynamic diameter < 10 μm, coarse fraction) is still unknown. It is important to conduct detailed and systematic PAHs profiles for particulate matter for the purpose of effective air pollution control and establishing air quality standards by assessing public exposure to PAHs and their associated health risks [23].

We have performed a four-season PM<sub>2.5</sub> and PM<sub>2.5-10</sub> sampling in 2004 and 2005 at 10 sites in five cities which covered different city zones of Liaoning Province. We focused on characteristic, temporal and spatial distribution as well as sources for both fine and coarse particulate PAHs. The main objectives of this study were to: (1) give the PAHs levels of PM in Liaoning Province; (2) identify the seasonal variation of PAHs concentration and distribution pattern associated with fine and coarse fraction; (3) compare the status of PAHs pollution in different city function zones; (4) identify their possible sources. It is expected that the results from this study will provide a baseline reference for a global database as well as for regulatory action to improve air quality in these cities.

**2. Experimental**

*2.1. Sampling area and sites description*

Liaoning province is located in the eastern shore of Eurasia, under the control of a continental monsoonal climate within a warm temperate zone. The terrain of the province is complex, including mountain, plain, hill and coast. Annual average temperature is between 5 and 10 °C, decreasing from coastal area to inland. The average yearly rainfall is between 500 and 1000 mm, decreasing from east to west. The precipitation is mainly in summer, accounting for 60–75%. Long cold period, strong wind in the plain area, wet in the east and dry in the west, concentrative precipitation in summer, plenitudinous sunlight and distinct four seasons are the main climate characteristics of the province. As the traditional heavy-industrial base of China, the major industry system of the province includes metallurgy, mechanics, petrochemical, construction material and so on.

Considering differences in topography, meteorology, industrial structure and air quality, five representative cities including Shenyang (122°25′–123°48′E, 41°11′–43°02′N), Anshan (122°10′–123°13′E, 40°27′–41°34′N), Fushun (123°39′–125°28′E, 41°41′–42°38′N), Jinzhou (120°42′–122°37′E, 40°48′–42°08′N) and Dalian (120°58′–123°31′E, 38°43′–40°10′N) were selected to study the characterization of PM-bound PAHs in Liaoning Province. Locations of these five cities are indicated in Fig. 1.

**Table 1** Geometric mean concentrations of PAHs in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> at 10 sites in five selected cities during sampling periods (ng m<sup>-3</sup>).

PAHs	PM <sub>2.5</sub>					PM <sub>2.5-10</sub>				
	Shenyang (n=53)	Anshan (n=51)	Fushun (n=53)	Jinzhou (n=51)	Dalian (n=50)	Shenyang (n=53)	Anshan (n=51)	Fushun (n=53)	Jinzhou (n=51)	Dalian (n=50)
Nap	3.49	4.81	0.73	0.65	1.52	3.57	0.39	2.62	0.55	1.04
Ace	4.05	3.56	2.33	2.53	1.79	1.52	1.54	3.45	0.35	1.66
Phc	69.98	15.19	21.08	10.73	7.09	48.46	5.03	15.41	2.57	4.43
Ant	1.76	64.07	8.39	3.50	0.98	0.51	1.09	2.74	0.74	0.62
Flu	20.39	311.77	70.45	42.53	12.51	5.16	14.27	17.71	4.98	4.38
Pyr	15.23	272.81	52.26	30.69	8.10	2.17	10.40	13.43	2.87	2.40
BaA	5.90	64.05	17.71	20.73	6.06	0.77	2.86	3.43	1.45	1.28
Chr	8.13	81.04	23.09	13.64	7.63	1.68	3.69	4.85	1.49	1.66
BbF	14.21	65.67	23.96	11.51	8.92	2.16	4.44	3.62	1.66	1.92
BkF	3.55	16.37	6.09	6.17	2.88	0.71	1.06	1.83	0.56	0.77
BaP	5.93	31.71	10.71	13.61	5.39	1.13	2.04	1.98	1.33	0.91
DbA	9.14	23.64	12.89	13.84	6.65	2.56	1.83	2.03	1.23	1.29
BghiP	1.40	4.76	4.42	2.61	1.63	0.70	0.72	1.06	0.38	0.35
Ind	7.35	16.89	8.98	10.75	4.83	1.18	1.66	1.54	0.91	1.22
∑ PAHs	170.50	1053.83	262.53	191.49	75.32	72.27	53.73	75.07	21.35	23.12

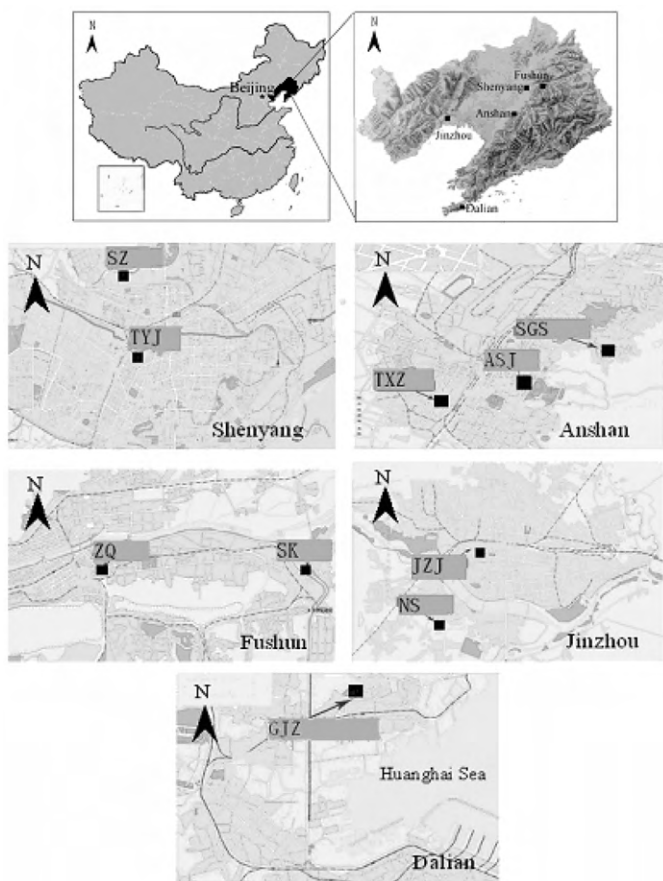


Fig. 1. Location of the five selected cities and the sampling sites.

Shenyang, as the capital city of Liaoning Province and the biggest city in the Northeast area of China, lies in the middle plain of the province. The main industry is mechanics. Locating at the west of Qianshan Mountain, Anshan is one of the most important iron and steel base in China. Fushun, a famous city owing to coal, is situated in the eastern mountainous area of the province with petrochemical and coal as its supporting industry. Jinzhou, which is the traffic ligament connecting Northeast District of China and other districts lies on the north of Bohai Sea, with metallurgy and petrochemical as its dominant industry. Dalian, a coastal city, lies in the south of Liaodong peninsula and the principal industries are shipbuilding, petrochemical and mechanics. According to the bulletins of environmental situation published by Liaoning Environmental Protection Bureau from 2000 to 2004, the primary air pollutant was  $PM_{10}$ . Except for Dalian,  $PM_{10}$  in the other four cities all exceeded the national annual secondary standards ( $0.1 \text{ mg m}^{-3}$  for  $PM_{10}$ ) [37].

Two sampling sites were selected for each city, except for Anshan and Dalian. All these sites are national routine monitoring stations. There were two sites in Shenyang: SZ (a residential area) and TYJ (a commercial area, near major roads with high traffic volume, lots of construction activities and barbecue sites); three sites in Anshan: SGS (a residential area), ASJ (a residential area) and TXZ (an industrial/commercial area, near Anshan steel smelt corporation, 17 coal combustion boilers within 1 km, annual total coal consumption was 16,000 tons); two sites in Fushun: SK (an urban background site, 10 km away from two power plant, about 20 coal combustion boilers within 1 km) and ZQ (a residential/commercial area, 2 km away from Fushun power plant, heavy traffic, tens of boilers for hotel and bathhouse); two sites in Jinzhou: NS (an urban background site, 12 coal combustion boilers within 1 km, annual

total coal consumption was 16,000 tons, an iron smelt stove about 1 km on the windward direction, a mixing site for bitumen within 0.9 km on the southeast) and JZJ (a residential area, 32 pollution sources including 16 coal combustion boilers within 1 km, annual total coal consumption was 70,000 tons); one site in Dalian: GJZ (an industrial area, special industry area, 60% of industry sources of Dalian concentrated here). There are total four residential sites, one residential and commercial mixed site, one commercial site, one commercial and industrial mixed site, one industrial site and two urban background sites, differing substantially in industry structure and were also expected to vary significantly in particulate associated PAHs. Sampling equipments were all placed on the rooftop of each site of the air quality monitoring network set by local government, 3–15 m above ground level.

## 2.2. Sampling

Measurements were carried out in five cities simultaneously between 2004 and 2005. Samplings were carried out during the first halves of January, April, July and October to represent four seasons. Each sampling began at 8:30 a.m. and continued for 24 h. These samples were collected on consecutive days in all four seasons except extreme meteorological conditions such as rain, snow or strong wind (wind speed higher than  $8 \text{ m s}^{-1}$ ). Ambient air particulate matter was continuously collected onto quartz filters ( $\varnothing 37 \text{ mm}$ , Pall Gelman Laboratory, Ann Arbor, MI) using dichotomous samplers (Model TH-15S, Wuhan Tianhong Instrument Factory) with a  $10 \mu\text{m}$  cut point before inlet at a rate of  $15.03 \text{ L/min}$  for fine particulate matter and  $1.67 \text{ L/min}$  for coarse fraction for 24 h. The flow rate of each dichotomous sampler, equipped with a mass flow controller, was calibrated automatically with bubble flow meters to ensure a constant flow rate. Flow rate variations throughout each 24 h sampling were within  $\pm 5\%$ .

Prior to sampling, quartz fiber filters were calcined at  $400^\circ\text{C}$  for 4 h to remove any organic compounds that may be present on the filters. Filters were weighted by a sensitive microbalance (Meter Toledo MX5) with balance sensitivity  $\pm 1 \mu\text{g}$ . Prior to weighing, the filters were equilibrated in a desiccator at room temperature within 48 h and then weighed before and after sample collection. After sampling, the filters were removed from the inlet, folded in half and wrapped in a laminar-flow clean hood until use. Filter blanks were assessed in the same procedure. After weighing, the filters were stored at  $-20^\circ\text{C}$  until analysis.

## 2.3. Analytical procedure

Half of each filter was cut into pieces to 5 mL centrifugal glass tube with 5 mL acetonitrile. PAHs were removed from the filter using ultrasonic extraction for 10 min and then reconcentrated for 10 min using a centrifuge with 600 r/min.  $10 \mu\text{L}$  extracts were filtered by a  $0.45 \mu\text{m}$  filter, injected into an ampoule bottle and stored in a refrigerator until analysis.

Separation and identification of 14 PAHs were achieved using a HPLC system equipped with a fluorescence detector (RF 2000) and a UV detector (PDA-100 Photodiode Array Detector) from Dionex Corporation, USA. The fluorescence of PAHs was monitored with an automatic adjustment of the wavelengths for each compound according to its retention time. The excitation wavelength was 245 nm, while the emission wavelength was 425 nm. Four wavelengths (207 nm, 220 nm, 230 nm, 254 nm) of the UV detector were selected. A gradient with acetonitrile and water was applied for separation of the analytes: 60% acetonitrile and 40% water in 0–3 min; 60% acetonitrile and 40% water in 3–15 min; 100% acetonitrile and 0% water in 15–38 min; 60% acetonitrile and 40% water at 38 min. The flow rate of mobile phase was set at  $1 \text{ mL min}^{-1}$ .

Quantification of PAHs was standardized by the retention times and peak areas of the calibration standards. In all analyses, a procedural blank was performed periodically to confirm that there was no contamination. An external standard mixture of selected PAHs which was diluted to  $500 \mu\text{g mL}^{-1}$  by acetonitrile was used.

Concentrations of 14 PAHs were quantified according to their elution orders as followed: naphthalene (Nap), acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), fluorene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DbA), benzo[ghi]perylene (BghiP), indeno[1,2,3-cd]pyrene (Ind). Data handling and statistical analysis were performed using the Statistical Package for Social Sciences software (SPSS version 13.0).

#### 2.4. Quality assurance

The recovery test was performed by spiking known amounts of a mixture of PAHs and then the spiked filter was treated the same way as mentioned above. The recovery experiment was repeated four times. When the concentrations of internal standards were  $0.500 \text{ mg L}^{-1}$ , the recovery for each PAHs fell between 86% and 95%, and the relative standard deviation was less than 10%. Field blank filters were placed unopened next to the samplers for the duration of sampling, after which they were returned to the laboratory and treated as regular samples to ensure that there was no significant background interference. Laboratory blanks (clean filters) were extracted and analyzed with every 10 samples. None of the target compounds was found in the blank filters. Consequently, the data was not subjected to any blank correction.

### 3. Results and discussion

#### 3.1. General characteristics of total PAHs in fine and coarse particulate matter

Concentrations of 14 PM-bound PAHs obtained in this study are presented in Table 1, arranged by sampling sites.

The total PAHs concentrations of  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  were in the range of  $75.32\text{--}1900.89 \text{ ng m}^{-3}$  and  $16.74\text{--}303.24 \text{ ng m}^{-3}$ , respectively. The highest concentrations for  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  were both found at a residential/commercial area (site 7, ZQ). The ZQ site held heavy traffic with tens of boilers for hotel and bathhouse as well as lots of barbecue plots. At the same time, it was 2 km away from Fushun power plant, which emitted about 5000 tons of soot each year accounting for 16% of the total soot emission of Fushun. The lowest concentration detected was at an industrial area (site 10, GJZ) and a residential area (site 9, JZJ) in Dalian and Jinzhou for  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , separately. Average concentration of individual PAHs in  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  varied from  $1.64 \text{ ng m}^{-3}$  (NaP) to  $128.09 \text{ ng m}^{-3}$  (Flu) and from  $1.28 \text{ ng m}^{-3}$  (Ant) to  $12.60 \text{ ng m}^{-3}$  (Flu). BaP had mean value of  $21.40 \text{ ng m}^{-3}$  for  $\text{PM}_{2.5}$ , which exceeded  $10 \text{ ng m}^{-3}$ , the state recommended air quality standard for BaP as day average [34].

It was observed that in the fine fraction, the highest concentrations of PAHs compounds were Flu (23%), Pyr (21%), Ace (8.3%), Chr (7.9%) and BaA (7.4%) which were associated with coal combustion sources [22]. The other nine compounds represented about 32.4% of the total concentration of this fraction. In the coarse fraction the dominant compounds were Flu (19.8%), Phe (19.0%), Pyr (16.7%), Ace (7.4%) and Chr (6.0%) indicating that coal combustion was one of the main sources [22] and the other nine compounds represent about 31.1% of the total concentration of this fraction. Flu, Pyr, Ace and Chr were also observed as predominant compounds in Xiamen [1], Hongkong [24] and Zonguldak [38] where the contribution of coal combustion, cooking sources and residential heating should

not be ignored. Yet some other studies found Ind, BbF and BghiP were the abundant species in Flanders [4], Taichung [10], Sao Paulo [13], Porto Alegre [13] and Rio de Janeiro [18] where vehicular emission was the main source for particulate PAHs. Different sources indicated that there were different inputs of PAHs in urban area.

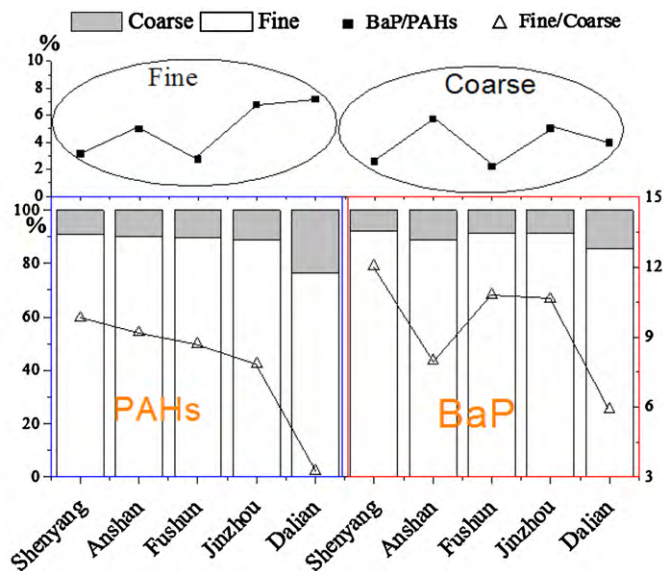
Sum of the carcinogenic PAHs (CANPAHs) including BaA, BbF, BkF, BaP, DbA and Ind accounted for 28.8% and 23.9% of the total PAHs concentrations in fine and coarse particulate matter, respectively. The obtained results suggested that coarse fraction can be hazardous to human health as the fine one. It also reflected PAHs with higher rings tend to be strongly absorbed by fine air particles, which was similar to the research of Wang et al. [5].

Another criterion to characterize each fraction was to group the PAHs compounds that were combustion derived, including Flu, Pyr, Chr, BbF, BkF, BaA, BeP, BaP, Ind and BghiP [13]. In this study, we summed all the species except for Chr and BeP. The sum of the main combustion-derived PAHs concentrations (COMPAHs) covered 69.8%, 54.1%, 70.2% and 68.4% of the total PAHs in  $\text{PM}_{2.5}$  for spring, summer, autumn and winter, respectively. It was 60.3%, 43.8%, 64.7% and 58.0% for  $\text{PM}_{2.5-10}$ . These proportions indicated that there was a clear difference in summer from the other seasons. Rogge et al. [39] determined the value of  $\text{COMPAH}/\Sigma\text{PAHs}$  ratio for non-catalyst (0.4) and catalyst-equipped (0.5) automobiles and for heavy-duty diesel trucks (0.3). In this study, the lower value of  $\text{COMPAH}/\Sigma\text{PAHs}$  in summer meant that vehicular emissions especially from catalyst-equipped vehicles may be a contribution while in other seasons emission sources were more complex.

Although it was pointed out that results on atmospheric PAHs could differ by 40% depending on sampling system, extraction solvents, analytical techniques and detectors [40], and also PAHs determined in airborne particles were influenced by regional climatic as well as source characteristics [13,41], the comparison was conducted with others as listed in Table 1 in Supplementary file to better understand the atmospheric particulate PAHs levels in Liaoning Province. The PAHs concentrations observed in this study were comparable to those reported in Beijing [5] and Taichung [23] but were significantly higher than those in urban environments of Hongkong [29] and Zonguldak [38]. Higher PAHs levels in this region were likely attributed to the combination of dense heavy industries, huge coal consumption due to long heating period, poorer atmospheric dispersion of pollutants, washout effects and less weak photo-degradation.

In general, the average fine particulate PAHs concentrations were all higher than coarse particulate PAHs concentrations [19,23,24,26,27,29]. Except NaP, the other 13 kinds of PAHs were consistent with other studies. The amount of PAHs associated with fine particles were 47.0%, 90.8%, 73.8%, 89.7%, 91.0%, 91.9%, 92.3%, 92.0%, 91.9%, 90.0%, 90.0%, 91.3%, 90.7% and 90.7% of the total for Nap, Ace, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DbA, BghiP and Ind, respectively. Fang et al. [10] gained the similar results in Beijing that almost all the  $\text{PM}_{2.5}$  concentrations of individual PAHs were higher than those in the coarse fraction, except for NaP, Ace, BaA and BbF. Zhou [25] pointed approximately 45.0–67.8% of total PAHs were present in the particles size less than  $1.1 \mu\text{m}$ , while the values were 68.4–84.7% for the particles size less than  $2.0 \mu\text{m}$  in Beijing. The results showed that total PAHs existed predominantly in fine particles, which were strongly related to a potential health risk. While Miguel et al. [44] observed higher PAH concentrations in coarse fraction and attributed this difference to chemical reactions which depleted PAHs from fine fraction. PAHs condensing on the surface of coarse fraction, dust resuspension by wind and vehicle emissions were also contributions to PAHs in coarse fraction [13].

Fig. 2 shows the spatial comparison of PAHs and BaP in fine and coarse fraction in the five cities. The concentrations of total PAHs and BaP in the fine fraction were higher than those in the coarse fraction and the fine to coarse ratio ranged from 3.3 to 9.8 for PAHs



**Fig. 2.** Spatial comparison of PAHs in fine and coarse particulates in five cities. The top line and symbol graph shows the percentage of BaP in PAHs for fine and coarse particulates. The bottom column represents the percentage of  $PM_{2.5}$  and  $PM_{2.5-10}$  for PAHs and BaP in five cities during sampling periods and the bottom line and symbol graph reflects the fine/coarse ratio. The blue box means PAHs distribution in fine and coarse particulate matter for each city and the red one is the representation of BaP. The left ellipse represent the percentage for BaP in PAHs in every city and the right one shows the percentage for BaP in PAHs on coarse fraction.

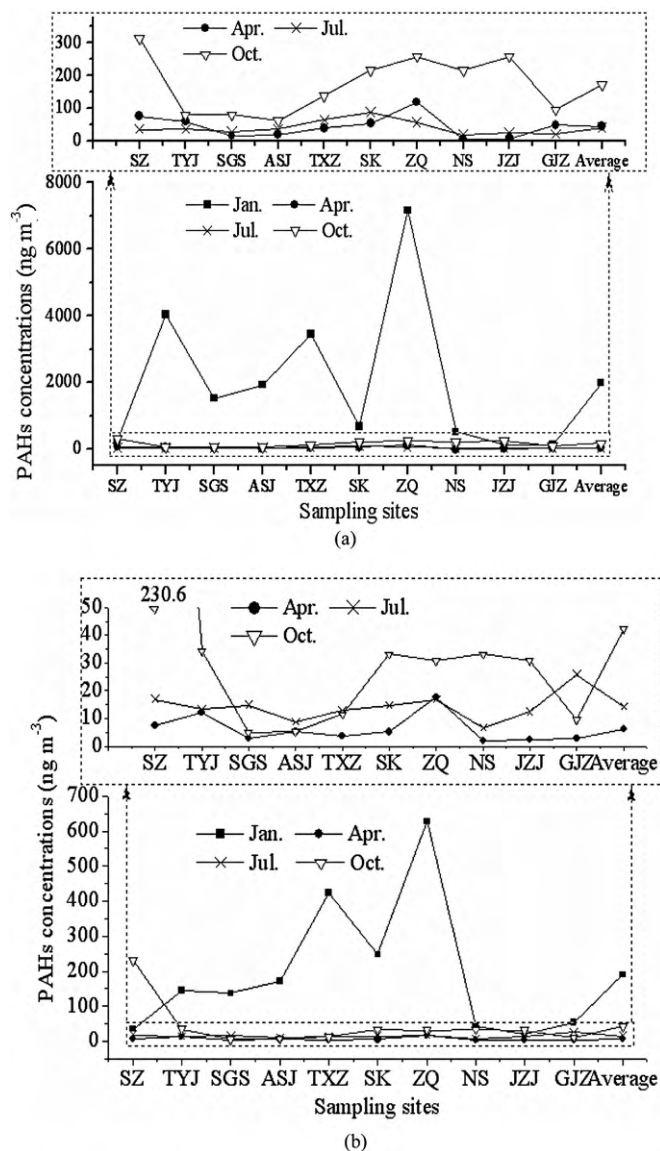
and from 5.9 to 12.0 for BaP, respectively. On the fine fraction, the BaP accounted for 2.7–6.7% of PAHs with value 2.2–5.7% on the coarse fraction.

### 3.2. Temporal variation for PAHs in fine and coarse fraction

Seasonal variations have been widely reported for many studies and the variability has been found to be mainly dependent upon the unique climatic changes and anthropogenic activities of the sampling sites under investigation [24]. In Liaoning, there are obvious four seasons with winter (from December to February), spring (from March to May), summer (from June to August) and autumn (from September to November). The results as illustrated in Fig. 3 indicated that lower PAHs concentrations were observed in July (summer) and April (Spring) while higher PAHs concentrations occurred in January (winter) and October (autumn) for both fine and coarse particulates.

Higher PAHs concentrations in winter and lower concentrations in summer were also widely observed in some Asia cities like Guangzhou [2], Taichung [10], Shizuoka [19], Hongkong [24], Beijing [25], Zonguldak [38], Delhi [45] and Kaohsiung [46] and cities in other continents such as Atlanta [11] and Florence [31]. For this reason we calculated the winter to summer ratio (w/s) as shown in Fig. 4 for both fine and coarse particulates. For total PAHs, the fine fraction had a ratio that varied from 6.5 (at GJZ) to 125.8 (at ZQ) and the coarse fraction had a ratio that varied from 1.7 (at JZJ) to 37.6 (at ZQ). This was in the same or higher level than that in Xiamen [1] (w/s: 2.0–15.8), Augsburg [15] (w/s: 8–20), HongKong [24] (w/s: 1.4–2.4), Birmingham [28] (w/s: 4.9), Zonguldak [38] (w/s: 7.0–70.7 for  $PM_{2.5}$ , 1.5–12.0 for  $PM_{2.5-10}$ ) and Bursa [47] (w/s: 8–30). Highest w/s ratio at site ZQ was related to its surrounding circumstances as explained before. Large coal consumption may explain the higher winter/summer ratio at this site. Site GJZ is near to sea. Therefore, the pollutants could be easily dispersed by the sea-breeze [2].

Source emissions and meteorological conditions as well as gas-particle partitioning may result in winter and summer difference



**Fig. 3.** Seasonal concentrations of atmospheric PAHs at 10 sites for fine (a) and coarse particulate matter (b). The tops were for April, July and October.

of PAHs concentrations [2]. Emissions increased obviously owing to the fossil fuel usage for space heating purposes [3,9,19,21,25] during its 4-month long heating periods in Liaoning Province which was one reason for the higher concentrations in winter. The cold start conditions for the vehicles in winter may also contribute to the higher PAHs concentrations [11,25,48].

Lower temperatures and atmospheric mixing heights as well as decreased photochemical oxidation intensity can also explain the higher PAHs concentrations in winter [9]. A higher ambient temperature could change the distribution of PAHs between the gaseous and particulate phases by increasing the vapour pressure of pollutants that adhered to atmospheric aerosols and favouring the volatilization of PAHs from the particulate to gaseous phase, but it could also increase the mixing height of the atmosphere resulting in excellent dilution and dispersion of PAHs and hence reduce them [1,24]. Furthermore, low atmospheric temperature can affect the distribution of PAHs between the gas and particle phases and result in a relatively larger portion of PAHs partitioning to the particle phase in winter [10,11]. There was a negative correlation between PAHs and temperature in many studies [1,2,4,9,20,21]. Greater wind speed could reduce PAHs levels by diluting air mass

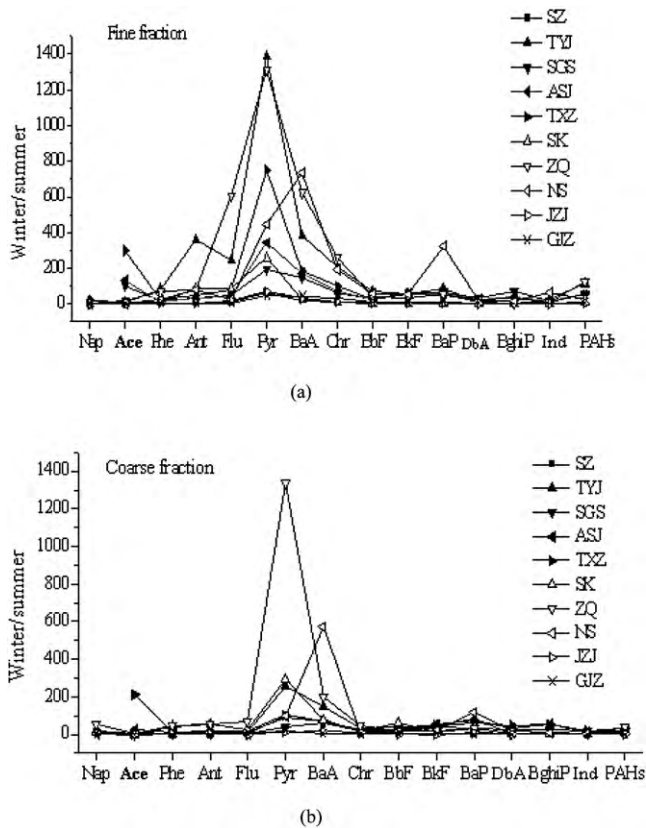


Fig. 4. Winter to summer ratios of atmospheric PAHs at ten sites for fine (a) and coarse particulate matter (b).

and enhancing dispersion efficiency [24] and a negative correlation between PAHs and wind speed were observed in former studies [2,35,45]. In addition, in summer, the frequent washing out effect for particulates results in the minimum aerosol concentrations [1,7]. There were also negative relationship between total PAHs concentrations and rainfall ( $r = -0.499$ ,  $P < 0.05$ ) [21]. It was well known that PAHs in the atmosphere were subjected to photochemical or thermic reactions with ozone, nitric oxides and hydroxyl radicals that lead to PAHs degradation, especially in the warmer seasons [48]. High solar radiation could enhance the reaction of volatile organic compounds in forming ozone active hydroxyl radicals that in turn react with PAHs and reduce their concentrations [24]. Physicochemical processes involving the preferential loss of the lower molecular weight PAHs had also been reported a lot [2,3,7,10,21]. Negative relationship ( $R = -0.31$ ) that exists between PAHs and solar radiation were found in Seoul [9].

In Fig. 4, the curve peaked at 4-rings PAHs including Pyr and BaA for both fine and coarse fraction, with the relative lower value at BbF and BkF. The possible reason was the gas-particle partitioning which exhibited a strong dependence on molecular weight and temperature [2]. PAHs with 3 or 4 rings are semi-volatile compounds and partition significantly in both the gas phase and the particle phase, while PAHs with more rings are roughly non-volatile and mostly reside in the particle phase. The seasonal average total concentrations of the semi-volatile PAHs increased 54 times from summer to winter, while the non-volatile PAHs increased 16 times [42]. Tan et al. [2] found lower molecular weight compounds such as Phe, Ant, Flu, Pyr and Chr in  $PM_{10}$  exhibited a negative correlation with temperature; higher molecular weight compounds such as BeP, Ind, DbA and BghiP were positively correlated with temperature. Hien et al. [21] observed five PAHs including Flu, Pyr, Tri, BaA and Chr increased sharply in the winter in Osaka. Sklorz

et al. [15] pointed BbF und BkF were comparably stable to oxidation. Additionally BaA was relatively sensitive to photo degradation and oxidation by reaction with ozone. Much higher increase of semi-volatile PAHs compared to non-volatile PAHs as well as the influence of temperature and photochemical reaction may explain the peaked values of Pyr and BaA as the temperature and sunshine intensity were lower in winter than in summer. BbF and BkF were more stable than other PAHs species. This may lead to their higher concentrations compared to other species in summer and correspondingly lower w/s ratios. Lower molecular weight PAHs (LMW-PAHs) were mostly emitted and enriched in vapour phase in winter [28] and atmospheric dry deposition velocities were higher for lower rings PAHs (with values 38.0% for 2-rings, 27.8% for 3-rings and 24.1% for 4-rings) [16] which may lead to lower concentrations compared to higher rings PAHs and this could explain the lower w/s ratios for LMW-PAHs.

The season has an impact on the size of the aerosols [6]. We compared all the w/s values between fine and coarse fraction, and found that 84% of value in fine fraction was higher than that in corresponding coarse fraction. This maybe explained by the shift from large to small particles in winter [6]. Manoli et al. [49] found in cold period, fine fraction of all PAH species ranged between 96.1% and 98.4%, whereas in the warm period it decreased slightly in the range of 92.2–97.8%. This decrease was probably due to repartition from the vapour phase onto larger particles under certain conditions, especially for the lower molecular weight PAHs. Similar seasonal effect on the size distribution of ambient PAHs has also been reported by other study [27].

### 3.3. Distribution in different rings

A PAHs classification was done based on their number of aromatic rings, which was used to construct the distribution pattern of the PAHs for each fraction. The 14 PAHs quantified in this study can be classified by their numbers of aromatic rings as follows: 2-rings including Nap; 3-rings including Ace, Phe and Ant; 4-rings including Flu, Pyr, BaA and Chr; 5-rings including BbF, BkF, BaP and DbA; 6-rings including BghiP and Ind. 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- and 6-rings PAHs) [46].

It can be observed that the PAHs with 3-, 4- and 5-rings are dominant in both fine and coarse fraction (Fig. 5). They occupied from 76% to 99% and from 67% to 97% of the total PAHs in fine and coarse fraction, respectively. It can also be seen that: (i) 4-rings PAHs were lower in summer than other seasons in fine fraction. PAHs with 4-rings are semi-volatile which distributed higher in gas phase in summer than in other seasons; (ii) HMW components were abundant in summer, but in winter 3- and 4-rings dominated in fine fraction. It reflected the sources variation of PAHs. The major source for HMW PAHs (BaP, BbF, BghiP and Ind) was gasoline vehicles [4,12], while the major source for 3- and 4-rings PAHs (Phe, Flu, Pyr, BaA and Chr) was coal combustion [4,22,50]. In winter coal combustion sources increased prominently owing to domestic heating; (iii) LMW were higher in coarse fraction than fine fraction. The LMW PAHs were subjected to volatilization processes from the fine particulates and subsequent partition to the coarse particulates [3]. This was in agreement with the behaviour observed in other studies in which PAHs with molecular weight  $\leq 202$  had a higher presence in coarse particles than heavier PAHs [3,44,51]; (iv) 5- and 6-rings were much richer in fine fraction than in coarse fraction at almost all the sites in four seasons. Same result was received at Taichung Harbor [10]. The carcinogenic 5- and 6-rings species are predominantly associated with particles especially those falling in the accumulation mode ( $0.5 \mu\text{m} < d < 1.0 \mu\text{m}$ ) [10].

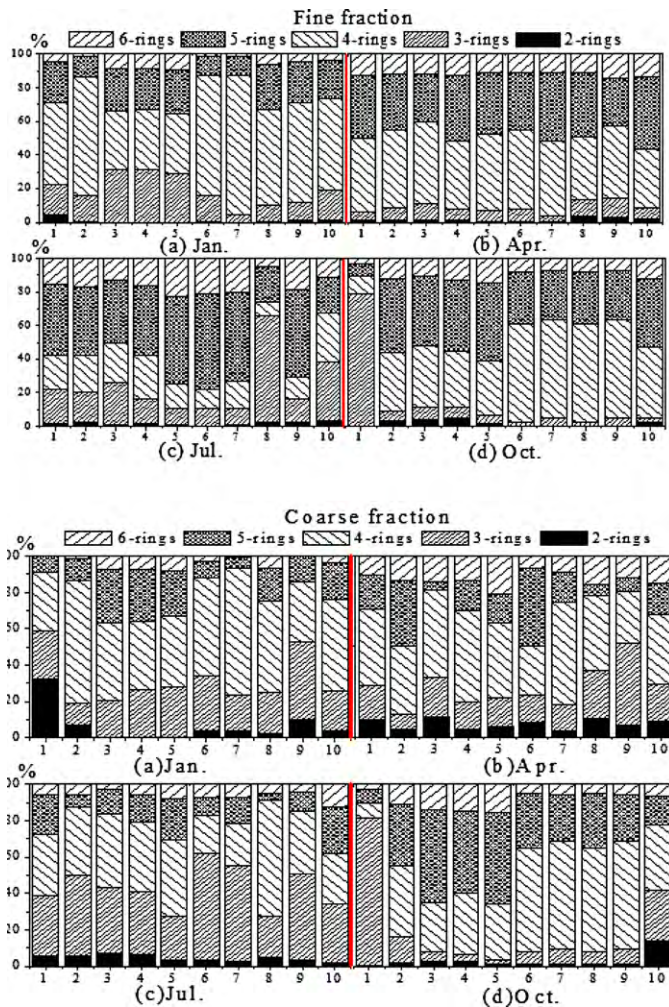


Fig. 5. Ring number distribution of PAHs in fine and coarse fraction. The vertical axes represent the percentage of different rings for total PAHs and the horizontal axes show the different sampling sites (1-SZ, 2-TYJ, 3-SGS, 4-ASJ, 5-TXZ, 6-SK, 7-ZQ, 8-NS, 9-JZJ, 10-GJZ).

### 3.4. Diversity in different function zones for PAHs and BaP

#### 3.4.1. Distribution of PAHs and BaP in different function zones

Owing to difference of population and traffic density as well as industry distribution, the PAHs contribution from anthropogenic inputs varied in different function zones. The 10 sites were classified into six function zones, including residential site ( $n=4$ , RA); residential/commercial site ( $n=1$ , RCA); commercial site ( $n=1$ , CA); industrial/commercial site ( $n=1$ , ICA); industrial site ( $n=1$ , IA); urban background site ( $n=2$ , UBS).

As shown in Fig. 6, significant differences appeared at the six function zones for PAHs and BaP in fine and coarse fraction. PAHs concentrations ranged from  $75.32 \text{ ng m}^{-3}$  to  $1900.89 \text{ ng m}^{-3}$  with the order: RCA ( $1900.89 \text{ ng m}^{-3}$ ) > CA ( $1053.83 \text{ ng m}^{-3}$ ) > ICA ( $923.01 \text{ ng m}^{-3}$ ) > RA ( $300.41 \text{ ng m}^{-3}$ ) > UBS ( $227.01 \text{ ng m}^{-3}$ ) > IA ( $75.32 \text{ ng m}^{-3}$ ) in fine fraction as well as the order RCA ( $173.24 \text{ ng m}^{-3}$ ) > ICA ( $112.72 \text{ ng m}^{-3}$ ) > CA ( $53.73 \text{ ng m}^{-3}$ ) > UBS ( $48.21 \text{ ng m}^{-3}$ ) > RA ( $44.22 \text{ ng m}^{-3}$ ) > IA ( $23.12 \text{ ng m}^{-3}$ ) in coarse fraction, respectively.

As for BaP, the order for six function zones was RCA ( $48.44 \text{ ng m}^{-3}$ ) > ICA ( $47.38 \text{ ng m}^{-3}$ ) > CA ( $31.71 \text{ ng m}^{-3}$ ) > RA ( $14.20 \text{ ng m}^{-3}$ ) > UBS ( $12.16 \text{ ng m}^{-3}$ ) > IA ( $5.39 \text{ ng m}^{-3}$ ) in fine fraction and ICA ( $6.01 \text{ ng m}^{-3}$ ) > RCA ( $3.44 \text{ ng m}^{-3}$ ) > CA ( $2.04 \text{ ng m}^{-3}$ ) > RA ( $1.83 \text{ ng m}^{-3}$ ) > UBS ( $1.55 \text{ ng m}^{-3}$ ) > IA

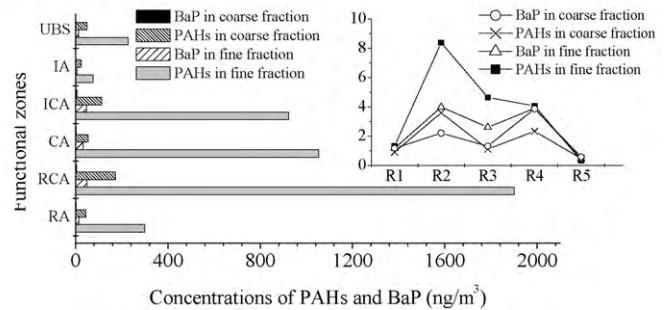


Fig. 6. Variation of total PAHs and BaP concentrations in different function zones. R1 = RA/UBS, R2 = RCA/UBS, R3 = CA/UBS, R4 = ICA/UBS, R5 = IA/UBS.

( $0.91 \text{ ng m}^{-3}$ ) in coarse fraction, respectively. We also calculated the ratios of PAHs and BaP concentrations at RA, RCA, CA, ICA and IA to those at UBS during sampling periods. It indicated that the line peaked at R2 (8.4 and 3.6 for PAHs in fine and coarse particulates, 4.0 and 2.2 for BaP, respectively) and R4 (4.1 and 2.3 for PAHs in fine and coarse particulates, 3.9 and 3.9 for BaP, respectively) which mean that residential/commercial areas and industrial/commercial areas were relatively more polluted. Lodovici et al. [31] concluded that the sum of PAHs in residential areas had values 2.5–3 times lower compared to a heavy traffic area. These differences largely related to the different sampling circumstance. The populated and heavily trafficked areas hold a high PAHs contribution from traffic emission and anthropogenic inputs [11]. The highest PAHs concentration occurred at residential/commercial area and industrial/commercial area meant domestic combustion (almost coal in this region), traffic exhausts and industry emissions were the major contributors for pollution of PAHs in Liaoning. Thus, the management of domestic heating, vehicle emission in commercial area and industries should be strengthened and further measures should be taken because of the high loads of PAHs.

The industry site here showed relative lower PAHs different from Sanderson et al. [30] as the cleaner oceanic air helped to dilute the pollutants along with its effective controlling measures. The urban background sites (SK and NS) in this study were already not clean as the BaP in  $\text{PM}_{2.5}$  was 11 times more than the standard compared to  $10 \text{ ng m}^{-3}$  [34]. For SK, it is 10 km away from two power plants which emitted about 15 tons of soot every year and there are about 20 coal combustion boilers within 1 km because of the rise of tourism. For NS, there are 12 coal combustion boilers within 1 km with 16,000 tons of annual total coal consumption volume, and there is an iron smelt stove about 1 km on the windward direction and a mixing site for bitumen plant within 0.9 km on the southeast. Ravindra et al. [8] pointed that the most important industrial sources of PAHs included primary aluminum production (in particular plants using Soderberg process), coke production (e.g. as part of iron and steel production), creosote and wood preservation, waste incineration, cement manufacture, petrochemical and related industries, bitumen and asphalt industries, rubber tire manufacturing and commercial heat/power production. The high density emission sources at urban background sites resulted in higher PAHs concentrations and it was improper to use them again as clean site for air quality management which should raise the attention of local government.

#### 3.4.2. Health risk assessment in different function zones

In principle, the health risk assessment of PAHs can be assessed based on its BaP equivalent concentration (BaP<sub>eq</sub>). BaP<sub>eq</sub> concentration for each PAHs is calculated by multiplying its concentration with the corresponding toxic equivalent factor (TEF) which rep-

resents the relative carcinogenic potency of the corresponding PAH suggested by Nisbet and LaGoy's TEFs that had been widely accepted by formers [1,7,21,32,43,50,51]. The carcinogenic potency of total PAHs can be assessed by the sum of the BaP<sub>eq</sub> concentrations of each PAHs.

The total BaP<sub>eq</sub> concentrations were found to be 20.66 ng m<sup>-3</sup>, 88.42 ng m<sup>-3</sup>, 50.18 ng m<sup>-3</sup>, 7.80 ng m<sup>-3</sup>, 66.97 ng m<sup>-3</sup> and 18.25 ng m<sup>-3</sup> for RA, RCA, CA, IA, ICA and UBS, respectively (Table 2). Meanwhile, it can be calculated that the potential health risk in RCA was 11 times higher than that in IA, and the reason was explained before. The annual mean  $\sum$ BaP<sub>eq</sub> concentration in Liaoning (40.05 ng m<sup>-3</sup>) was higher when compared to particulate samples from other urban atmospheres, such as Florence (0.916 ng m<sup>-3</sup>) [31], Zonguldak (14.1 ng m<sup>-3</sup>) [38] and Nanjing (7.1 ng m<sup>-3</sup>) [43].

The highest total BaP<sub>eq</sub> concentrations in residential/commercial area were an alarming signal for pollution risks in relation to human health as the high levels of PAHs increases human health risk caused by exposure to such toxic chemicals.

The contribution of carcinogenic potency of BaP alone in this study varied from 0.55 to 0.71 in agreement with literature data [31,52]. It can be concluded that the risk assessment of PAHs mixtures on the basis of the atmospheric BaP concentration without taking into account of the profile variability was valid, even though underestimated, and that BaP was a good marker to assess PAHs-related health risk in this region. As for the CANPAHs (BbF, BkF, BaP, BghiP and Ind), they accounted for more than 96% of the total BaP<sub>eq</sub> concentrations which was similar to 97% in HCMC and 93% in Osaka [21]. These results implied that particle-bound PAHs with high molecular weight did play an important role on total BaP<sub>eq</sub> concentration from health-risk assessment point of view.

### 3.5. Coefficient of divergence analysis

In this study, similarities between two sampling sites within each city and between fine and coarse fraction were also compared by using coefficient of divergence, a self-normalizing parameter used to measure the spread of the data points for two datasets. The parameter is determined as follows:

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}$$

where  $j$  and  $k$  stand for the two profiles for sampling sites or fractions,  $p$  is the number of investigated components, and  $x_{ij}$  and  $x_{ik}$  represent the average mass concentrations of chemical

component  $i$  for  $j$  and  $k$  [53,54]. In addition, mass concentration diagrams are characterized by scatter plots of PAHs components mass concentrations for  $j$  against  $k$  as shown in Figs. 1–3 in Supplementary file. If  $CD_{jk}$  approaches zero, sources  $j$  and  $k$  are similar, and if it approaches one, they are significantly different [53–55]. Wongphatarakul et al. [53] pointed the CD value 0.269 reflected the similarity between particles between two cities.

In all five cities, the  $CD_{jk}$  values between fine and coarse fraction are higher than 0.5, indicating that the two fractions in each city had desimilar PAHs species concentrations. For the sites comparison, the  $CD_{jk}$  values were all higher than 0.3 except for the value of ASJ vs. SGS for fine fraction ( $CD_{jk} = 0.1$ ) and the values of TYJ vs. SZ ( $CD_{jk} = 0.16$ ) and ASJ vs. SGS ( $CD_{jk} = 0.13$ ) for coarse fraction. From the CD values, it is also concluded that significant difference in PAHs composition exists between fine and coarse fraction in all five cities, as well as different sampling sites with TYJ vs. SZ, ASJ vs. SGS excluded. So the study of fine and coarse particulate matter synchronously was essential. Of course, the sites selected could in principle represented different function zones as the diversity of CD values.

### 3.6. Source identification

Since most of PAHs are released due to a variety of combustion processes, their levels in the ambient environment depend on a great extent on a number of factors such as type of fuel, amount of oxygen available for combustion and temperature [45]. Considering the variability in the PAHs levels coupled with the fact that similar assemblages of PAHs can arise from different combustion sources, the identification of the sources may not be easy. Nevertheless, it is worth having an insight into the nature of the sources and their relative contributions to the PAHs levels observed in present study. To achieve this, ratios and principal component analysis (PCA) were used.

#### 3.6.1. Diagnostic ratios analysis

Diagnostic ratios have been a convenient approach to help identify possible emission sources in former studies [1,35,41] although the ratios should be used with much attention as PAH profiles were different from those in the sources and can be altered due to the chemical reaction with other atmospheric pollutants, such as NO<sub>x</sub>, O<sub>3</sub>, etc. [1,8,20]. Diagnostic ratios for PAHs, such as Ind/(Ind + BghiP), Ind/BghiP, BaP/BghiP, BaP/(BaP + Chr), Flu/(Flu + Pyr), Ant/(Ant + Phe), BaA/Chr, BbF/BkF, BeP/(BeP + BaP), Cor/BeP and BghiP/BeP were widely used. As the BeP and Cor were not detected here, the last three ratios were not calculated. Others were calculated in Table 3 on the premise that different PAHs ratios in Table 3 explained different sources.

**Table 2**  
The BaP<sub>eq</sub> concentrations of PAHs at six functional zones in fine fraction.

PAHs	TEF	BaP <sub>eq</sub> concentration (ng m <sup>-3</sup> )					
		RA	RCA	CA	IA	ICA	UBS
Phe	0.001	0.03	0.07	0.09	0.01	0.03	0.02
Ant	0.01	0.18	0.10	0.64	0.01	0.10	0.06
Flu	0.001	0.04	0.56	0.31	0.01	0.12	0.06
Pyr	0.001	0.04	0.58	0.27	0.01	0.11	0.04
BaA	0.1	1.60	19.02	6.4	0.61	5.05	1.92
Chr	0.01	0.16	2.04	0.81	0.08	0.50	0.18
BbF	0.1	2.01	11.52	6.57	0.89	5.67	2.17
BkF	0.1	1.23	3.36	1.64	0.29	4.42	0.61
BaP	1	14.2	48.44	31.71	5.39	47.38	12.16
BghiP	0.01	0.14	0.09	0.05	0.02	0.60	0.04
Ind	0.1	1.03	2.64	1.69	0.48	2.99	0.99
Total		20.66	88.42	50.18	7.80	66.97	18.25
BaP/total (%)		69	55	63	69	71	67
CANPAHs/total (%)		97	96	96	98	97	98



**Table 3**  
Diagnostic ratios of PM-bound PAHs in Liaoning Province in summer and winter.

Diagnostic ratios	Ind/(Ind + BghiP)	BaP/BghiP	Flu/(Flu + Pyr)	Ant/(Ant + Phe)	BaA/(BaA + Chr)
Gasoline engine	0.18 [5,18]	0.5–0.6 [8]	<0.5 [4,8]	0.5 [29]	0.49 [35,12]
Diesel engine	0.35–0.7 [4,5,8,18,35,57]	0.3–0.4 [13]	>0.5 [4,8]	0.35 [29]	0.68 [35,12]
Coal/coke	0.33 [58]	>1.25 [8]	0.53 [57]	–	0.5 [58]
Coal burning	0.56 [5,8,18,35,51]	0.9–6.6 [51]	0.57 [14]	0.24 [29]	0.46 [14]
Non-burned fossil fuels inputs	–	0.58 [20]	–	<0.1 [35]	–
Wood combustion	0.62 [8,20,18,51]	–	0.51 [14]	0.16 [14]	0.43 [20,51]
Natural gas combustion	0.32 [14]	–	0.49 [14]	0.12 [14]	0.39 [14]
Fine (summer, average ± SD)	0.71 ± 0.28	0.46 ± 0.21	0.84 ± 0.08	0.33 ± 0.37	0.32 ± 0.04
Fine (winter, average ± SD)	0.56 ± 0.07	4.72 ± 4.87	0.52 ± 0.03	0.24 ± 0.25	0.50 ± 0.06
Coarse (summer, average ± SD)	0.59 ± 0.27	0.63 ± 0.27	0.93 ± 0.04	0.32 ± 0.31	0.20 ± 0.10
Coarse (winter, average ± SD)	0.61 ± 0.15	1.86 ± 1.02	0.52 ± 0.05	0.43 ± 0.24	0.50 ± 0.05

SD—standard deviation.

For fine fraction, the ratios Ind/(Ind + BghiP) (0.71 in summer and 0.56 in winter), BaP/BghiP (0.46 in summer and 4.72 in winter), Flu/(Flu + Pyr) (0.84 in summer and 0.52 in winter), Ant/(Ant + Phe) (0.33 in summer and 0.24 in winter), BaA/(BaA + Chr) (0.32 in summer and 0.50 in winter) indicated a significant contribution of coal burning in winter and vehicular emissions in summer. It was the same for coarse fraction. Also, the natural gas combustion was one of the sources in winter according to the ratios. For coarse fraction, the main sources were coal combustion in winter and vehicular emissions in summer as the ratios Ind/(Ind + BghiP) (0.59 in summer and 0.61 in winter), BaP/BghiP (0.63 in summer and 1.86 in winter), Flu/(Flu + Pyr) (0.93 in summer and 0.52 in winter), Ant/(Ant + Phe) (0.32 in summer and 0.43 in winter), BaA/(BaA + Chr) (0.20 in summer and 0.50 in winter) were mostly consistent with those by others. Moreover, wood combustion was maybe one source for this fraction because the calculated values all meet the diagnostic ratios including Ind/(Ind + BghiP), Flu/(Flu + Pyr), Ant/(Ant + Phe) and BaA/(BaA + Chr). The strongest seasonality was observed for the BaP/BghiP ratio (its winter and summer ratio was 2.95 for coarse fraction and 10.26 for fine fraction) as a result of the combined higher contribution of coal combustion and enhanced atmospheric degradability during warm time period. Higher values for BaA/Chr indicated that relatively little photochemical processing of the air mass and major contribution from local emissions, whereas lower ratios were reflective of more aged PAHs [47]. In this study, BaA/Chr ratios were higher for winter ( $1.00 \pm 0.27$  for fine fraction,  $0.99 \pm 0.19$  for coarse fraction) than summer ( $0.46 \pm 0.10$  for fine fraction,  $0.25 \pm 0.16$  for coarse fraction). Thus, looking to these ratios one can conclude that the air masses sampled during summer were relatively aged. In addition to this, Lohmann et al. [59] stated that BaA/Chr ratio higher than 0.40 indicated freshly emitted pollution. A ratio much close to 0.40 for summer samples also indicated that major sources of PAHs were not local or the air masses were aged. As explained earlier, BaA/Chr ratio in summer indicated that sampled air masses traveled further from their sources and had higher residence time in the atmosphere [47].

Overall, the results suggested that the major sources of PAHs were coal combustion, vehicular emissions, and wood combustion and natural gas combustion influenced the PAHs concentration to some extent. Vehicular emissions and coal combustion were dominated in summer and winter, respectively. However, in order to identify the exact sources, a study has to be conducted on specific sources of PAHs in this region.

### 3.6.2. Principal component analysis (PCA)

Using PCA, it is possible to simplify the interpretation of complex systems and to reduce the set of variables to few new ones, called factors. Each of these factors can be identified as either an emission source, or a chemical interaction. Many of these factors indicate

more than one possible cause [4]. In addition to use the diagnostic ratios between PAHs, principal component analysis (PCA) was undertaken to further identify the major sources of pollutant emissions for both fine and coarse fraction. In this study, each factor from PCA is associated with a source characterization by its most representative PAHs compounds.

Some PAHs compounds and their combinations were frequently used as source markers such as Flu, Chr and Pyr for diesel exhaust [21,29], Flu, Pyr, BbF and BkF for heavy-duty diesel vehicles [1,4,13], BghiP for gasoline vehicles [4,21,22], Flu and BaP [1,13] or Ant, Phe, Flu and Pyr [4,5,13,12] or NaP and Ant [12] for wood combustion, Ant, Phe, Flu, Pyr, BaA and Chr for coal combustion [4,5,12,22], Phe and Flu [4,12] for coke production, Flu and Pyr [4,5] for oil burning, Ant, Phe, BaP, BghiP and Chr [4] for steel industry emissions.

Results from standardized PAHs concentrations were presented in Table 4. Variables with loading higher than 0.7 were considered relevant in the interpretation of each factor.

For the fine fraction, three factors explaining 96.30% of the data variance were obtained. Factor 1 including Flu, Pyr, BaA, Chr and BbF accounted for 43.58% of the variance. This factor was interpreted as coal combustion sources [10]. Factor 2 grouped Ace, BkF, BaP, DbA, Ind and BghiP. This factor explained 35.67% of the variance and was identified as vehicular emissions [10]. Factor 3 included NaP and Ant. This component accounted for 17.05% of the total variance and was attributed to wood combustion.

For the coarse fraction, two components were identified. Factor 1 was mostly associated with high molecular weight PAHs and accounted for 46.54% of the total variance. BghiP, DbA, Ace, BkF,

**Table 4**  
Factorial weights matrix obtained from PM<sub>2.5</sub> and PM<sub>2.5–10</sub> samples in Liaoning Province.

Variables	PM <sub>2.5</sub>			PM <sub>2.5–10</sub>	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Nap			0.888		0.934
Ace		0.992		0.974	
Phe					
Ant			0.883		0.898
Flu	0.934				0.966
Pyr	0.956				0.952
BaA	0.963				0.863
Chr	0.962				0.917
BbF	0.869			0.730	
BkF		0.827		0.939	
BaP		0.700		0.884	
DbA		0.962		0.986	
BghiP		0.993		0.992	
Ind		0.766		0.903	
Total variance (%)	43.58	35.67	17.05	46.54	45.07
Cumulative (%)	43.58	79.25	96.30	46.54	91.61

Factor loading > 0.7 listed.

Extraction method: principal component analysis.

Rotation method: varimax with Kaiser normalization.

Ind, BaP and BbF were all indicators of vehicular emissions in which BbF and BkF were mostly from diesel powered vehicles while BaA, BaP, BghiP, DbA and Ind were associated from gasoline powered vehicles in this factor [60]. Consequently, this factor was attributed to vehicular emission sources. Several studies received the same conclusion that high molecular weight PAHs indicated vehicular emission sources [1,5,10]. Factor 2 explained 45.07% of the variance, with higher loadings of Flu, Pyr, NaP, Chr, Ant and BaA. These PAHs were components of fossil fuels and a portion of them was associated with combustion sources.

To summarize, it can be inferred from the above analysis that vehicles emission and coal combustion are two principal sources of PAHs for both fine and coarse particulate matter. This is not too unexpected in view of the fact that coal was widely used to meet local heating/energy requirements. In the year of 2005, the consumption of raw coal, crude oil and gasoline were 12116.61, 5410.89 and 357.17 ten thousands of tons in Liaoning Province, accounting for 5.6%, 18.0%, and 7.4% of China, respectively [61]. The results obtained with PCA for both fine and coarse fractions of the particulate matter reinforced the ones obtained from ratios analysis. However, the different categories of sources that have been identified in this study were based on the PAHs source fingerprints found in international literature and not on local profiles of PAHs. Local or regional profiles of PAHs for each type of emitting sources needed to be determined to allow a more accurate identification of the characteristic PAHs for each source type and thus to quantify the contribution from each emitting sources.

#### 4. Conclusions

Fourteen priority polycyclic aromatic hydrocarbons (PAHs) in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were identified and quantified at five cities of Liaoning Province in four seasons in 2004 and 2005 to determine the composition, temporal and spatial distribution and sources.

The total PAHs concentrations in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were in the range of 75.32–1900.89 ng m<sup>-3</sup> and 16.74–303.24 ng m<sup>-3</sup>, respectively. 90% of the PAHs were in the fine fraction with 3-, 4- and 5-rings dominated in both fractions. A strong seasonal trend of PAHs was observed. The fine fraction had a w/s ratio varying from 6.5 to 125.8 and the coarse fraction had a ratio varying from 1.7 to 37.6.

PAHs concentrations in different functional zones changed with the following order: residential/commercial area (1900.89 ng m<sup>-3</sup>) > commercial area (1053.83 ng m<sup>-3</sup>) > industrial/commercial area (923.01 ng m<sup>-3</sup>) > residential area (300.41 ng m<sup>-3</sup>) > urban background sites (227.01 ng m<sup>-3</sup>) > industrial area (75.32 ng m<sup>-3</sup>) for fine fraction as well as the order residential/commercial area (173.24 ng m<sup>-3</sup>) > industrial/commercial area (112.72 ng m<sup>-3</sup>) > commercial area (53.73 ng m<sup>-3</sup>) > urban background sites (48.21 ng m<sup>-3</sup>) > residential area (44.22 ng m<sup>-3</sup>) > industrial area (23.12 ng m<sup>-3</sup>) in coarse fraction, respectively.

The highest total BaP<sub>eq</sub> concentrations in residential/commercial areas were an alarming signal for pollution risks. Similarities of PAHs profiles between two sampling sites within each city and between fine and coarse fraction were also compared by coefficient of divergence revealing that the two sites in each city had dissimilar PAHs species concentrations and significant difference exists between fine and coarse fraction in all five cities.

Results obtained from diagnostic ratios associated with PCA revealed that coal combustion and vehicle emissions were the major sources for both PM<sub>2.5</sub> and PM<sub>2.5-10</sub>. Other sources like gas burning and wood combustion were identified as common sources in these five cities. Local or regional profiles of PM-bound PAHs for

each type of emitting sources needed to be determined for more accurate source identification results. A further study is being conducted for the detailed information of particle as well as gas phase PAHs compositions for both sources and receptors.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.06.107.

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