



Particulate polycyclic aromatic hydrocarbons in the urban Northeast Region of China: Profiles, distributions and sources

Weifang Li^{a,c}, Yue Peng^b, Jianwu Shi^a, Weiguang Qiu^b, Jun Wang^a, Zhipeng Bai^{a,*}

^aState Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

^bLiaoning Provincial Environmental Monitoring Center, Shenyang 110031, China

^cTianjin Academy of Environmental Science, 300191, China

ARTICLE INFO

Article history:

Received 30 June 2010

Received in revised form

31 March 2011

Accepted 1 April 2011

Keywords:

Polycyclic aromatic hydrocarbons

PM₁₀

Ambient concentrations

Distributions

Northeast Region of China

ABSTRACT

In this study, concentrations of polycyclic aromatic hydrocarbons (PAHs) associated with PM₁₀ were measured to examine the status, characteristics and sources of atmospheric PAH pollution in the industrial Northeast Region of China. Mean concentrations of total PAHs were 65.5, 40.0, 73.0 and 436.7 ng m⁻³ in the four seasons respectively. The calculated BaP_{eq} concentrations in winter all exceeded the national standard, imposing serious PAH exposure risk. PAH concentrations varied between the cities, but PAH concentrations in different functional areas within a city did not show significant difference. In general, particulate PAH profiles were dominated by 4- and 5-ring compounds. Elevated proportions of 3-ring PAHs and 5-ring PAHs were found in winter and in summer respectively. Diagnostic ratios and principal component analysis (PCA) were used to identify potential sources of PAHs. Coal combustion activities were the main contributors of particle-associated PAHs in this region.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic pollutants (POPs), primarily derived from incomplete combustion of fossil fuels and biofuels (U.S. National Academy of Sciences, 1983). PAHs were widely studied with focus on their health-related impacts, and many of them were proved or possible mutagens and carcinogens (Ivanstcki et al., 2009; Nisbet and LaGoy, 1992; US EPA, 1984). Atmospheric PAHs present in both particle and gas phases, while carcinogenic species are mainly associated with the particle phase (Dickhut et al., 2000; Zhang et al., 2009). In addition, most of the carcinogenic PAH species are concentrated in the fine size and ultra fine size of particulate matters (Venkataraman et al., 1994). Those particulate matters could be inhaled into the deeper respiratory tract regions (Cecinato et al., 1999). As a result, particulate PAHs has been a serious concern to both scientists and policy makers. In addition to localized risk, PAHs can disperse regionally and intercontinentally through atmospheric transportation (Lohmann et al., 2007). Recently, high levels of atmospheric PAH concentrations and emission rates have been reported in developing countries especially in China (Bourotte

et al., 2005; Sharma et al., 2007; Zhang and Tao, 2009), which has caused health concerns for a large population (Li et al., 2005; Xu et al., 2006).

The Northeast Region of China (NRC) encompasses three big northeastern provinces, i.e. Liaoning, Jilin and Heilongjiang and east area of Inner Mongolia (Fig. 1). This region is bordered by Russia, Mongolia and North Korea to the north, northwest and southeast, respectively. It covers an area of 1,250,000 km² and occupies 13% of the national total land area, with a population of about 120 million. NRC has the earliest heavy industry foundation in China, characterized by resource-reliant leading industries including iron/steel, coal, crude oil, machinery, metallurgy and chemical production. As an important producer of energy and raw material, NRC played an important role in the national economic development and industrialization process. However, the traditional economic growth mode not only depletes the un-reproducible natural resources but also causes severe environmental problems including deteriorated air, water and soil quality. NRC is one of the regions with the highest PAH emission intensity and population-normalized emission in China (Xu et al., 2006), which poses significant health risk for people both within this region and in adjacent areas. Based on the previous knowledge and emerging demand, a region-wide survey of atmospheric PAHs was, for the first time, initiated to fully understand the status and characteristics of PAH pollution, especially focus on the more

* Corresponding author. Tel./fax: +86 22 23503397.

E-mail addresses: liweifang@nankai.edu.cn (W. Li), zbai@nankai.edu.cn (Z. Bai).

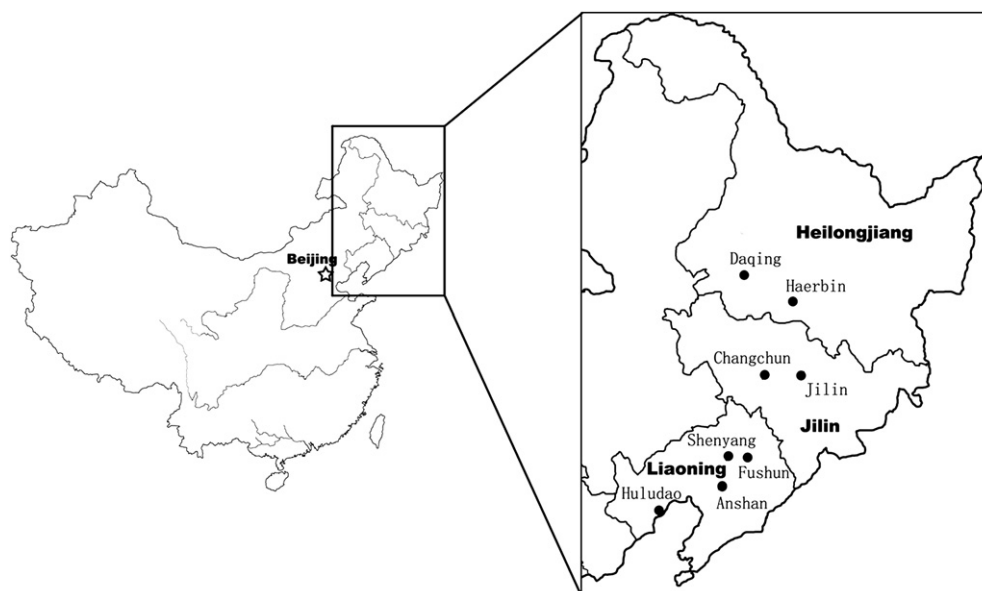


Fig. 1. Location of the Northeast Region and the eight typical industrial cities studied.

carcinogenic particulate PAHs in this heavy industry impacted area. Four intensive field campaigns were performed during April 2008 to January 2009 at 30 urban sites located in eight industrial cities. In this study, observation of the concentrations and profiles of particulate PAHs and their temporal and spatial distributions were presented, major contributing sources are identified and quantified using the multivariate method. This information was vital in terms of pollution control and risk management.

2. Experimental

2.1. Studied area and sampling procedure

The cities within this region are mostly sprawled around local mineral field. Nearly one third of the typical resource cities in China are located in the northeast region. Location and information of the eight typical industrial cities examined in this study were shown in Fig. 1 and Table 1. Most of the studied areas are located on flat plains, except Fushun and Jilin are mountainous. All the cities experience a continental monsoon climate of middle latitude

temperate zone, characterized by a long and chilly winter (about five to six month) when coal are heavily used for heating purpose.

A sampling network composed of 30 urban sites was designed and set with three or five sites in each city (Table 1). The sampling sites were selected from the existing automatic air quality monitoring sites and located in different functional areas, i.e. industrial, residential, cultural, mixed and relatively clean areas. Sampling devices were placed on rooftops of two- or three-story monitoring buildings. The sampling inlets were located approximately 8–12 m above the ground level. Four intensive field campaigns were carried out in the spring (April 15–20, 2008), summer (July 21–26, 2008), autumn (October 10–16, 2008), and winter (January 12–17, 2009). The seasonal differences in ambient temperature were large, with the minimum temperature (–5–20 °C) in January and the maximum temperature in July (20–26 °C). Air sampling was almost simultaneously conducted at the 30 sites in each campaign. The 24 h integrated PM₁₀ (aerodynamic diameter <10 μm) samples were taken continuously for five days.

Particulate PAHs were captured on prebaked (800 °C, 3 h) quartz-fiber filters (Φ90 mm, Pall Life Sciences, USA) using median-volume PM samplers (TH-150CIII, China) operated at a flow rate of

Table 1

Description of the eight cities examined in this study.

City	Location	Urban area	Population	Main industry	Sampling site ^a
Shenyang	41°11'–43°02'N, 122°25'–123°48'E	3945 km ²	7.8 million	Equipment manufacturing, metal smelting, medical	Industrial (2), residential (1), cultural (1), clean site (1)
Fushun	41°41'–42°38'N, 123°39'–125°28'E	675 km ²	1.4 million	Coal mining, petrochemical, fine chemicals, aluminum	Industrial (1), residential(2)
Anshan	40°27'–41°34'N, 122°10'–123°13'E	624.3 km ²	1.3 million	Iron and steel, minerals processing	Industrial (1), residential (2)
Huludao	39°59'–41°12'N, 119°12'–121°02'E	2303 km ²	1.6 million	Petrochemical, equipment manufacturing, zinc	Industrial (1), residential (2)
Changchun	43°05'–45°15'N, 124°18'–127°02'E	4906 km ²	4.9 million	Automobile, medical, food, photoelectronic	Industrial (1), residential (2), cultural (1), clean site (1)
Jilin	42°31'–44°40'N, 125°40'–127°56'E	3636 km ²	2.4 million	Petrochemical, metallurgy, automobile, carbon production	Industrial (1), residential(1), clean site(1)
Harbin	44°04'–46°40'N, 125°42'–130°10'E	7086 km ²	4.8 million	Equipment manufacturing, medical, food, petrochemical	Industrial (1), residential(2), cultural(1), mixed site(1)
Daqing	45°46'–46°55'N, 124°19'–125°12'E	5107 km ²	1.2 million	Oil extraction, petrochemical	Industrial (2), mixed site(1)

^a With the number of this type of site in parentheses.

100 Lpm. All the samplers were checked and calibrated before field operations. Field blank filters were collected with the same manner as ambient samples but without air flow. The exposed filters were wrapped in aluminum foil and stored below -15°C until extraction. A total of 700 aerosol samples were analyzed for PAH concentrations.

2.2. PAH analysis

The seventeen PAHs measured in this study included naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorine (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DBA), benzo(g,h,i)perylene (BghiP), indeno(1,2,3-cd)pyrene (IcdP), and coronene (COR). NAP, ACE and ACY existed predominantly in the vapor phase, and their concentrations were generally below the method detection limits in this study. Those three PAH compounds were excluded for further data analysis.

Detailed description of the sample extraction, analytical procedure, and quality control were given by Hu et al. (2007). Briefly, filter aliquots were extracted ultrasonically with dichloromethane, concentrated using a rotary evaporator, purified with silica chromatography column, and finally adjusted to 1 ml under a gentle nitrogen stream. GC/MS analyses were performed on a 6890N GC coupled with 5975I mass selection detector and 7683B autoinjector (Agilent Technologies, Palo Alto, CA, USA). The chromatographic separations were carried out on a DB-5MS column ($30\text{ m} \times 0.25\text{ mm i.d.}, 0.25\text{ }\mu\text{m}$ film thickness) using helium (1 mL min^{-1}) as the carrier gas. Identification of individual PAHs was based on comparison between the GC retention times coupled with mass spectra of PAHs in samples and pure PAH standards. Quantification of 17 PAH compounds was performed using the selected ion monitoring (SIM) mode. PAH concentrations were determined based on the standard calibration curve and the peak area of each PAH compound. The method detection limits for the analytical method ranged from 0.039 (BkF) to 0.113(FLO) ng m^{-3} , based on 24 h air sampling with a 100 Lpm flow rate. The coefficients of variation (RSD%), evaluated by 7 parallel measurements of the standard solution, ranged from 3.6% (IcdP) to 9.5% (FLO). These results for individual PAHs were shown in supporting information. Most of the target compounds were not detected in both the field and the laboratory blank filters.

2.3. Statistical analysis

Principal components analysis (PCA) is commonly used as an exploratory tool to identify the major sources of PAHs and to select statistically independent source tracers (Guo et al., 2003; Harrison et al., 1996; Larsen and Baker, 2003; Zuo et al., 2007). PCA was employed in this study to identify possible sources of particulate PAHs. The multivariate and other statistical analysis including hierarchical cluster and correlation analysis were performed using the statistical software SPSS 13.0.

3. Results and discussion

3.1. Seasonal variation of PAH concentrations

Concentrations of total and individual PAHs in PM_{10} during each sampling season were shown in Table 2. Total PAH concentrations were in the range of 16.3–168.4 ng m^{-3} in spring, 16.3–79.2 ng m^{-3} in summer, 28.5–121.7 ng m^{-3} in autumn and 152.1–712.1 ng m^{-3} in winter, with an average of 65.5, 40.0, 73.0 and 436.7 ng m^{-3} , respectively. The winter to summer ratios of total PAH concentrations ranged between 5.0–14.5, which were in accordance with results reported by other studies in Hongkong (Guo et al., 2003), Birmingham (Harrison et al., 1996) and Atlanta (Li et al., 2009). The elevated particulate PAH concentrations during the winter time can be attributed to: (a) increased emissions from heating sources; (b) shift of gas/particle partitioning toward the particulate phase induced by low atmospheric temperature; (c) reduced photochemical degradation of some PAHs by solar radiation in winter. In contrast, the lowest concentrations in summer were attributable to absence of seasonal sources (i.e. residential heating, cold start of vehicles), higher percentage in vapor phase, wash out effect, and photochemical degradation.

The winter to summer ratio of individual PAHs ranged from 1 to 52, indicating significant seasonal variations of individual PAHs. In the studied areas, the main difference between winter and other seasons was a great deal of coal consumption for heating in winter, which brought severe PAH contamination. The seasonal distributions of BbF and BkF were totally different from those of other PAH species. BbF often had higher concentrations in autumn while the concentration levels of BkF were rather stable in various seasons. This observation suggested that major sources for BbF and BkF were other than coal combustion such as traffic. The two largest winter/summer ratios were found for PYR(52) and FLA(47) which exhibiting

Table 2
Statistical summary of particulate PAH concentrations (ng m^{-3}) measured in the four intensive campaigns in the urban Northeast Region of China: mean (minimum–maximum).

Compound	Spring (N = 175 ^a)	Summer (N = 173)	Autumn (N = 174)	Winter (N = 175)
FLO	0.4 (0.2–0.6)	0.3 (0.2–0.6)	0.5 (0.1–1.3)	5.6 (2.4–10.3)
PHE	4.1 (1.3–10.0)	2.8 (0.9–8.7)	2.9 (1.1–7.5)	88.5 (33.0–155.7)
ANT	4.3 (1.4–10.2)	3.2 (1.0–11.0)	4.1 (1.6–10.5)	37.1 (28.1–46.9)
FLA	5.9 (1.7–11.0)	2.2 (0.9–5.3)	4.9 (2.1–7.6)	98.1 (23.9–176.0)
PYR	4.4 (1.3–9.6)	1.5 (0.8–3.0)	4.3 (1.9–6.9)	78.0 (19.5–135.3)
BaA	9.4 (1.4–24.9)	2.4 (0.9–3.8)	11.3 (1.7–25.5)	27.0 (8.0–44.4)
CHR	6.9 (1.3–24.0)	2.3 (0.8–3.7)	8.6 (3.2–16.0)	27.0 (8.0–44.5)
BbF	6.8 (1.4–21.8)	8.7 (1.1–24.9)	10.7 (4.2–17.2)	9.3 (6.7–13.7)
BkF	5.4 (1.5–15.3)	4.7 (0.8–10.7)	5.3 (3.2–7.9)	6.1 (3.8–9.2)
BaP	5.1 (0.8–13.9)	3.4 (0.7–7.9)	4.9 (2.1–10.4)	19.8 (4.7–33.5)
IcdP	7.5 (1.5–20.3)	5.1 (0.6–11.9)	8.3 (2.1–16.0)	16.3 (3.9–21.5)
DBA	0.6 (0.1–2.5)	0.3 (0.1–0.6)	0.7 (0.2–1.6)	3.2 (0.4–5.2)
BghiP	3.5 (0.7–11.7)	2.5 (0.3–5.5)	5.0 (2.1–9.7)	14.8 (3.6–20.8)
COR	1.2 (0.2–4.4)	0.7 (0.2–1.6)	1.7 (0.5–4.7)	6.6 (0.9–8.9)
BaPeq ^b	8.8 (1.7–24.5)	5.9 (1.2–13.7)	9.3 (3.7–18.1)	29.7 (7.9–49.0)
Σ 14PAHs	65.5 (16.3–168.4)	40.0 (16.3–79.2)	73.0 (28.5–121.7)	436.7 (152.1–712.1)

^a N: sample size.

^b BaP equivalent concentrations.

a stronger seasonal fluctuating than other species. One reason for this finding was that partitioning of the two medium volatility compounds was more sensitive to the change in temperature, as several studies have proved (Odabasi et al., 1999; Bi et al., 2003). High emission rates of the two compounds from residential coal combustion could be another reason.

BaP concentrations during non-heating seasons were 0.7–13.9 ng m⁻³, and an average of 4.5 ng m⁻³. The values were generally lower than the national standard of 10 ng m⁻³, but exceeded WHO annual maximum limit of 1 ng m⁻³. However, BaP concentrations in the heating season (4.7–33.5 ng m⁻³, average of 19.8 ng m⁻³) were about 3 to 5 times higher than those in non-heating seasons. For better quantification of aerosol carcinogenicity related to whole PAH fraction, BaP equivalent concentrations (BaP_{eq}) were calculated based on the toxic equivalent factors (TEFs) of individual compounds (Nisbet and LaGoy, 1992). The mean BaP_{eq} values were 8.8, 5.9, 9.3 and 29.7 ng m⁻³ in the spring, summer, autumn and winter, respectively. It clearly showed residential coal heating increased considerably the PAH exposure risk. The relative contributions of individual PAHs to BaP_{eq} were shown in Fig. 2, and similar profiles were observed in different sampling periods. BaP dominated the ambient particulate BaP_{eq} levels, with percentages in the range of 52.7–65.6%. This was in agreement with the previous studies (Lodovici et al., 2003). The sum of the other five carcinogens BaA, BbF, BkF, IcdP and DBA contributed 31–45% to BaP_{eq}.

3.2. Comparison of PAH concentrations between cities and sites

PAH concentrations varied considerably among the cities. Concentrations of selected and total PAHs averaged for the whole sampling periods in each city are shown in Table 3. By the use of cluster analysis, the 8 cities were divided into three groups corresponding to high, medium and low PAH levels. The highest PAHs concentrations were found in Fushun and Jilin. Both cities are heavily impacted by industries with high emissions intensity such as coal and coke production in Fushun, ferroalloy, charcoal and aluminum production in Jilin. Topography of the two cities is alike, being surrounded on three sides by mountains, which is unfavorable for pollutants dispersion. The lowest concentrations were found in Daqing, a city principally affected by petroleum industry. The absence of other heavy industry and its vast territory were contributing factors to the low PAH levels in Daqing. Medium and

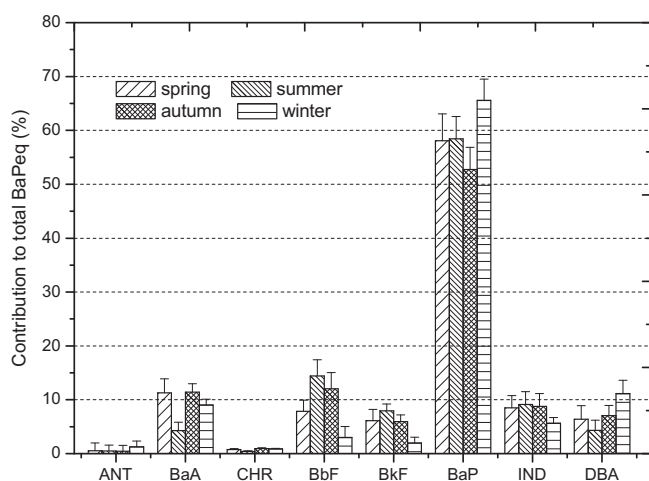


Fig. 2. Relative contributions of individual PAHs to particulate BaP_{eq}.

Table 3

Concentrations (ng m⁻³) of selected and total PAHs averaged for the whole sampling periods in each city.

city	ANT	CHR	BbF + BkF	BaP	BghiP + COR	Total PAHs
Fushun	12.99	21.45	28.26	16.31	16.72	268.83
Jilin	13.98	18.81	21.83	13.66	11.29	245.64
Harbin	13.24	10.14	12.00	7.60	8.83	148.27
Huludao	9.20	10.23	10.93	7.58	9.52	137.73
Changchun	12.45	7.99	9.31	6.70	8.35	134.47
Shenyang	9.89	10.65	14.26	6.98	9.42	126.57
Anshan	11.22	6.71	11.11	5.46	5.87	102.68
Daqing	14.47	3.71	6.03	2.27	2.33	66.02

comparable PAH levels were found in the three provincial capital cities—Shenyang, Changchun, and Harbin—all with a high population density. Anshan, a city heavily impacted by iron and steel industry, had the second lowest PAH concentrations. Being one of the largest iron and steel companies, Ansteel has implemented rigorous pollutant emission controls, which substantially reduces the amount of pollutants including PAHs discharged into the atmosphere. Generally, the levels of PAH contamination in these cities were closely related to local emission intensity, meteorological and topographic situations that determine the extent of pollution diffusion.

Comparison of PAH concentrations in different functional areas within one city provided some insight on the spatial distribution as well as local factors influencing PAH pollution. Fig. 3 used the three types of sites—industrial, cultural and relatively clean sites in Shenyang as an example to show PAH distributions over one city. The industrial site is located in the west of the urban area, with chemical plants and a big monosodium glutamate factory situated to the south, north and west of this site. The cultural site is situated on campus of Northeastern University lying in the south of the city. The clean site lying in the north of the city, is situated in the scenery area of Beiling park with a main traffic road to the east. Locations of the monitoring sites were given in supporting information. In the summer campaign (Fig. 3a), measured PAH concentrations at the three locations were rather similar. This result suggested a relatively uniform spatial distribution and similar principal emission sources in different urban areas. Meanwhile, the distinctly higher levels of BaA at the cultural site and BbF at the clean site indicated influences of special local sources, such as diesel vehicles at the clean site due to its adjacent to a main road. In the winter campaign (Fig. 3b), the PAH distribution patterns were somewhat different from those in summer. PAH concentrations at the industrial site were at higher levels compared with other sites, while PAH levels between the cultural and clean sites kept unanimous with each other. During both of the summer and winter campaigns, the dominant wind direction over the city was from southwest. The elevated industrial PAH concentrations, especially coal combustion markers, i.e. PHE, FLA and PYR, were consistent with stronger coal consumption activities in industrial plants.

3.3. PAH profiles

The proportions of various PAHs (3 to 7 ring) to the total PAH concentrations were calculated to show the seasonal variations in PAH profiles (Fig. 4). In general, 4- and 5-ring PAHs were the most abundant compounds constituting 63.6–78.2% of total PAHs, whereas 3-ring and 6-7-ring PAHs were less abundant. Such PAH profile was similar to that found in a study conducted in Taiwan (Fang et al., 2006). Obvious seasonal differences in PAH profiles could also be seen. 5-ring PAHs were predominant in summer accounting for an average of 50.8% of total PAHs. The PAH profiles in spring and autumn were characterized by analogous abundances of

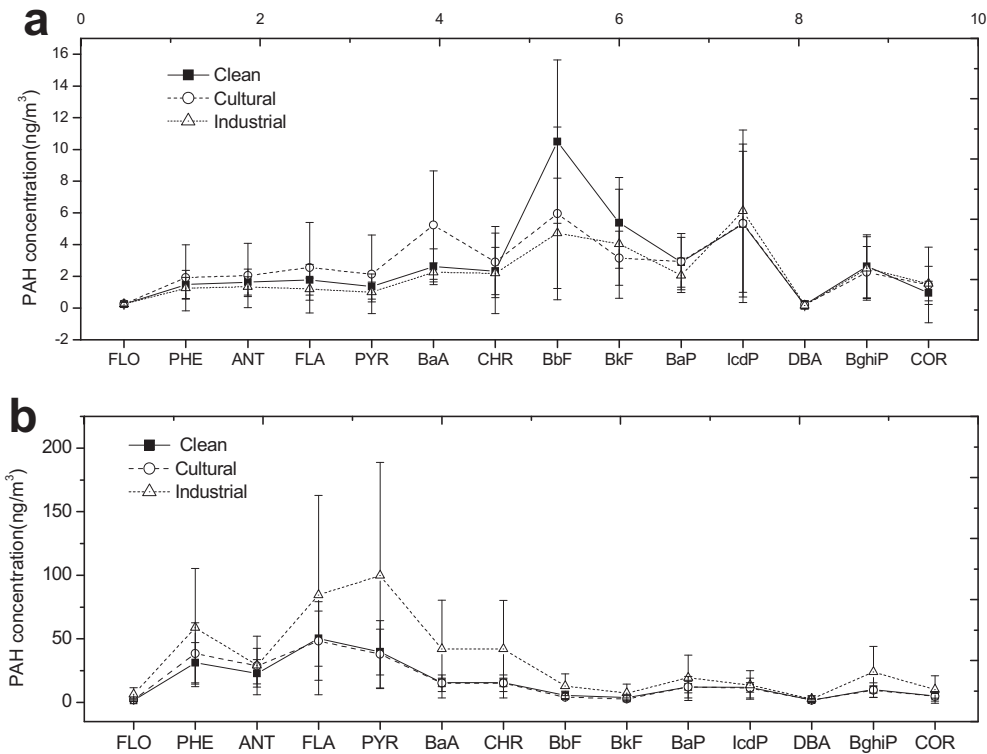


Fig. 3. Distributions of PAH concentrations in different functional areas within a city, taking Shenyang as an example.

4- and 5-ring PAHs. The winter PAH profile was distinguished by elevated proportions of lower molecular weight PAHs (3-, 4-ring) and significantly decreased proportions of higher molecular weight PAHs (5-, 6-, 7-ring). The seasonal variation in ambient temperature contributed much of the observed variation in PAH profiles. The temperature dependency of vapor pressure was controlling gas/particle partitioning of PAH compounds (Odabasi et al., 1999).

For an evaluation of the temperature effects on PAH profiles, relationships between relative abundances of various PAHs and ambient temperature were studied. Representative results at Shenyang were shown in Fig. 5, and similar tendency could be observed at other cities. The figure showed that the relative abundances of 3- and 4-ring PAHs in total PAH concentrations

generally decreased with temperature increasing, presenting a negative correlation with ambient temperature. With higher vapor pressure and volatility, gas-particle partitioning of these compounds was more sensitive to the temperature changing. The increased particle phase partitioning under low ambient temperature resulted in high proportions of volatile PAHs in aerosols during winter season. In addition, residential coal emission was also enriched by lower molecular weight PAHs (i.e. PHE, FLA, PYR, etc.) (Chen et al., 2004). In contrast, the mass percentages of 5-ring PAHs increased with temperature, reaching to the maximum values in summer. The reason may be those compounds were associated primarily with particulates, and will not volatilize to the gas phase in summer as it was for compounds with lower molecular weights. The 6–7 ring PAHs contributed less than 10% to total PAH concentrations, and did not vary significantly with temperature.

The differences in PAH profiles across the cities were small with the exception of Daqing, suggesting a similarity in PAH sources. Although PAHs may be contributed from many sources, coal, coke ovens, vehicles and biomass burning have been considered as major sources in this region (Xu et al., 2006). Representative PAH profiles for Jilin, Shenyang and Daqing were compared in Table 4. Differing from other cities, the composition of particulate PAHs in Daqing atmosphere were primarily consisted of 3-ring PAHs constituting 36.7–48.3% of total PAH concentrations, with PHE and ANT being the most abundant compounds in various sampling periods. Daqing had the largest oil field in China, and the unique composition of PAHs could be related to crude oil exploitation and petroleum industry. There was a strong resemblance of PAH profiles between cities during both of the cold and warm seasons. FLA was the most abundant compound in winter and BbF was the most abundant compound in summer. This result could be explained by the assertion that influences of local emissions and processes were offset by residential coal burning in winter and by the high temperature effect in summer. In spring and autumn, the

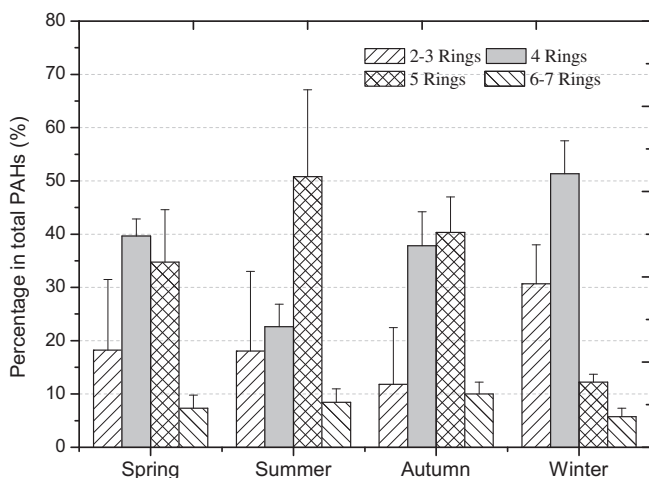


Fig. 4. Seasonal distribution of various PAHs grouped by ring size.

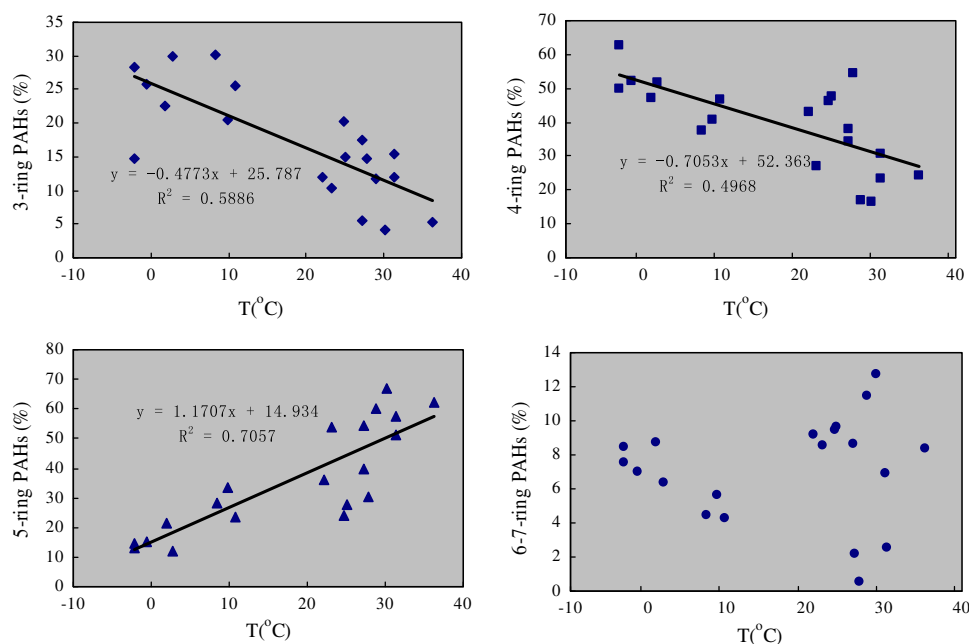


Fig. 5. Relationship between relative concentrations of various PAHs and ambient temperature.

predominant compound varied with locations, indicating the differing extents of influence of various sources in these cities.

3.4. Potential sources of PAHs

The diagnostic ratios between PAHs are useful indicators of PAH sources. The ratio of IcdP/(IcdP + BghiP) has been used to distinguish PAH emission sources. Ratios of 0.18, 0.37 and 0.56 were reported for gasoline vehicles, diesel vehicles and coal burning, respectively (Grimmer et al., 1983). In this study, IcdP/(IcdP + BghiP) ratios averaged for each campaign were 0.65, 0.65, 0.58 and 0.52 in the four seasons respectively, indicating a predominant contribution from coal combustion sources. As one of the heavy industrial base in China, energy consumption in NRC heavily relies on coal. It appears that coal is the most important energy as well as PAH source in the urban Northeast Region.

Source analysis with PCA in this study was limited to such species as CHR, BaA, BbF, BkF, BaP, IcdP and BghiP. These species

were largely associated with particles in the environment. PCA procedure was run using those PAH concentrations measured in non-heating periods to avoid the influence of seasonal source. Three principal components were identified for each city, which accounted for 85–96% of the total variability. Representative results for Shenyang, Jilin and Daqing were presented in Table 5. Profiles of the factor loadings and specific indicative PAH species were used to infer the factors obtained and to distinguish possible PAH sources, such as CHR and BaA for coal combustion, BaP and BghiP for coke production, BbF and BkF for diesel-powered vehicles, BghiP and COR for petrol-powered cars (Duval and Friedlander, 1981).

For Shenyang, factor 1 had high loading on BghiP and IcdP, with IcdP/(IcdP + BghiP) ratio (~ 0.51) calculated from the factor loading similar to those for coal combustion. Factor 1 explained about 35% of the total variance. Factor 2 had high loading on BbF and BkF, indicative of vehicular emissions. Similar loading profiles were also found in factor 2 for Jilin and Daqing. Factor 3 was heavily loaded by

Table 4

Proportions of individual PAH to the total PAHs concentrations for Jilin, Shenyang and Daqing.^a

PAHs	Spring			Summer			Autumn			Winter		
	Jilin	Shenyang	Daqing	Jilin	Shenyang	Daqing	Jilin	Shenyang	Daqing	Jilin	Shenyang	Daqing
FLO	0.2	0.6	1.4	0.6	0.7	1.7	0.3	0.9	2.4	1.3	1.1	1.6
PHE	3.2	5.5	23.2	3.5	4.4	22.4	2.0	5.0	14.2	22.5	16.0	21.7
ANT	3.2	6.0	23.7	3.7	4.8	23.4	2.9	7.3	20.0	6.8	8.6	21.9
FLA	8.0	9.3	17.3	3.9	4.9	13.2	6.2	9.3	9.5	24.6	19.4	15.7
PYR	6.4	7.6	6.1	3.0	3.9	6.6	5.7	7.9	7.5	18.1	18.4	12.8
BaA	15.4	17.5	7.9	6.6	9.4	5.4	10.9	8.7	5.0	6.4	7.6	5.2
CHR	10.1	9.4	4.5	6.4	7.1	5.1	13.1	11.4	7.8	6.4	7.6	5.2
BbF	9.3	12.5	3.3	23.2	19.4	6.6	14.1	18.1	10.7	1.9	2.3	4.4
BkF	8.4	7.5	3.4	16.6	12.1	4.7	6.5	7.9	6.1	1.3	1.5	2.5
BaP	11.5	7.2	3.1	10.0	7.9	4.6	6.7	6.2	4.3	4.0	4.7	3.1
IcdP	16.8	9.7	3.4	14.6	15.0	3.5	13.1	8.7	5.7	2.7	5.4	2.6
DahA	0.9	0.6	0.2	0.7	0.5	0.6	0.9	0.6	0.3	0.6	0.8	0.3
BghiP	5.2	5.3	1.5	5.7	6.7	1.9	5.7	6.4	5.1	2.6	4.8	2.4
COR	1.3	1.6	0.8	1.4	3.2	0.9	1.9	1.6	1.3	1.0	2.3	0.6

^a The eight cities in this program were divided according to profile similarity into three groups: group 1 (Jilin and Fushun), group 2 (Shenyang, Changchun, Harbin, Anshan, Huludao) and group 3 (Daqing).

Table 5
Rotated component matrix of particulate PAHs collected in the nonheating season for Shenyang, Jilin and Daqing.

	Shenyang			Jilin			Daqing		
	F1	F2	F3	F1	F2	F3	F1	F2	F3
CHR	0.63	0.55	0.44	0.87	0.08	0.28	0.15	0.09	0.98
BaA	0.12	0.33	0.93	0.90	0.10	0.17	0.82	0.41	0.31
BbF	0.21	0.92	0.22	0.30	0.91	−0.10	0.74	0.63	0.08
BkF	0.20	0.86	0.27	−0.05	0.86	0.40	0.43	0.88	0.10
BaP	0.54	0.63	0.44	0.45	0.11	0.86	0.58	0.65	0.44
BghiP	0.91	0.27	0.15	0.67	0.18	0.65	0.73	0.60	0.08
IcdP	0.93	0.13	0.05	0.81	0.19	0.41	0.89	0.35	0.19
Variance (%)	35.58	35.38	19.88	42.14	23.77	23.13	44.39	31.95	18.69
Cumulative (%)	35.58	70.96	90.84	42.14	65.91	89.04	44.39	76.34	95.03

Extraction method: Principal component analysis.

Rotation method: Varimax with Kaiser normalization.

Factor loading ≥ 0.8 are bold faced.

BaA, which were used to indicate coal combustion or natural gas combustion (Simcik et al., 1999). It was difficult to judge this factor without additional information.

For Jilin, PAHs with high factor loading for Factor 1 were CHR and BaA, which are typical markers for coal combustion. Factor 1 explained 42% of the variance. Factor 3 had high loading on BaP and BghiP, which might be associated with coke production (Duval and Friedlander, 1981).

For Daqing, Factor 1 was featured in high loading on BaA and IcdP, and moderate loading on BbF and BghiP. This profile seemed to be a combination of both coal combustion (BaA, BghiP) and traffic oil (BbF, IcdP). Factor 1 explained 44% of the total variance. Factor 3 was simply correlated with CHR, a marker for coal combustion.

The PCA results indicated that coal combustion and vehicular emissions could be the significant PAH sources in this region.

4. Conclusions

To characterize the atmospheric PAHs associated with particulate matter, four intensive observation campaigns were performed between April 2008 and January 2009 at 30 urban sites in the Northeast Region, the heavy industrial base of China. The mean concentrations of total PAHs were 65.5, 40.0, 73.0, and 436.7 ng m^{−3} in spring, summer, autumn and winter, respectively. A clear seasonal pattern was observed for all PAHs except BbF and BkF, with the maximum concentrations in winter and the minimum in summer. Generally, 4- and 5-ring PAHs were the most abundant compounds. PAH profiles in summer were most enriched by 5-ring PAHs and 3-4 ring PAHs were predominant in winter. Increased emissions from residential heating, ambient temperature changing, and PAH volatility were the major reasons for such seasonal variations. BaP concentrations in the heating season generally exceeded the national standard of 10 ng m^{−3}, posing the highest health risk of PAHs exposure. The differences in particulate PAH profiles between the cities were small with the exception of the petroleum impacted Daqing, indicating a similarity in PAH sources. Coal combustion and vehicular emissions, identified by isomer ratios and PCA, could be the major PAH sources in the urban Northeast Region of China. Investigation of PAH source profiles in this region is performed and will be included in future paper.

Acknowledgements

Thanks are given to the personnel at Liaoning Provincial Environmental Monitoring Center for their vital assistance in the field campaign. This project is supported by the Commonweal Project of National Environment Protection (200709013) and the National Basic Research Program (973) of China (No. 2011CB503801).

Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2011.04.004.

References

- Bourotte, C., Forti, M.C., Taniguchi, S., Bicego, C.M., Lotufo, P.A., 2005. A wintertime study of PAHs in fine and coarse aerosols in São Paulo city, Brazil. *Atmos. Environ.* 39, 3799–3811.
- Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J.M., 2003. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos. Environ.* 37, 289–298.
- Cecinato, A., Marino, F., Di Filippo, P., Lepore, L., Possanzini, M., 1999. Distribution of n-alkanes, polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particles. *J. Chromatogr.* 826, 255–264.
- Chen, Y., Bi, X., Mai, B., Sheng, G., Fu, J., 2004. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* 83, 781–790.
- Dickhut, R.M., Canuel, E.A., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., Edgcombe, G., Gaylor, M.O., Macdonald, H., 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. *Environ. Sci. Technol.* 34, 4635–4640.
- Duval, M.M., Friedlander, S.K., 1981. Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmosphere: application of a CMB with First Order Decay. U.S. EPA Report EPA-600/2-81-161, Washington, DC.
- Fang, G.C., Wu, Y.S., Chen, J.C., Chang, C.N., Ho, T.T., 2006. Characteristic of polycyclic aromatic hydrocarbon concentrations and source identification for fine and coarse particulates at Taichung Harbor near Taiwan Strait during 2004–2005. *Sci. Total Environ.* 366, 729–738.
- Grimmer, G., Jacob, J., Naujack, K.W., 1983. Profile of the polycyclic aromatic compounds from crude oils. 3. Inventory by GC, GC/MS-PAH in environmental materials. *Fresenius Zeitschrift Fur Analytische Chemie* 316, 29–36.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, S.C., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* 37, 5307–5317.
- Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ. Sci. Technol.* 30, 825–832.
- Hu, Y., Bai, Z., Zhang, L., Wang, X., Zhang, L., Yu, Q., Zhu, T., 2007. Health risk assessment for traffic policemen exposed to polycyclic aromatic hydrocarbons (PAHs) in Tianjin, China. *Sci. Total Environ.* 382, 240–250.
- Ianistcki, M., Dallarosa, J., Sauer, C., Teixeira, C.E., da Silva, J., 2009. Genotoxic effect of polycyclic aromatic hydrocarbons in the metropolitan area of Porto Alegre, Brazil, evaluated by *Helix aspersa* (Müller, 1774). *Environ. Pollut.* 157, 2037–2042.
- Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: current and future research directions. *Environ. Pollut.* 150, 150–165.
- Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ. Sci. Technol.* 37, 1873–1881.
- Li, X., Guo, M., Tao, S., Li, B., Cao, J., Wang, X., Liu, W., Xu, F., Wu, Y., 2005. Population exposure to PAHs in Tianjin area. *Acta Sci. Circum.* 25, 989–993.
- Li, Z., Sjodin, A., Porter, E.N., Patterson, D.G., Needham, L.L., Lee, S., Russell, A.G., Mulholland, J.A., 2009. Characterization of PM_{2.5}-bound polycyclic aromatic hydrocarbons in Atlanta. *Atmos. Environ.* 43, 1043–1050.
- Lodovici, M., Venturini, M., Marini, E., Grechi, D., Dolari, P., 2003. Polycyclic aromatic hydrocarbons air levels in Florence, Italy, and their correlation with other air pollutants. *Chemosphere* 50, 377–382.
- Nisbet, C., LaGoy, P., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* 16, 290–300.
- Odabasi, M., Vardar, N., Sofuoglu, A., Tasdemir, Y., Holsen, T.M., 1999. Polycyclic aromatic hydrocarbons_PAHs in Chicago air. *Sci. Total Environ.* 227, 57–67.

- Sharma, H., Jain, V.K., Khan, Z.H., 2007. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in the urban environment of Delhi. *Chemosphere* 66, 302–310.
- Simcik, M.F., Eisenreich, S.J., Lioy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* 33, 5071–5079.
- US EPA, 1984. Health effects assessments for polycyclic aromatic hydrocarbons (PAHs). US Environmental Protection Agency (EPA), Environmental Criteria and Assessment Office, EPA 549/1-86-013, Cincinnati.
- U.S. National Academy of Sciences, 1983. In: Committee on Biological Effects of Atmospheric Pollution: Particulate Polycyclic Organic Matter. U.S. Government Printing Office, Washington, DC.
- Venkataraman, C., Lyons, J.M., Friedlander, S.K., 1994. Size distribution of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. *Environ. Sci. Technol.* 28, 555–562.
- Xu, S., Liu, W., Tao, S., 2006. Emission of Polycyclic Aromatic Hydrocarbons in China. *Environ. Sci. Technol.* 40, 702–708.
- Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* 43, 812–819.
- Zhang, S., Zhang, W., Wang, K., Shen, Y., Hu, L., Wang, X., 2009. Concentration, distribution and source apportionment of atmospheric polycyclic aromatic hydrocarbons in the southeast suburb of Beijing, China. *Environ. Monit. Assess.* 151, 197–207.
- Zuo, Q., Duan, Y., Yang, Y., Wang, X., Tao, S., 2007. Source apportionment of polycyclic aromatic hydrocarbons in surface soil in Tianjin, China. *Environ. Pollut.* 147, 303–310.