



## Characterization of PM<sub>10</sub> fraction of road dust for polycyclic aromatic hydrocarbons (PAHs) from Anshan, China

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### ARTICLE INFO

#### Article history:

Received 17 September 2008

Received in revised form 17 March 2009

Accepted 13 May 2009

Available online 21 May 2009

#### Keywords:

Road dust

Polycyclic aromatic hydrocarbons

Diagnostic ratios

Principal component analysis

### ABSTRACT

Nineteen road dust samples were collected during 2005 in different parts of the urban area of Anshan, Liaoning Province, China, and 11 polycyclic aromatic hydrocarbons (PAHs) species were quantitatively analyzed using GC–MS. The results indicated that the total average concentration of PAHs over the investigated sites ranged from 48.73 to 638.26  $\mu\text{g/g}$ , with a mean value of 144.25  $\mu\text{g/g}$ , higher than the concentrations measured in previous studies. PAHs concentrations were higher with high molecular weight homologues (4–6 rings PAHs), accounting for 83.24–96.98%, showing combustion of petroleum fuels was a potential source. Organic carbon in road dust was considered one of the important factors that influenced the concentrations of PAHs in this study, and it was found that concentrations of total PAHs were correlated with those of organic carbon in road dust. The results of diagnostic ratios analysis showed traffic emission (gasoline or diesel) was one of the most important sources of road dust PAHs. Principal component analysis (PCA) indicated that the major sources of road dust PAHs might be emission from traffic, steel industry, cooking and coal combustion.

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## 1. Introduction

Substantial researches show the fugitive dust (or geological dust) is a major contributor to ambient particulate matter in urban areas [1–14]. Paved road dust is an important type of fugitive dust. This kind of dust is chemically similar to the primary portion of the atmospheric aerosol in many aspects, and has a dynamic relationship with atmospheric aerosol by resuspension into and redeposition from the atmosphere [15].

In China, most studies have focused on heavy metal elements contained in road dust, while the available data or relative researches on PAHs in road dusts are quite limited. On urban road surfaces, PAHs from various origins (e.g. weathered materials of road surfaces, automobile exhaust, lubricating oils, gasoline, diesel fuel, tire particles, construction materials and deposited materials) are present as road dust [16]. Moreover, some road dust PAHs will return to the atmosphere by evaporation or wind raise [17].

Liu et al. [18] collected road dust samples from central Shanghai in winter (January) and summer (August), respectively, and analyzed the 16 PAHs in the United States Environmental Pro-

tection Agency (USEPA) priority pollutants list, finding that road dust PAHs in central Shanghai mainly a mixture from traffic and coal combustion. Hassanien and Abdel-Latif [19] collected road dust samples and analyzed PAHs in 17 sites over Greater Cairo, Egypt, and concluded that vehicular traffic, industrial emissions and the incomplete combustion of open waste burning were the main sources of road dust PAHs. Furthermore, PAHs concentration in road dust was found to vary with the distance from the source of pollution [20]. Butler et al. [21] have demonstrated higher benzo(a)pyrene (BaP) concentrations in road dust near complex road interchanges than those in remote areas.

In this study, a road dust sampling campaign was conducted in Anshan, an important iron and steel city in northeastern China. The objectives of this study were (1) to determine the concentration, distribution, carcinogenic risk of road dust PAHs in the urban area of Anshan; (2) to elucidate potential sources of road dust PAHs; (3) to establish an environmental evaluation and serve as essential information for future study, such as health risk assessment.

## 2. Materials and methods

### 2.1. Study area description

Anshan is the third largest city in Liaoning province of China. Situated in the central area of the province, Anshan is about 92 km

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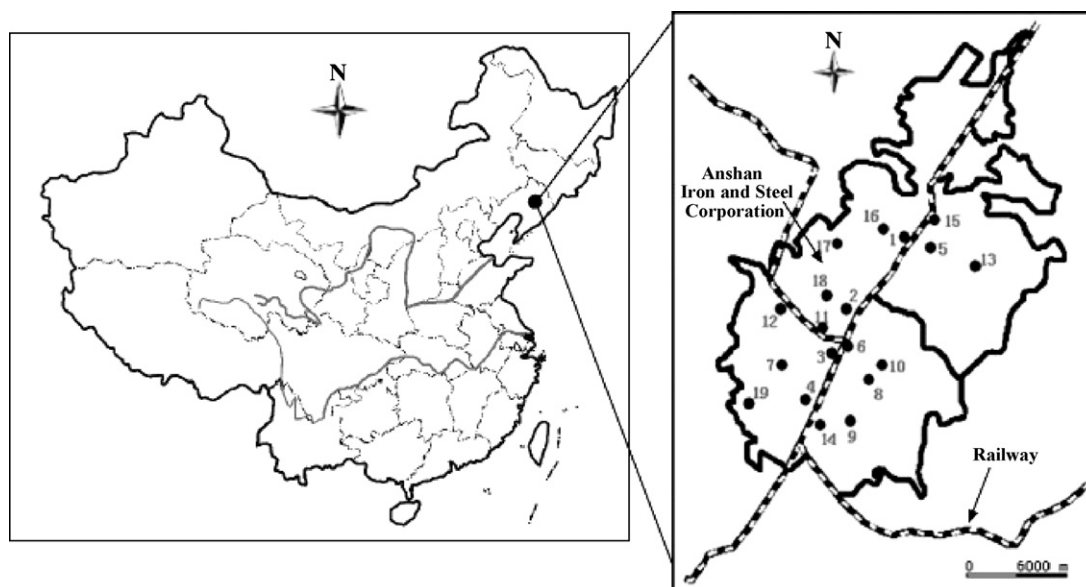


Fig. 1. (a) Locations of Anshan (b) the general study area and road dust sampling sites.

south of Shenyang, the province's capital. Anshan is on the boundary between the Mountains of eastern Liaoning and the plains of the west. Steel manufacture, metallurgy, mining, and chemical engineering are its dominant industries, all of which are high energy consumers and high pollution emitters. Due to the rapid growth of industrial production, building activities, population and traffic density, the air quality has been deteriorating during recent years [22].

Fig. 1 illustrated the detailed location of Anshan (N40°27'–41°34', E122°10'–123°13'): the city lies in the central area of Liaoning Province with Qianshan Mountain in the east. It has 1.45 million residents in its 624 km<sup>2</sup> areas. The prevailing wind directions in Anshan are south in summer, and north in winter. Temperature inversion occurs frequently during the wintertime.

As shown in Fig. 1, Anshan Iron and Steel Corporation is located in the northwestern part of the city and has an area of 29 km<sup>2</sup>, nearly a quarter of the urban area. It is one of the largest iron–steel enterprises of China, including power generation, mining, beneficiating, sinterability, coking, iron-smelting, steel-making, steel-rolling, etc., with the iron and steel producing ability of 12 million tons per year. Meanwhile, the corporation emitted large amount of air pollutant and industrial dusts, with yearly emissions of  $2.4 \times 10^5$  tons of coal combustion fly ash and  $6.8 \times 10^5$  tons of industrial dusts in 2005 [22].

## 2.2. Sampling

Paved road dust samples were collected from the 19 sampling areas chosen across the urban area of Anshan as shown in Fig. 1 in August, 2005. All sampling sites were selected to represent different functional area. Classification of sites was shown in Table 1. Sites 16, 17 and 18 were set in the area of Anshan Iron and Steel Corporation, representing highly industrialized area of Anshan. Except these three sites, all sites were located close to the main stem or intersection. Sites 1, 2, 3, 5, 6, 11, 12 and 15 were located close to Anshan Iron and Steel Corporation, and 3, 7, 8, 13, 14, 15 were in residential area with high density population. All 19 samples were swept from representative portions of major paved road surfaces with a plastic brush and dustpan.

Each dust sample was weighed after being dried in the vacuum freeze dryer to remove the moisture. After drying, the samples

were sieved through a 160-mesh screen to remove hair, fibers and other larger particles. Then the sieved samples were suspended in a resuspension chamber [23–25] and sampled through PM<sub>10</sub> inlets onto quartz-fiber filters. Filters were weighed both before and after sampling by a sensitive microbalance (Mettler M5). The balance sensitivity was  $\pm 0.010$  mg.

## 2.3. Polycyclic aromatic hydrocarbons analysis

### 2.3.1. Sample analysis

For PAHs analysis, the filters were extracted ultrasonically with dichloromethane, concentrated using a rotary evaporator, purified with a silica gel cleanup technique, reconcentrated by rotary evaporation, and finally condensed to exactly 1 mL under a gentle nitrogen stream in 60 °C water bath. The extracts were transferred into two ampoule bottles and stored in refrigerator until GC/MS analysis [26].

A gas chromatography coupled to mass spectrometry (trace 2000 GC–MS, Thermo Finnigan, USA) was used for determining

Table 1  
Locations and character of sites over the urban area of Anshan.

ID	Site name	Functional zone
1	Lishan Bridge	Industrial zone
2	Labor Union	Mixed zone <sup>a</sup>
3	Old Man Center	Residential zone
4	Jiefang Road Bridge	Mixed zone
5	Lishan culture center	Mixed zone
6	City square	Mixed zone
7	Qianlonghu community	Residential zone
8	Environmental monitoring center	Residential zone
9	Traffic management agency	Mixed zone
10	February 19th Park	Mixed zone
11	South gate of Anshan Iron and Steel Corporation	Industrial zone
12	Tiexi Government	Mixed zone
13	High School of Anshan Iron and Steel Corporation	Residential zone
14	Zhangda Square	Residential zone
15	Tuanjie Primary School	Residential zone
16	Steel-making section	Industrial zone
17	Sinterability section	Industrial zone
18	Iron-making section	Industrial zone
19	Xingsheng Road developing area	Mixed zone

<sup>a</sup> Mixed zone: industrial and residential mixed zone.

**Table 2**  
Concentrations of individual PAH ( $\mu\text{g/g}$ ) in road dust of different sites (sampling period: August, 2005).

Site	PHE	ANT	FLU	PYR	CHR	PER	BkF	BaP	DbahA	BghiP	IND	$\Sigma\text{PAHs}$	OC (%)
1	21.18	2.01	39.91	29.11	20.93	24.13	15.91	13.56	34.12	31.32	13.38	245.55	7.61
2	10.62	1.21	18.69	14.38	8.39	9.71	7.23	14.13	16.25	14.40	5.95	120.96	4.26
3	12.66	1.33	21.89	16.26	10.32	12.25	7.69	6.83	18.63	14.69	6.51	129.05	4.88
4	12.34	1.38	23.18	19.47	12.84	14.34	26.67	8.27	24.21	20.02	8.50	171.21	7.43
5	9.89	1.24	14.58	16.12	8.45	13.90	7.27	11.08	15.28	12.42	4.86	115.08	4.22
6	12.54	3.16	– <sup>a</sup>	33.53	14.47	22.59	13.17	12.03	–	26.99	10.05	148.53	5.25
7	11.23	1.44	23.53	25.69	13.20	22.30	–	11.46	–	12.84	5.22	126.91	4.70
8	12.16	1.38	22.79	16.41	12.93	19.57	9.19	8.42	21.50	19.04	7.74	151.13	6.16
9	9.22	1.07	–	17.74	7.12	10.92	–	7.15	14.68	11.41	4.65	83.97	3.59
10	4.05	0.82	5.02	5.39	1.93	10.90	11.13	7.47	–	2.03	–	48.73	3.27
11	4.58	1.13	7.17	4.46	1.95	11.62	11.91	7.08	7.36	1.89	–	59.15	3.47
12	5.59	1.58	10.99	5.61	5.18	19.14	16.72	10.72	–	1.92	–	77.44	3.52
13	9.64	0.57	4.32	4.26	1.84	10.44	12.19	3.39	12.21	2.08	–	60.95	3.51
14	5.58	0.58	5.31	6.54	7.58	24.01	16.38	9.35	5.79	4.26	–	85.38	3.89
15	4.66	0.99	7.83	8.43	7.30	25.21	18.16	12.62	5.51	3.83	–	94.55	3.97
16	35.36	5.36	70.63	73.92	53.79	163.76	67.73	44.21	49.60	49.93	23.97	638.26	7.67
17	9.90	2.78	22.67	14.61	8.49	30.26	24.75	16.48	20.62	8.17	–	158.74	6.35
18	3.89	0.49	–	18.43	10.92	46.19	33.00	22.61	9.63	–	–	145.16	4.98
19	6.77	2.59	12.43	12.15	1.57	15.96	15.68	10.65	–	2.21	–	80.01	3.52
Average	10.62	1.64	16.36	18.03	11.01	26.70	16.57	12.50	13.44	12.60	4.78	144.25	4.86

<sup>a</sup> “–” no detected.

PAHs with selected ion monitoring (SIM). A fused-silica DB-5MS capillary column (30 m  $\times$  0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness) was used. Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.0 mL  $\text{min}^{-1}$ . A 2  $\mu\text{L}$  volume was injected by applying a hot splitless injection technique. The temperature program of the oven was started at 70  $^{\circ}\text{C}$  (for 1 min) and increased at a rate 10–300  $^{\circ}\text{C min}^{-1}$  and was held for 10 min. The mass spectrometer was operated in the electronic impact (EI) mode with an ion source at 200  $^{\circ}\text{C}$  and the electron impact energy was set at 70 eV. Identification of the PAHs compounds using GC-MS was based on a combination of retention times and relative abundances of selected ions. Quantification of individual compounds was based on the comparison of peak areas with those of the internal standards [27]. The method of GC/MS analysis was according to the Method TO-13A [28]. For each sample, the procedures of sampling, pretreatment, and analysis had been completed within one month.

The PAH determined in the process were: phenanthrene (Phe), fluoranthene (Flu), anthracene (ANT), pyrene (Pyr), chrysene (Chr), perylene (Per), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IND), dibenz(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP).

The content of organic carbon (OC) in road dust was also measured using an Element Analyzer (Elementar Analysensysteme GmbH VarioE1, Germany), in order to study the relationship between OC and total PAHs in road dust.

### 2.3.2. Quality assurance

Field blanks (quartz-fiber filters, 45 mm in diameter, type 2500QAT-UP, Pall Life Sciences, U.S.A.), which accompanied samples to the sampling sites, were used to determine any background contamination using same analysis method with samples. Concentrations of PAHs in the blanks were below the detection limits in all analysis.

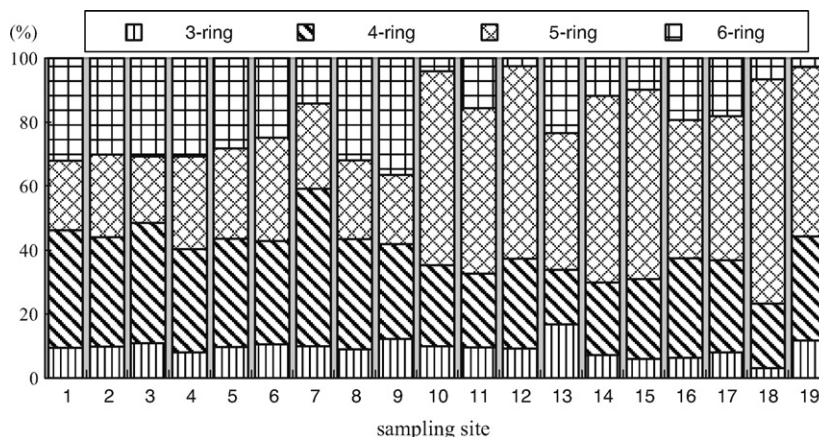
Each standard and sample was measured in duplicate, and the sample was re-analyzed if the relative standard deviation of the two measurements was higher than 5%. In the present study, all laboratory tools used in sample collection, analysis, and storage were soaked in 10%  $\text{HNO}_3$  for two days and then rinsed thoroughly with distilled and double distilled water, respectively.

For every set of 10 samples, a reference sample was run to check the interference, cross-contamination and minimize any errors due to losses during the extraction, cleaning, and concentration procedures. The averaged recoveries for the studied PAH compounds were 93.5–98.4%.

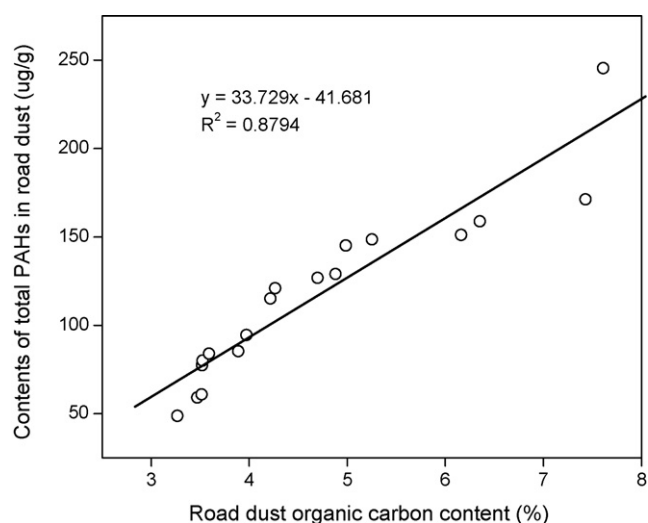
## 3. Results and discussion

### 3.1. Concentration of PAHs in road dust

PAHs concentrations in road dust for all sites were presented in Table 2. Different levels of 11 PAHs species were detected in road



**Fig. 2.** Percentage of different rings in road dust total PAHs.



**Fig. 3.** Relationship between road dust organic carbon and total concentrations of PAHs in road dust samples at different locations in urban areas of Anshan.

dust samples of all 19 sites. Total PAHs concentrations ranged from 48.73 to 638.26  $\mu\text{g/g}$ . The highest concentration was observed at site 16, which was located inside the Anshan Iron and Steel Corporation and close to the coking section. The lowest value was recorded at site 10, which could be attributed to the low traffic density and absence of industrial activities influence. Except sites 11 and 12, all sites inside or close to Anshan Iron and Steel Corporation (sites 1, 2, 3, 5, 6, 15, 16, 17 and 18) had high concentration of total road dust PAHs. Another three sites, 4, 7 and 8, located in the intersection, were also high in the concentration of total road dust PAHs. According to the results shown in Table 2, the concentrations of total PAHs in road dust are higher than those measured in other studies. For example, 70.4  $\mu\text{g/g}$  in Cairo (Egypt) [19], 58.7  $\mu\text{g/g}$  in urban Pasadena, CA (USA) [29], 14.1  $\mu\text{g/g}$  in summer and 20.6  $\mu\text{g/g}$  in winter in central Shanghai area (China) [18], 16.1–65.8  $\mu\text{g/g}$  in Taichuan, central Taiwan (China) [30], and 12.6–93.7  $\mu\text{g/g}$  in urban Birmingham (UK) [31].

The highest average concentrations for PAH species in Anshan's road dust were for PER of 26.70  $\mu\text{g/g}$  followed by PYR and BkF with average levels of 18.03 and 16.57  $\mu\text{g/g}$ , respectively. Meanwhile, the lowest measurable species in dust were ANT and IND with average concentrations of 1.64 and 4.78  $\mu\text{g/g}$ .

Examined PAHs could be classified according to their number of aromatic rings as follows: 3-ring including PHE and ANT; 4-ring including FLU, PYR, and CHR; 5-ring including PER, BkF and BaP, 6 rings including DbahA, BghiP, IND. The percentage of different rings total PAHs was shown in Fig. 2. Low molecular weight PAHs homologues (including 3 ring PAHs) took up lower fraction in total

PAHs, whereas high molecular weight PAHs homologues (including 4–6 ring PAHs) accounted for higher fraction, ranging from 83.24% to 96.98%. The high fraction of high molecular weight PAHs in total PAHs indicated that they mostly came from the combustion of petroleum fuels [18].

### 3.2. Effect of organic carbon (OC) in road dust

Several studies have shown that PAHs are strongly retained by the soil matrix [32,33]. The partitioning concept of soil sorption of organic contaminants indicates that the sorption of hydrophobic organic molecules is determined by the organic carbon content of the substrate [34]. The organic matter concentration is considered to be a very important variable related to PAHs pollution of soils [35]. In this study, the relationship between organic carbon and total PAHs in road dust was calculated.

Organic carbon in road dust varied highly, ranging from 3.27% to 7.67% with a mean of 4.86% (Table 2). A regression analysis was conducted to investigate the relationship between  $\sum$ PAHs concentrations (11 compounds,  $\mu\text{g/g}$ ) and organic carbon contents (OC, %). The result showed a positive exponential relationship (Fig. 3).

This result demonstrated that higher  $\sum$ PAHs concentrations were mainly observed in road dust with higher organic carbon, which can be described by the following equation (the  $\sum$ PAHs value of 16th site was an outlier, and was deleted in the linear regression):

$$\sum \text{PAHs} = 33.729 \times \text{OC}^{-41.681}, \quad n = 18, \quad R^2 = 0.880$$

where  $\sum$ PAHs is the total concentrations of 11 PAHs in road dust ( $\mu\text{g/g}$ ), and OC is the amounts of organic carbon in road dust (%). This relationship illustrated that the level of road dust contamination with PAHs may be affected by organic carbon contents, although the input of PAHs to each site is rather different.

### 3.3. Source analysis

#### 3.3.1. Diagnostic ratios

The diagnostic ratio method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions [36]. It is possible to use PAHs in distinguishing emissions [31,36–38]. The concentrations of several marker compounds and their ratios can give several indication about the influence of different sources. Table 3 provides several information on diagnostic ratios for PAHs, such as IND/(IND + BghiP), BaP/(BaP + CHR), BaP/BghiP, IND/BghiP and Flu/(Flu + PYR).

IND/BghiP values obtained in this study were 0.37–0.48, which were similar to that for gasoline engine emission. BaP/(BaP + CHR) values were between 0.39 and 0.87, which were between the value of gasoline and diesel engine emission. BaP/BghiP ratios ranged

**Table 3**  
Diagnostic ratios of road dust PAHs in the urban area of Anshan.

Diagnostic ratios	IND/(IND + BghiP) <sup>a</sup>	BaP/(BaP + CHR) <sup>b</sup>	BaP/BghiP <sup>c</sup>	IND/BghiP <sup>d</sup>	Flu/(Flu + PYR) <sup>e</sup>
This study	0.27–0.32	0.39–0.87	0.41–5.57	0.37–0.48	0.45–0.66
Other studies					
Gasoline engine	0.18	0.73	0.5–0.6	0.27–0.4	0.4
Diesel engine	0.35–0.7	0.5	–	1	0.6–0.7
Coal/coke	0.56	–	>1.25	1.06–1.12	–
Smelter	–	–	–	0.88–1.18	–

<sup>a</sup> Refs. [41–44].

<sup>b</sup> Refs. [45,46].

<sup>c</sup> Refs. [47,48].

<sup>d</sup> Refs. [49].

<sup>e</sup> Refs. [29,30,42,43,50,51].



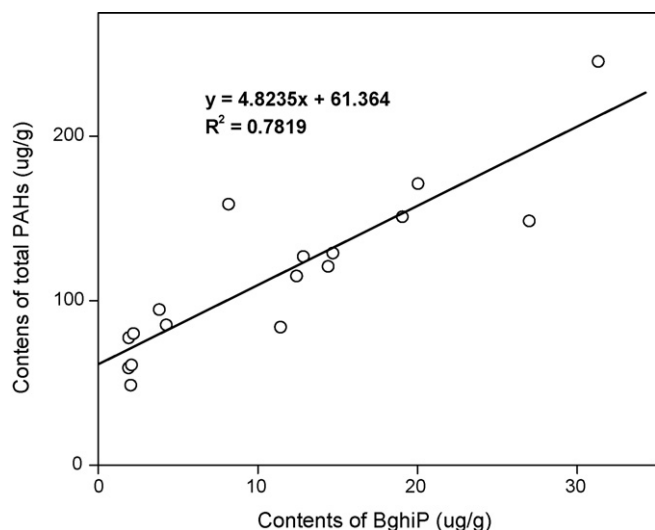


Fig. 4. Correlation between BghiP and total PAHs in road dust.

from 0.41 to 5.57, covering the sources of gasoline engine emission and coal combustion. While for values of IND/BghiP and Flu/(Flu + PYR), they were also in the range of traffic emission. The diagnostic ratios obtained in this study implied that traffic emission (from gasoline or diesel engine) and coal combustion were major sources of road dust PAHs. Moreover, in addition to the emissions related to transportation, additional emissions of PAHs due to abrasion of rubber tires, asphalt road surfaces, and brake linings should not be ignored [39,40].

Furthermore, typical combustion emitted PAHs can be indicated by  $\sum$ COMB (combustible PAHs species: FLA, PYR, BaA, CHR, BbF, BkF and BbP) [52]. High ratios of  $\sum$ COMB to  $\sum$ PAHs suggest more combustion activities [53]. While  $\sum$ COMB/ $\sum$ PAHs ratios of road dust in this study were found to range from 0.31 to 0.59. The mean ratio over Anshan was 0.42, showing the influence of traffic emission on PAHs concentration [19].

Correlation factors between BghiP and total PAHs was calculated in this study (the  $\sum$ PAHs value of 16th site was an outlier, and the BghiP in 18th sample was not detected). Therefore, these two samples were deleted in the linear regression, and good correlation was observed ( $R^2 = 0.7819$ ) as shown in Fig. 4. Considering BghiP is associated with vehicular emissions [54], it is concluded that vehicular emissions are the dominant source of particulate PAHs if there was good correlation between BghiP and total PAHs. Therefore vehicular emissions may be an important source for PAHs in Anshan.

### 3.3.2. Principal component analysis (PCA)

The principal component analysis (PCA) was conducted in this study to identify the potential sources for road dust PAH. The PAH profile was determined by calculating the ratios of individual PAH concentration to the total PAHs concentration [55]. The score and loading plots can show the similarities between ambient PAH profiles.

The results from PCA analysis on road dust PAHs are presented in Table 4, where four principal components, which probably represented the four source categories, were identified.

A high factor loading of Flu, Pyr, and especially BghiP has been considered for gasoline-powered vehicles [45,56], whereas Guo et al. [46] also included BaA, B[a]P, BbF, BghiP, and IND as source markers for gasoline emission. The high loading factors of source markers for vehicular emissions in Factor 1 such as PYR, BghiP and IND in Table 4 indicated that vehicle emission was one of the major sources of road dust PAHs.

Table 4

PCA analysis of road dust PAHs in the urban area of Anshan.

Species	Factor 1	Factor 2	Factor 3	Factor 4
Percent of variance (%)	34.73	31.30	19.62	8.59
PHE	0.74	0.34	0.43	0.27
ANT	0.48	0.45	0.11	<b>0.73</b>
FLU	0.52	0.37	0.49	0.25
PYR	<b>0.76<sup>a</sup></b>	0.54	0.16	0.28
CHR	0.69	0.60	0.28	0.16
PER	0.40	<b>0.84</b>	0.20	0.20
BkF	0.18	<b>0.90</b>	0.28	0.19
BaP	0.35	<b>0.86</b>	0.17	0.20
DbahA	0.48	0.32	<b>0.81</b>	0.07
BghiP	<b>0.87</b>	0.24	0.32	0.26
IND	<b>0.88</b>	0.27	0.31	0.18

<sup>a</sup> Factor loadings are higher in the factor shown in bold.

A high level of Ant, Phe, B[a]P, BghiP, and CHR has been suggested for steel industry emissions [42]. Several studies suggested that Flu, PYR with high factor loading of BbF and BkF indicated diesel-powered vehicles [45,56]. Therefore, high loading factors of PER, BkF and BaP in Factor 2 were likely to be related to the source makers of steel industry emissions or diesel emission.

In Factor 3, high loading factor of DbahA was observed. It probably originated from some other DbahA emission sources. According to several researches in China, vapors from rapeseed oil were mutagenic [57,58], and DbahA was extracted from rapeseed oil [59]. This is caused by Chinese traditional cooking style, and people exposed to the emitted fumes of cooking oils are at increased risk of contracting lung cancer [60]. Therefore, Factor 3 can be considered as the cooking emission.

For Factor 4, the loading factor of ANT was larger than 0.50. According to Duval and Friedlander [56] and Khalili et al. [45], ANT had been identified in coal combustion, coke production or wood combustion.

## 4. Conclusions

The concentrations of road dust PAHs in the urban area of Anshan were high, compared to other studies. The average concentration of total 11 PAHs was 144.25  $\mu$ g/g. PAH species with the higher average concentrations were PER, PYR and BkF, while the lowest species were ANT and IND. Furthermore, the concentrations of PAH species with 4–6 rings were higher at all sites. Total concentrations of PAHs in road dust were highly correlated with road dust organic carbon, indicating that road dust organic carbon might be an important factor determining the retention of PAHs in road dust. Diagnostic ratios and PCA results indicated the major possible sources for road dust PAHs in Anshan were traffic emission, steel industry emissions, cooking emission and coal combustion.

Therefore, this study suggested that the mitigation of road dust PAHs pollution in Anshan should emphasize on controlling the traffic exhausts, industrial emissions and coal combustion.

## Acknowledgements

This study was funded by “Pre study on air quality criteria for particulate matter.” (2007–2008 Special Environmental Research Fund for Public Welfare, No. 200709048) and “study on pollution prevention and control approaches and technologies for atmospheric p-PAHs and VOCs in Northeastern China” (2007–2008 Special Environmental Research Fund for Public Welfare, No. 200709013). This study was also supported by Anshan Environmental Protection Bureau, Liaoning Province, China. The authors are grateful to the staff from Environmental Monitoring Center of Anshan for conducting sampling during the study.

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