Source Identification of Polycyclic Aromatic Hydrocarbons in Urban Particulate Matter of Tangshan, China

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ABSTRACT

The presence of particle-associated polycyclic aromatic hydrocarbons (PAHs) was investigated in mixed residential/light industrial, industrial and commercial zones in summer 2000 and winter 2001 in Tangshan, China. Thirteen PAHs were measured with the total average concentrations (ng/m^3) of PAHs ranged from 26.5 to 313.6 in summer and from 142.4 to 672.4 in winter. The average concentrations of ∑PAHs were 161.97 in summer and 326.80 in winter. PAH concentrations in mixed residential/light industrial zones were the lowest. Mixed residential/light industrial is a major land-use pattern in many cities in China. This study paid more attention to the source category in the mixed residential/light industrial zone. Particle PAH emissions may be contributed from industrial or domestic activities. Diagnostic ratio analysis, principal component analysis (PCA) and hierarchical clustering analysis (HCA) show major sources to be crude oil (by industrial activities mainly) in summer; and coal combustion (by domestic activities mainly) in winter. In addition, coal combustion was a principal source in the industrial zone. Traffic (combustion engine) was an important source in commercial zones. Finally, analysis by coefficient of divergence got similar results.

Keywords: Polycyclic aromatic hydrocarbons (PAH); Particulate matter; Diagnostic ratios; Principal component analysis (PCA); Hierarchical clustering analysis (HCA); Coefficient of divergence.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are extensively studied compounds, and have been studied for a long time (Wang *et al.*, 2007). They are considered hazardous air pollutants in the group of non-halogenated organic compounds along with benzene, phenols, aldehydes, etc. PAHs exist in the atmosphere in both vapor- and particulate- phase (Bidleman *et al.*, 1986). Generally speaking, carcinogenic PAHs are found predominantly in respirable particles. In urban and industrial atmospheres, PAHs are almost entirely anthropogenic (Jones *et al.*, 1989; Guo *et al.*, 2003); giving importance to characterizing potential PAH sources in urban and industrial areas. In China's urban areas, a large amount of air pollution is emitted from natural sources (e.g., soil dust), as well as anthropogenic sources (e.g., coal combustion and vehicle exhaust emission) (Okuda et al., 2004).

Several methods and models have been developed and applied for air quality analysis (Hopke, 2003; Vouitsis *et al.*, 2008; Wang and Chen, 2008; Xu *et al.*, 2008). Among these methods, receptor models are useful tools for source identification. These include the chemical mass balance (CMB) model (Watson *et al.*, 2002; Wang *et al.*, 2008; Zhang *et al.*, 2008), PCA-MLR model (Thurston and Spengler, 1985; Srivastava *et. al.*, 2008), Unmix (Henry, 2003) and PMF models (Paatero, 1997; Begum *et al.*, 2007). Some receptor models usually need a mass of samples (such as PCA-MLR, PMF, Unmix and so on), or information about the sources (such as CMB). Besides these receptor models, some other analysis techniques and multivariate statistics

methods are also applied to identify source categories. Principal component analysis (PCA) and hierarchical clustering analysis (HCA) can study the ambient PAH profiles qualitatively. Some studies show that PCA and HCA can obtain good results without requesting a mass of samples or long-term measurements (Lee *et al.*, 2004; Ohura *et al.*, 2004). The ratio values of individual PAH species in ambient samples are also frequently employed to identify the PAH sources in ambient air (Azevedo *et al.*, 1999; Papageorgopoulou *et al.*, 1999; Kendall *et al.*, 2001; Guo *et al.*, 2003; Manoli *et al.*, 2004). The coefficient of divergence (CD) has also been applied to address similarities among three sampling zones included in the current study in Tangshan ((mixed residential/light industrial, industrial, and commercial).

As an important heavy-industrial base, Tangshan, China (centrally located in the Bohai Bay region) has experienced an economic and social boom in recent years. It has become one of the largest cities in northern China and is famous for the production of energy and raw materials. Its "pillar" industries include coal, steel, power, oil industry and ceramics. At the same time, the levels of PAH concentrations are relatively high. Tangshan's land-use pattern is mainly mixed residential/light industrial. In the mixed residential/light industrial zone, some light industrial areas are close to residential buildings. In this area, particle PAH emissions might be contributed from both industrial and domestic activities. Contributions from domestic heating may be more important during winter in comparison with summer emissions. According to some studies, domestic coal combustion is a major PAH source in some northern cities in China (Xu *et al.*, 2006). So, understanding the PAH level and contributions of various sources (contributions may come from industrial or domestic activities in different seasons) in the mixed residential/light industrial region is necessary for air management in China. In this study, industrial and commercial zones in

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Tangshan were investigated.

EXPERIMENTAL

Sampling

In this study, ambient PM_{10}-associated PAH samples were obtained from three sampling sites in Tangshan during the summer of 2000 and winter 2001 (see Fig. 1). Tangshan (117°31'-119°19'E, 38°55'-40°28'N) lies east of Heibei Province. Its population is about 3.01 million. The urban area is 3874 km^3 in size. Its climate is temperate, semi-humid, and semi-arid. During the sampling periods, the temperature ranged from -6°C to 2°C in winter, 19°C to 35°C in summer; and the prevailing wind directions in winter and summer were W and S, respectively.

The sampling sites are described as follows: Site A located in a mixed residential/light industrial zone. There are some light industrial factories and a high density of residents. Industrial and domestic activities occur in this area simultaneously. Site B is located in the industrial region. Many factories, such as coal, steel, power, oil, and few residents are present in this area. Most of the industrial activities in site B consume coal mainly. Compared with coal combustion, other anthropogenic sources around site B (such as vehicle) might be less important. Site C is in a commercial area close to the city center, characterized by high traffic density and commercial activities.

Samples were collected by filtration with a high volume air sampler situated at a height of 5 m from the ground. The pump was set at 100 L/min and run continuously for 24 h. Particulate matter was collected by pumping air through a quartz-fiber filter (Pallflex 2500QAT-UP), which was preheated at 550°C for 6 h. Sample collections were repeated for 5 consecutive days in summer 2000 (17-21 July) and winter 2001 (3-7 December). Detailed weather conditions during these sampling days are shown in Table 1. After sampling, each quartz-fiber filter was preserved at 4°C without illumination. The quartz-fiber filters were extracted in Soxhlets for 24 hours. This method of extraction is described in Caricchia *et al.* (1999).

Analysis

A gas chromatography coupled to mass spectrometry (Trace 2000 GC–MS, Thermo Finnigan, USA) was used for determining PAHs with selected ion monitoring (SIM). A fused-silica DB-5MS capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used. Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.0 mL/min. A 2μL volume was injected by applying a hot splitless injection technique. The temperature program of the oven was started at 70°C (for 1 min) and increased at a rate of 10°C/min to 300°C and was held for 10 min. The mass spectrometer was operated in the electronic impact (EI) mode with an ion source at 200°C and the electron impact energy set at 70 eV. Identification of PAH compounds was performed by comparing GC retention time with hose of authentic standards. Quantification of individual compounds was based on comparison of peak areas with those of the internal standards (Cao *et al.*, 2005). The method of GC/MS analysis was according to the Method TO-13A (EPA/625/R-96/010b). For each sample, the procedures of sampling, pretreatment, and analysis had been completed in one month.

Thirteen PAHs were determined: Phenanthrene (Phe), Fluoranthene (Flu), Pyrene (Pyr), Benz(a)anthracene (BaA), Chrysene (Chr), Benzo[b+k]fluoranthene (B[b+k]F), Benzo(e)pyrene (BeP), Benzo(a)pyrene (BaP), Perylene (Pery), Indeno(1,2,3,-c,d)pyrene (IcdP), Dibenz(a,h)anthracene (DahA), Benzo(g,h,i)perylene (BghiP), Coronene (Cor).

In this study, the recovery efficiencies ranged 76-101% and averaged 84%. The method detection limits (MDLs) were expressed as 3 times the mean blank concentration. They were (pg/m^3): Phe-10, Flu-60, Pyr-30, BaA-5, Chr-9, B[b+k]F-1, BeP-5, BaP-6, Pery-3, IcdP-4, DahA-2, BghiP-10, Cor-70.

RESULTS AND DISCUSSION

PAH Concentrations

Polycyclic aromatic hydrocarbons can be formed by the thermal decomposition of many organic materials containing carbon and hydrogen. There are two main mechanisms in the formation of PAHs: (1) hydrolysis and incomplete combustion,
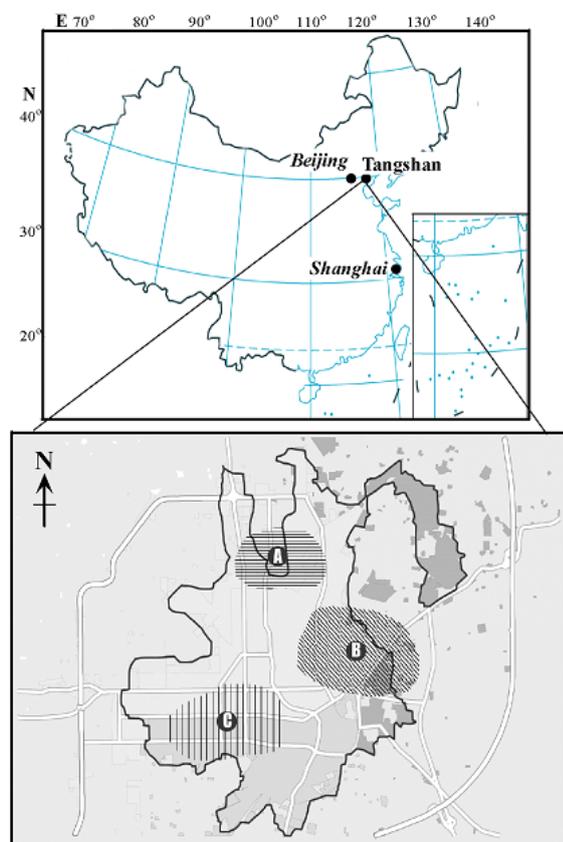

Fig. 1. Map of the three sampling sites in the city of Tangshan, China. Site A represents mixed residential/light industrial region; Site B represents industrial region; Site C represents commercial region.

Table 1. Summary of weather conditions during sampling days.

Date	Wind direction	Wind Speed (m/s)	Temperature (°C)
17/7/00	S	2.3	26.0
18/7/00	ES	3.0	26.1
19/7/00	S/ES	2.8	26.6
20/7/00	S	2.3	27.9
21/7/00	S/ES	2.3	29.8
3/12/01	WN	1.8	0.3
4/12/01	WN	0.8	-1.6
5/12/01	W	3.0	-3.1
6/12/01	W/WN	1.8	-2.9
7/12/01	W	0.8	-3.2

and (2) carbonization process. The average concentrations (ng/m3) of the 13 PAHs identified in this study are listed in Table 2 for site A, B and C in different seasons. The average ΣPAH concentrations were in the range of 26.5-672.4 ng/m^3. It can be seen that the PAH concentrations at site A (mixed residential/light industrial region) were much lower than those at other sites, especially during summer. The average ΣPAH concentration at site C, located at the center of the city and characterized by dense traffic and busy streets, showed the highest level among the three sites. Compared to site C, relatively lower values were identified at site B (certainly higher than those at site A), because the industrial zone was further from the city

center. Levels of BaP were in the range of 0.7-49.4 ng/m^3. Table 2 also lists the average concentrations of PAHs and ΣPAHs in Tangshan. The average ΣPAH concentration was 244.38 ng/m^3. Comparing results of published data on ΣPAH concentrations in other cities (Simcik *et al.*, 1997; Manoli *et al.*, 2004; Tan, *et al.*, 2006; Tekasakul, *et al.*, 2008), angshan has relative high ΣPAH concentrations.

Table 2 shows that the higher PAH concentrations were found in the winter than summer for each site. This result is similar to other studies in China. Feng *et al.* (2006) collected 7 ambient samples in summer and Winter and found that PAHs with higher concentrations in winter (Feng *et al.*, 2006). It is believed that the

Table 2. Particulate concentrations (ng/m^3) of 13 PAHs for three sites during two seasons in Tangshan: average concentration, (average mass fraction %), and min. to max. concentration.

	site A			site B			site C			*average concentration*
	Summer (n = 5) *min-max*	Winter (n = 5) *min-max*	ratio*	Summer (n = 5) *min-max*	Winter (n = 5) *min-max*	ratio*	Summer (n = 5) *min-max*	Winter (n = 5) *min-max*	ratio*	
Phe	10.9 (41.21%) *5.8-16.1*	27.3 (19.14%) *18.1-41.0*	2.50	30.3 (20.75%) *14.7-48.6*	38.6 (23.31%) *21.0-50.5*	1.27	27.4 (8.75%) *17.1-35.3*	37.5 (5.58%) *18.4-51.9*	1.37	*28.67*
Flu	2.3 (8.82%) *1.3-3.0*	9.8 (6.86%) *6.4-18.4*	4.26	15.2 (10.42%) *9.6-23.9*	15.4 (9.28%) *8.1-21.1*	1.01	15.1 (4.81%) *8.3-23.3*	25.9 (3.85%) *11.7-7.8*	1.72	*13.95*
Pyr	0.7 (2.68%) *0.3-1.2*	5.5 (3.87%) *2.7-10.0*	7.86	11.6 (7.92%) *6.1-22.1*	12.8 (7.72%) *5.3-25.0*	1.10	17.7 (5.65%) *8.7-31.9*	20.4 (3.03%) *9.1-45.0*	1.15	*11.45*
BaA	0.5 (1.96%) *0.3-0.9*	4.3 (3.03%) *2.1-6.7*	8.60	7.2 (4.93%) *3.9-12.4*	8.1 (4.87%) *2.9-15.0*	1.13	9.3 (2.97%) *4.4-17.8*	19.2 (2.85%) *8.5-29.8*	2.06	*8.10*
Chr	3.1 (11.54%) *1.6-4.9*	16.0 (11.20%) *6.6-27.1*	5.16	15.0 (10.30%) *8.7-24.8*	16.9 (10.19%) *7.7-29.1*	1.13	30.0 (9.57%) *17.1-47.3*	42.7 (6.36%) *21.5-83.8*	1.42	*20.62*
B[b+k]F	5.0 (18.74%) *3.0 -8.0*	32.1 (22.56%) *15.6-49.5*	6.42	30.5 (20.90%) *19.6-44.8*	33.0 (19.91%) *21.5-47.9*	1.08	50.0 (15.94%) *27.2-78.8*	172.9 (25.71%) *122.1-251.4*	3.46	*53.92*
BeP	1.6 (6.00%) *0.9-2.5*	9.8 (6.84%) *6.0-16.9*	6.13	15.9 (10.92%) *12.3-22.5*	16.9 (10.21%) *8.7-25.8*	1.06	20.1 (6.40%) *11.8-36.1*	38.7 (5.75%) *16.8-72.3*	1.93	*17.17*
BaP	0.9 (3.47%) *0.4-1.5*	0.7 (0.51%) *0.2-1.4*	0.78	8.3 (5.67%) *4.8-12.2*	9.2 (5.53%) *5.2-14.7*	1.11	21.5 (6.85%) *12.7-38.7*	49.4 (7.34%) *19.8-86.7*	2.30	*15.00*
Pery	0.4 (1.66%) *ND-0.9*	6.0 (4.21%) *3.0-8.6*	15.00	0.2 (0.15%) *ND-0.7*	1.1 (0.67%) *0.4-2.3*	5.50	10.1 (3.21%) *4.2-19.2*	21.5 (3.19%) *11.5-45.6*	2.13	*6.55*
IcdP	0.4 (1.55%) *0.2-0.8*	9.4 (6.61%) *4.6-15.8*	23.50	4.7 (3.19%) *2.0-8.7*	5.7 (3.41%) *3.8-9.3*	1.21	18.9 (6.0%) *9.6-25.1*	50.1 (7.46%) *21.4-97.1*	2.65	*14.87*
DahA	0.2 (0.79%) *ND-0.6*	12.2 (8.55%) *7.6-17.4*	61.00	1.0 (0.69%) *0.3-2.1*	1.0 (0.62%) *0.4-2.0*	1.00	40.1 (12.78%) *21.7-63.5*	72.5 (10.78%) *24.3-164.5*	1.81	*21.17*
BghiP	0.4 (1.43%) *0.1-1.2*	8.7 (6.09%) *3.7-18.3*	21.75	3.7 (2.56%) *2.7-5.3*	4.1 (2.45%) *0.7-8.0*	1.11	33.3 (10.63%) *18.6-52.2*	83.20 (12.37%) *49.5-128.8*	2.50	*22.23*
Cor	0.1 (0.15%) *ND-0.1*	0.8 (0.53%) *0.3-1.4*	8.00	2.3 (1.59%) *1.1-3.9*	3.1 (1.85%) *1.2-6.1*	1.35	20.2 (6.43%) *10.4-33.6*	38.4 (5.71%) *20.2-62.3*	1.90	*10.82*
ΣPAHs	26.5 *14.4-37.3*	142.4 *84.2-202.9*	5.37	145.8 *108.1-193.0*	165.6 *93.8-230.6*	1.14	313.6 *195.9-459.6*	672.4 *397.2-1069.8*	2.14	*244.38*

site A represents mixed residential/light industrial region; site B represents industrial region; site C represents commercial region.
* the ratio is the winter/summer ratio. Phe—phenanthrene, Flu—fluoranthene, Pyr—pyrene , BaA—benz(a)anthracene, Chr—chrysene, B[b+k]F—benzo[b+k]fluoranthene, BeP—benzo(e)pyrene, BaP—benzo(a)pyrene, Pery—perylene, IcdP—Indeno(1,2,3,-c,d)pyrene, DahA—dibenz(a,h)anthracene, BghiP—benzo(g,h,i)perylene, Cor—coronene, ND—non-detectable

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seasonal distributions of particle-associated PAHs are controlled by the combination of emission factors, dispersion conditions and chemical mechanisms (Caricchia *et al.*, 1999; Menichini *et al.*, 1999; Guo, *et al.*, 2003).

For sites A and C, the residential activities and traffic density occur, respectively. The relatively low PAH concentrations in summer might be attributed to different meteorological conditions (including fewer daylight hours, reduced ambient temperatures, and lower volatilization and photochemical activities) and the absence of emissions from seasonal sources, such as residential heating (Caricchia *et al.*, 1999; Papageorgopoulou *et al.*, 1999; Guo *et al.*, 2003; Manoli *et al.*, 2004). Masclet *et al.* (1986) also found that the absolute PAH levels in urban area are always lower in summer than winter. This decrease is not only due to smaller quantities being emitted (no domestic heating) but also to some physicochemical and meteorological factors, such as: 1) dilution, which is the more important factor, 2) photochemical degradations are stronger, and 3) the gas/particle ratio increases with temperature (Masclet *et al.*, 1986). For site B, higher PAH concentrations were found in winter.

The winter/summer ratios of the three sites are listed in Table 2. Average ∑PAHs of site B were 1.14, which is not very high. Site B was located in the industrial region distant from the urban center and where a smaller population resides. So some residential activities (such as domestic heating) might be ignored during winter at site B. Emissions from fossil-fuel burning power stations were the main source there. In addition, industrial activities do not vary greatly across different seasons. Some studies have also found a relatively higher winter/summer ratio in the city center (4.22) than in the industrial area (2.52) (Rehwagen *et al.*, 2005).

Source Analysis
Diagnostic Ratios

It is suggested that the concentrations of some PAH marker compounds and their ratios can give some indication about the impact of different sources of airborne compounds (Guo *et al.*, 2003). Table 3 provides the values of diagnostic ratios for PAHs, such as BaA/(BaA+Chr), BghiP/BeP, Flu/(Flu+Pyr) and IcdP/(IcdP+BghiP), which can be applied to investigate their origin, or as an indication of the aging of air samples (Cotham and Bidleman, 1995). The BaA/(BaA+Chr) values were determined to be 0.15 in summer and 0.21 in winter at site A, which are similar to the values reported for crude oil emission (0.16 ± 0.08) (Sicre *et al.*, 1987). The IcdP/(IcdP+BghiP) ratios obtained in this study were 0.55 in summer and 0.58 in winter at site B. These values are similar to those for coal combustion emissions (Yunker *et al.*, 2002). In addition, the Flu/(Flu+Pyr) ratios at site B are also in the range for coal combustion (Yunker *et al.*, 2002). So, the major source at site B might be the coal combustion in summer and winter. On the other hand, the IcdP/(IcdP+BghiP) ratios were 0.36 in summer and 0.38 in winter

at site C, which are in vehicle-emission range (0.19-0.5) (Yunker *et al.*, 2002). This implies that vehicle emissions might be the major PAH source at site C. The Flu/(Flu + Pyr) ratios were 0.46 and 0.56 at site C (summer and winter, respectively), which are also in the range of vehicle emissions (0.2-0.58) (Yunker *et al.*, 2002; Manoli, 2004). The high BghiP/BeP ratio can be used as an indicator for traffic (Nielsen *et al.*, 1996). The mean BghiP/BeP ratio reached 1.91 at site C (1.66 and 2.15 in summer and winter, respectively), which was the highest ratio among the three sites.

Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA)

To identify the potential PAH sources for the three ambient environments in different seasons, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were employed in this study. PCA was performed on a normalized original matrix composed of 13 columns (number of PAH species) and 30 lines (number of PAH profiles of ambient samples). The PAH profile was determined by calculating the ratios of individual PAH concentrations to the total concentration of all PAHs measured (Manoli *et al.*, 2004). Values below the detection limit were replaced by half of the method detection limits (MDLs) for the statistical analysis. The score and loading plots obtained by PCA can show the similarities or dissimilarities between ambient PAH profiles. Some receptor models use the chemical and physical haracteristics of particles measured at source and receptor to identify the source contributions to the receptor. Particle characteristics must be such that: 1) they are present in different proportions in different source emissions; 2) these proportions remain relatively constant for each source type, and; 3) changes in these proportions between source and receptor are negligible or can be approximated (US EPA, 2001). Based on his hypothesis, the PAH profiles of different source categories are dissimilar to each other. If the ambient sample received contributions of PAH from one source predominantly, the ambient PAH profile would be similar to the source profile.

On the score plot, the data points with similar PAH profiles are closely located, while those having divergent patterns are located further apart. The data points are classified according to the position of their corresponding coordinates with respect to the factor axis. The use of PCA for identification of PAH sources is simply based on the similarity in the PAH profiles of emission source and receptors (Lee *et al.*, 2004).

The results of the PCA are described in Fig. 2. The first two PCs represented 39.87% and 18.38% of the variability, respectively.

Three groups are delineated in Fig. 2: group 1 contains A1-A5; A6-A10, B1-B5; B6-B10 are included in group 2, and; the C1-C5 and C6-C10 cluster are in group 3. The ambient PAH profiles got PAH contributions from the same source cluster in one group. Nevertheless, unlike the points of the other sampling sites, the points of A1-A5 and A6-A10 do not cluster together. It means that the PAH profiles in winter might differ from those in

Table 3. Mean diagnostic ratios of PAHs identified for three sites in different seasons.

	BaA/(BaA+Chr)	Flu/(Flu+Pyr)	IcdP/(IcdP+BghiP)	BghiP/BeP
diagnostic source type	crude oil emission	vehicle emissions	coal combustion emissions	vehicle emissions
site A summer	0.15	0.77	0.52	0.24
site A winter	0.21	0.64	0.52	0.89
site B summer	0.32	0.57	0.55	0.23
site B winter	0.32	0.55	0.58	0.24
site C summer	0.24	0.46	0.36	1.66
site C winter	0.31	0.56	0.38	2.15

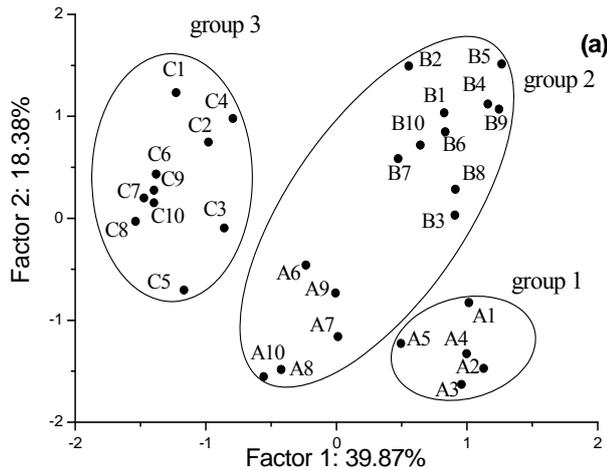site A, B, C represent the same as in Table 2.

Fig. 2. Factor score plot. A1-A5: site A, summer; A6-A10: site A, winter; B1-B5: site B, summer; B6-B10: site B, winter; C1-C5: site A, summer; C6-C10: site A, winter.

summer at site A. This might be due to the fact that principal sources at site A in summer and winter were different. A similar result was obtained by hierarchical clustering analysis (HCA), using complete linkage and Euclidean distances (Fig. 3). The distances between different sites show the similarity between the PAH profiles at different sampling sites. Generally, the shorter the distance between objects, the more similar they are (Otto, 1999).

From Fig. 2, points of the C1-C5 and C6-C10 cluster at the second quadrant are similar to each other. So the samples from site C in different seasons (summer and winter) might get significantly more contributions from the same source. On the other hand, points B1-B5 and B6-B10 appear to be defined by the positive axes of both factors. Points A1-A5 and A6-A10 occupy disparate groups. So the main sources at site A in winter and summer are different. The A6-A10 and B1-B10 points are in a group and these PAH profiles are more similar to each other, so the dominating source at site A in winter might be similar for site B (both summer and winter). According to these results, this source seems to be coal combustion emission. Although they were in one group, A6-A10 occupied a different quadrant from B1-B10. This is reasonable, considering the coal combustion for domestic heating at site A in winter (Xu *et al.*, 2006), and industrial activities at site B in both summer and winter. The PAH profile of domestic coal combustion is a little different from the PAH profiles of industrial coal combustion and coal-fired power stations. However, coal combustion might not be the only major source at site A in winter. The contributions from oil emission cannot be neglected.

Combined results of the PCA, HCA and diagnostic ratios show that only the samples from site A might get contributions from different major sources during the two seasons. This can be confirmed by Fig. 3, where the PAH profiles of samples from site A in winter are closer to those from site B (both in summer and winter), rather than site A in summer. This discrepancy is likely due to the characteristics of mixed residential/light industrial area; that is, the presence of both industrial and domestic activities in this area.

To sum up, the results of the PCA and HCA are consistent with that obtained by diagnostic ratios in some aspects.

Coefficient of Divergence (CD) and Mass Fraction Diagrams

In addition to the analysis above, similarities between summer and winter at the three sampling sites were also calculated using the coefficient of divergence (CD). CD is self-normalizing and
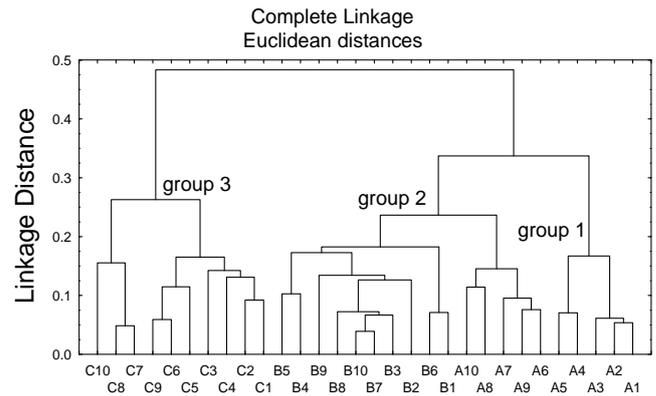

Fig. 3. Hierarchical clustering of all the profiles. A1-A5, A6-A10, B1-B5, B6-B10, C1-C5, C6-C10 represent the same as those in Fig. 2.

can be calculated from short-term measurements or long-term averages. The CD is determined as follows:

$$CD_{fj} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}(\frac{X_{if}-X_{ij}}{X_{if}-X_{ij}})^2} \qquad (1)$$

where x_{if} is the average concentration of the i th chemical component measured at the f th site. f and j represent two sampling sites, and p is the number of chemical components.

In this work, the similarity or dissimilarity of mass fractions of PAH species (normalized PAH profile) in different seasons at each sampling site were studied. So, in Eq. (1), the x_{if} is the average mass fraction of the i th PAH component measured at the f th site (Zhang *et al.*, 2000).

In addition, mass fraction diagrams are log-log scatter plots of mass fraction or concentration of the chemical components at one sampling site against those at another. More detailed introduction of CD and Mass fraction diagrams can be found elsewhere (Wongphatarakul *et al.*, 1998; Zhang *et al.*, 2000).

Figs. 4-6 show mass fraction scatter diagrams between summer and winter for sites A, B and C. The values of CD show that a stronger dissimilarity of the mass fraction (PAH profiles)
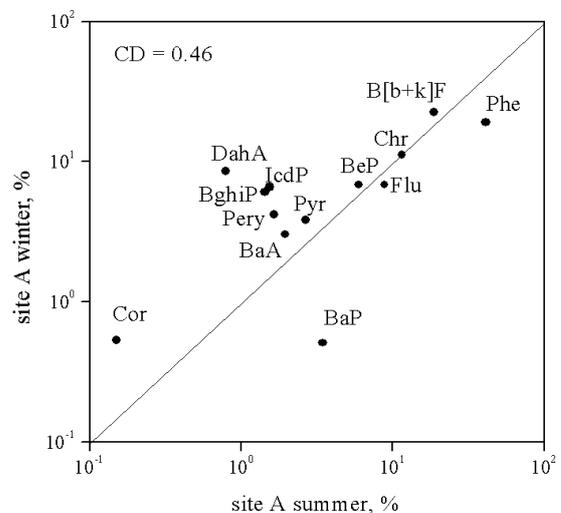

Fig. 4. For site A (mixed residential/light industrial), mass fractions of PAH species in summer and winter have less similar characteristic PAH profiles.
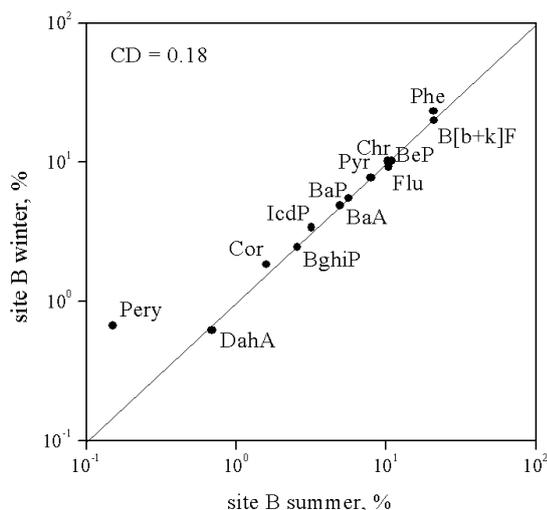
Fig. 5. For site B (industrial zone), mass fractions of PAH species in summer and winter show relatively strong similar characteristic PAH profiles.
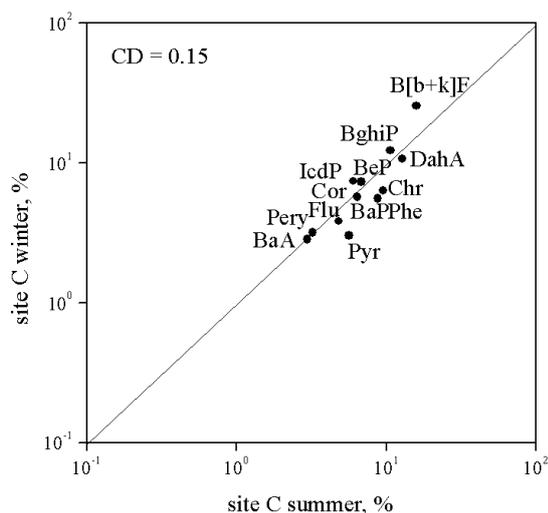

Fig. 6. For site C (commercial zone), mass fractions of PAH species in summer and winter show relatively strong similar characteristics.

between summer and winter at site A (CD is 0.46) than at site B (0.18) and C (0.15). It is because that the major sources at site A were different in summer and winter (the ambient PAH profiles were less similar to each other). These conclusions agree with the results obtained from the analysis methods mentioned above.

CONCLUSIONS

The PAH concentrations in winter were higher than in summer at three sampling sites (mixed residential/light industrial, industrial and commercial zonesa) in Tangshan, China during summer 2000 and winter 2001. Relatively lower PAH levels were found in summer than winter for each zone. The PAH concentrations in mixed residential/light industrial were the lowest level among the three zones. Diagnostic ratio analysis, PCA and HCA show that the major emission sources for the residential/light industrial zone during the two seasons (summer and winter) are different. The major PAH source might be crude oil (by industrial activities mainly) in summer, while coal

combustion (by domestic activities mainly) in winter. This is a reasonable conclusion due to the presence of residential heating (coal combustion) in winter. It also indicates that coal combustion was a major contributor to the industrial zone (both in summer and winter), and vehicular emission was the major source for the commercial zone (both in summer and winter). In addition, CD values were applied for the three sampling sites to study the similarities of PAH profiles between different seasons. Conclusions obtained by diagnostic ratios, PCA and HCA were consistent.

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