

Daily Variation of Airborne Particle-Associated Polycyclic Aromatic Hydrocarbons (PAHs) - Impacts of Sources and Meteorological Condition

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Abstract: Prediction of air pollution of polycyclic aromatic hydrocarbons (PAHs) is limited by the lack of information on the impacts of meteorological condition and emission sources on PAHs in the air. Therefore, more studies are needed. In this paper, airborne particulate matter with the aerodynamic diameter less than 10 μm (PM_{10}) was collected in Changping district, Beijing during a pollution episode in winter 2009. The samples were analyzed for the 16 US EPA priority PAHs, benzo[e]pyrene and coronene using gas chromatography – mass spectrometry (GC-MS). The results showed that the PM_{10} -associated benzo[a]pyrene concentrations were 4.06-33.0 ng/m^3 , which exceeded the NAAQS value (10 ng/m^3) on 50% of the sampling days. The major sources of PAHs were coal combustion, traffic emission, crop residue burning and cooking. During the pollution episode, a significant daily variation of the PAH concentrations was observed, which was greatly influenced by meteorological condition rather than source emission. The PAH concentrations showed a significant negative correlation with wind speed and a positive correlation with relative humidity. The impact of temperature on the daily variation was insignificant during the pollution episode.

Keywords: daily variation; meteorological condition; emission sources; PAHs

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known carcinogens and/or mutagens in environment. Epidemiological and toxicological studies have reported that exposure to high concentrations of PAHs in the ambient air can cause health risks associated with cancers^[1,2]. In order to reduce the risks, understanding temporal variation of PAHs in the air and its causes are very important. The knowledge would be beneficial to predicting the occurrence of pollution episode of PAHs in the air in advance and to further preventing the public from high exposure.

Many previous studies have focused on temporal variation, especially seasonality, of PAHs in the ambient air^[3,4]. With the extensive work, it is well demonstrated that the concentrations of particle-associated PAHs varies significantly with seasons, with the highest concentrations in winter and the lowest concentrations in summer. The reasons for the seasonality are commonly explained as domestic heating and unfavorable dispersion condition in winter as well as low source emissions and high decay rates of PAHs in summer. However, very limited studies have addressed daily and even diurnal variations of PAHs in the air, probably due to the expensive and time-consuming procedures of PAHs determination. Moreover, compared with the impacts of emission sources on seasonal variation of

PAHs which have been fully discussed previously, the impacts of meteorological condition remain unclear. Researchers^[5-9] have put their efforts on understanding the association between PAHs pollution in the air and meteorological parameters such as temperature, humidity, wind speed and direction, precipitation etc.. But the conclusions from the studies are inconsistent or even controversial. Therefore, more measurements are needed to refine our knowledge of the impacts of meteorological condition on PAHs in the ambient air.

In this paper, particle-associated PAHs were measured in Changping district, Beijing in a typical episode in winter to investigate the impacts of emission sources and meteorological condition on daily variation of PAHs. The information provided in this paper would be helpful to better understand the causes for severe pollution of PAHs in the air and to validate models predicting ambient concentrations of PAHs.

2 Experiments

2.1 Study Area and Sampling Site

Airborne particulate matter with the aerodynamic diameter less than 10 μm (PM_{10}) was collected in Changping district, Beijing. Changping district is located in the northwest of Beijing with an area of 1,344 km^2 . In the recent years, Changping district has been experiencing a rapid economic development and population growth. The local GDP increased from 21.32 billion RMB in 2006 to

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34.04 billion RMB in 2009, and the population increased from 829,000 in 2006 to 1,021,000 in 2009. Coal combustion (especially domestic heating in winter) and traffic emissions are major sources of PAHs in this area.

The sampling site was located on the rooftop of a 6-storey building in the campus of China University of Petroleum-Beijing. It was close to residential communities, schools, restaurants, and shopping malls, and was surrounded by four main roads of Kangshan, Yanping, Fuxue, and Xihuan in the east, west, north and south, respectively.

2.2 Sample Collection

The PM₁₀ samples were collected for 24 hours from noon to noon using a high-volume sampler (Thermo-Anderson HV-PM10 sampler, Fisher Scientific Inc.) during a pollution episode in winter from January 4th to January 13th, 2009. Before sampling, the flow rate of the sampler was calibrated to make sure of the correct particle cut-off point in sampling. Quartz fiber filters (Whatman Inc.) were used to collect PM₁₀ for PAHs measurements. The filters were pre-baked at 450°C for 5 hours to eliminate organic contamination and were pre-weighed. After sampling, the filters were retrieved from field, post-weighed in lab, and then stored at -20°C for PAHs determination.

2.3 Sample Analysis

The PM₁₀ samples were spiked with deuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂, SUPELCO Inc.) as surrogates to determine the loss of target compounds in sample processing. After the spiking, the samples were extracted in a sonication bath for 20 min and the extraction procedure was repeated for three times. The resulting extracts were filtered, combined, and concentrated to 1 mL. The concentrated extracts were then cleaned using a column packed with silica and alumina and the elution fraction of PAHs was collected for further analysis by gas chromatography – mass spectrometry (GC-MS).

A total of 18 PAH species were quantified with Agilent 6890N GC equipped with Agilent 5975i MSD (Agilent Inc.). The target species are naphthalene (NAP), acenaphthylene (ACE), acenaphthene (ACEN), fluorene (FLN), phenanthrene (PHE), anthracene (AN), fluoranthene (FLUA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IND), dibenzo[a,h]anthracene (DBahA), benzo[g,h,i]perylene (BghiP), and coronene (COR). The column used was 60-m DB-5MS capillary column with an inner diameter of 0.25 mm and a film thickness of 0.25 μm. The flow rate of carrier gas (helium) was 1 mL/min. The column

temperature was initially set to be 50°C for 1 min, and then increased to 120°C at 20°C/min and further to 310°C at 3°C/min, and finally remained 310°C for 25 min. The injector temperature was 300°C. The electronic impact (EI) ionization mode was used for mass spectrometric detection.

2.4 Quality Assurance/Quality Control (QA/QC)

To detect possible contamination in the sampling and the analysis procedures, field blanks, lab blanks and solvent blanks were employed. No target PAHs were detected in the blanks. The instrument detection limits (IDL) was defined as a signal-to-noise ratio of 3:1. As no target compounds were detected in the blank samples, the method detection limits (MDL) could be calculated as 3 times the standard deviation of replicate spiked samples. The recoveries were 28±13% for naphthalene-d₈, 51±20% for acenaphthene-d₁₀, 63±25% for phenanthrene-d₁₀, 61±25% for chrysene-d₁₂, and 84±28% for perylene-d₁₂.

3 Results and Discussions

3.1 PAH Concentrations in a Pollution Episode

A significant daily variation of the ambient concentrations of PM₁₀-associated PAHs was observed during the pollution episode from January 4th to January 13th, 2009 (Table 1). The ambient concentration of BaP was 20.1 ng/m³ on January 4th, and gradually increased to 28.3-33.0 ng/m³ on the following 3 days. The concentrations exceeded the National Ambient Air Quality Standard (NAAQS) value of 10 ng/m³ by 101%-230%. However, on January 8th, the concentration decreased dramatically from 28.3 ng/m³ to 5.49 ng/m³. On the rest of the sampling days, the concentration of BaP remained at low levels (4.06-12.7 ng/m³) with a slight increase on January 9th and 12th, which generally met with the NAAQS. Such a pattern of the daily variation was also observed for other 4-, 5-, 6- and 7-ring PAHs measured in this study. For 3-ring PAHs, however, the ambient concentrations tended to decrease gradually on the beginning 4 days (from January 4th to 7th). The reason for the daily variations will be discussed detailed in the following parts.

3.2 Emission Sources of PAHs

In general, changes in emission strength and source contributions are considered important reasons for temporal variation of PAHs in the air. Based on the chemical composition of the measured PAH species (Figure 1), major sources were identified for the samples collected.

Table 1. Concentrations of PM₁₀-associated PAHs (ng/m³)

PAHs	Average ±Standard Deviation	Median	Range
NAP	0.31±0.14	0.63	0.12-0.60
ACE	1.00±0.60	1.00	0.31-1.66
ACEN	0.09±0.04	0.08	0.05-0.12
FLN	1.58±0.89	1.40	0.51-2.52
PHE	14.8±9.27	14.2	3.84-23.6
AN	1.81±1.33	1.57	0.43-3.83
FLUA	20.0±14.6	15.6	4.61-41.0
PYR	23.5±17.7	17.6	5.51-47.0
BaA	13.2±10.4	9.75	3.16-29.5
CHR	8.43±6.14	6.26	2.28-17.7
BbF	17.7±11.1	12.8	4.09-51.9
BkF	14.0±13.9	12.5	3.99-37.5
BeP	19.0±11.5	14.5	5.60-40.6
BaP	15.1±11.5	11.1	4.06-33.0
IND	6.54±5.10	4.97	1.23-14.4
DBahA	1.14±0.86	0.74	0.24-2.56
BghiP	30.5±21.8	23.4	9.23-61.3
COR	44.8±33.5	35.0	11.6-93.1

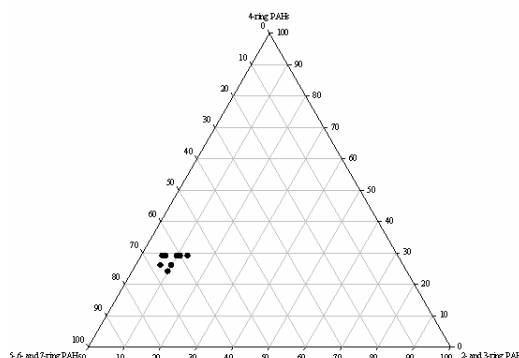


Figure 1. Chemical composition of PAHs with different fused benzene rings

3.3 Impacts of Meteorological Condition

As discussed in section 3.2, the major sources of PAHs and their emissions were stable during the pollution episode. However, the meteorological condition experienced remarkable variation during the period. In order to examine if the daily variation of PAHs observed was associated with the meteorological condition, regression analysis was applied to the PAH concentrations and meteorological parameters which were reported by the National Meteorological Center of China Meteorological Administration (CMA) (Table 2).

3.3.1 Wind Speed

The ambient concentrations of PAHs were negatively associated with wind speed with the Pearson correlation coefficients of 0.63-0.88 ($p < 0.05$, except for NAP, Table 2), suggesting the significant dispersion effects of wind on air pollutants. During the pollution episode, the wind speed was 1.3-2.0 m/s from January 4th to 7th, and increased to 4.8 m/s on January 8th, and then fluctuated between 1.6 m/s and 3.9 m/s from January 9th to 13th. Accordingly, the elevated concentrations of PAHs were observed on January 4th, 5th, 6th, 7th and 12th when the wind speed was lower than 2 m/s, while the decreases in concentrations occurred on January 8th, 10th and 11th when the wind speed was higher than 3 m/s. This was agreeable with those reported in previous studies^[5-7].

3.3.2 Wind Direction

Wind direction also influenced air pollution of PM₁₀-associated PAHs. During the pollution episode, the predominant wind direction was north, northeast, east, and northwest from January 4th to January 7th. However, southwest wind and south wind also affected Changping district from January 5th to January 7th with the frequency of 10-20%. Accordingly, it was observed that the concentrations on January 4th were 8-58% lower than those

The distribution of PAHs with different benzene rings in PM₁₀ was identical during the pollution episode (Figure 1), suggesting same emission sources affected the area in this period. The 4- and 5-ring PAHs were the most abundant species accounting for 23-31% of the total amount of PAHs, followed by the 6- and 7-ring PAHs. The 2- and 3-ring PAHs accounted for only 9%. In previous studies, it has been reported that coal combustion is characterized by high emissions of 4- and 5-ring PAHs, while vehicle exhausts enrich 4- and 6-ring PAHs^[10,11]. Therefore, the chemical composition of the measured PAHs observed in this study suggested coal combustion and vehicle exhausts were major sources of PAHs during the pollution episodes. In addition, the high concentrations of PHE and PYR in the samples indicated the contribution of crop residue burning and cooking nearby^[12,13]. This is consistent with the anthropogenic activities near the sampling site including busy traffic and commercial activities and domestic heating in winter. Also, the high concentration of SO₂ during the pollution episode gave more supports of the impacts of coal combustion on air quality.

on the following 3 days for 4- to 7-ring PAHs, although the wind speed was lowest on January 4th (1.3 m/s). Changping district is located in the northwest of Beijing, and therefore PAHs transported from industrial and urban areas in the south would affect air quality in Chingping district with south and southwest wind.

Table 2. Correlation coefficients (*R*) between concentrations of PM₁₀-associated PAHs and meteorological condition

PAHs	Wind speed	Relative humidity	Temperature
NAP	-0.54	0.11	0.14
ACE	-0.81*	0.90*	0.08
ACEN	-0.88*	0.84*	0.00
FLN	-0.82*	0.93*	0.15
PHE	-0.80*	0.96*	0.23
AN	-0.74*	0.88*	0.17
FLUA	-0.74*	0.93*	0.37
PYR	-0.75*	0.95*	0.37
BaA	-0.69*	0.90*	0.50
CHR	-0.74*	0.94*	0.44
BbF	-0.65*	0.78*	0.31
BkF	-0.63*	0.83*	0.57
BeP	-0.69*	0.90*	0.51
BaP	-0.71*	0.91*	0.47
IND	-0.74*	0.87*	0.49
DBahA	-0.67*	0.79*	0.53
BghiP	-0.72*	0.93*	0.46
COR	-0.73*	0.93*	0.47

Notes: **p* value < 0.05.

3.3.3 Relative Humidity

The relative humidity remained 37-41% from January 4th to 7th and reduced to be 20-30% since January 8th. The Pearson correlation coefficients between relative humidity and PM₁₀-associated PAH concentrations were 0.78-0.96 (*p* < 0.05, except for NAP, Table 2), indicating humidity played an important role in the accumulation of PAHs during the episode. The impacts of relative humidity on particle-associated PAH concentrations have been reported in previous studies^[5-9]. In winter, relative humidity frequently presents a negative correlation with wind speed, and wind speed is negatively associated with air pollutant concentrations. Thus, the inter-correlation

between meteorological parameters can result in positive correlation between relative humidity and air pollutant concentrations. In this study, the wind speed and relative humidity was negatively associated with the Pearson correlation coefficient of 0.79 (*p* < 0.05), which would be a reason for the significant positive association between relative humidity and PM₁₀-associated PAH concentrations in the pollution episode. Such a positive association has also been reported previously^[6,8,9]. However, on the other hand, increasing relative humidity can suppress the adsorption of gas phase organic species onto particle surface^[14], and is unfavorable to enhancing the concentrations of semi-volatile PAHs, such as 4-ring PAHs, in particulate matter. Thus, a negative correlation between relative humidity and particle-associated PAH concentrations were unsurprisingly reported in some studies^[5]. Given the complicated mechanisms, further study on the effect of relative humidity is obviously needed.

3.3.4 Temperature

The temperature increased gradually from -4.0°C to -1.7°C during the beginning 4 days (January 4th to 7th), and dropped back to -4.1°C on January 8th with the arrival of a cold front, and then remained around -4°C on January 9th, 11th and 12th. The temperature was slightly high on January 10th (-2.5°C) and 13th (-1.9°C). The concentrations gradually decreased for the PM₁₀-associated 3-ring PAHs, but increased for 4- to 7-ring PAHs during the beginning 4 days. The lowest concentrations were observed on January 8th, 10th, 12th and 13th for most of the measured PAHs. The Pearson correlation coefficients between temperature and PAH concentrations ranged from 0.08 to 0.57 (*p* > 0.05, Table 2), suggesting an insignificant impact of temperature on air pollution of PAHs during the episode.

4 Conclusions

The 24-hour averaged ambient concentrations of PM₁₀-associated PAHs were high during the pollution episode. The concentration of BaP exceeded the NAAQS by up to 230%. The major sources of PAHs were coal combustion and vehicle exhaust. Crop residue burning and cooking near the sampling site contributed to the high contents of PHE and PYR in PM₁₀.

Under the condition that the source contributions remained stable, the meteorological condition played an important role in the daily variation of PM₁₀-associated PAHs in the pollution episode. Relative humidity and wind speed were strongly associated with the PAH concentrations. The highest concentrations of PAHs were exclusively found concurrent with low wind speed and high relative humidity. Transport of particle-associated PAHs would worsen the local air pollution. However, in winter when local source emission were high and wind direction was predominated by north, northwest and

northeast, the impact of long-term transport was limited in Changping district. The impact of temperature on air pollution of PM₁₀-associated PAHs was not statistically significant during the pollution episode.

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