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Short Communication

The Characterization and Sources of Polycyclic Aromatic Hydrocarbons in PM_{10} in Rural, China

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Abstract

Polycyclic aromatic hydrocarbon (PAH) samples in particles were collected with a PM_{10} sampler in rural areas of Beijing. PAH samples collected on quartz fiber filters were first extracted using dichloromethane with ultrasonic methods, and then were fractionated on an alumina-silica column. Finally, the aromatic and n-alkane fractions were analyzed by gas chromatography with mass spectrometry and gas chromatography-combustion-isotope ratio mass spectrometry. The level of PAHs showed distinctly seasonal changes throughout the year, with the highest concentrations in January and lowest concentration in July. ∑16PAH concentrations ranged from 153.23 to 867.41 $ng \cdot m^{-3}$ in January, from 21.53 to 527.42 $ng \cdot m^{-3}$ in April, from 1.84 to 32.02 $ng \cdot m^{-3}$ in July, and from 14.86 to 114.81 $ng \cdot m^{-3}$ in November. Potential PAH emission sources were identified using normal alkane distribution analysis, positive matrix factorization, and compound-specific stable carbon isotope analysis. The results revealed that vehicular emission was the major contributor, and it explained about 48.41% PAH source contribution. The petroleum source explaining 38.63% of the total PAHs was another major PAH source contributor. Coal combustion also was a major PAH contributor, totalling 30.45% of the contribution of PAHs in winter.

Keywords: PAHs, seasonal variations, emission sources, n-alkane distribution analysis, PMF model

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread pollutants in the environment. Exposure to ambient PAHs is a potential health concern for communities because many PAHs are known to be mutagenic and carcinogenic [1-3]. PAH sources include emissions from automobiles, industrial processes, domestic heating systems, waste incineration facilities, and tobacco smoking, plus several natural sources, including forest fires and volcanic eruptions [4-6]. Many authors have reported PAH concentration distribution in Asian urban areas [7-10], and they have provided much information about PAHs of particles in urban areas. With the rapid development of the economy of rural areas, private have cars increased quickly and the use of petroleum products has increased substantially in these areas. The contributions of persistent organic pollutants from these regions to pollution of the rural area environment have been paid great attention [10,

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11]. Beijing being a famous and important city of China, the pollution of PAHs in this city had been focused on by many scholars for a long time [12-16]. However, only a little information about PAHs in PM_{10} in Beijing rural areas was given. In order to investigate more information of PAHs in rural areas, in this study we collected PAHs in PM_{10} in rural areas of Beijing to investigate seasonal variation in the PAH concentrations and to characterize potential PAH emission sources.

Experimental Procedures

Sample Collection

All sampling sites were selected from the rural area in Changping district of Beijing. Site 1 is in a hot spring resort. Site 2 is close to the Ming Tombs reservoir, and site 3 is located in the Ming Tombs weather station. SO_2, NO_x, and TSP of the sampling site are lower than the urban area of Beijing. The map of sample sites is shown in Fig. 1. PAHs in PM_{10} were collected by a Thermo Andersen PM_{10} sampler equipped with a quartz fiber filter which was replaced every 24 hr, and was preheated at 450ºC for 4 hr. Suction flow rate was 566 L/min. The samples were collected in winter (January), spring (April), summer (July), and autumn (November) from 2009 to 2010.

PAH Analysis

Samples in the filter were first extracted using dichloromethane with ultrasonic methods three times. Each time lasted for 20 min. Surrogate PAHs including Acenaphthene-D_{10}, Chrysene-D_{12}, Naphthalene-D_8, Perylene-D_{12}, Phenanthrene-D_{10}, and 1,4-Dichloro-benzene-D_4, $C_{24}D_{50}$ were added prior to extraction. The extract was then concentrated to 2 ml on a Buchi Rotary evaporator (bath temperature ≤ 30ºC).

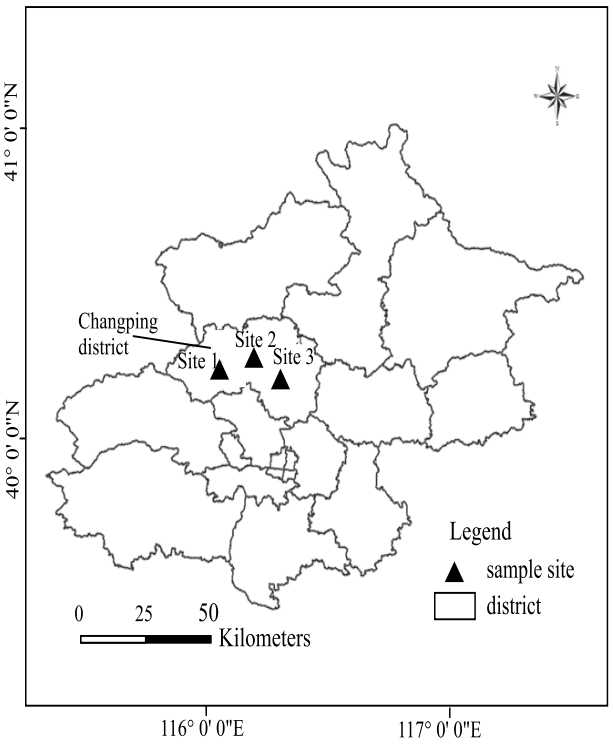

Fig. 1. Sampling site of PAHs.

Samples were fractioned on an alumina-silica column. Two fractions were eluted. Fraction I was eluted by 70 ml of hexane containing the n-alkanes, while fraction II was eluted by 70 ml of dichloromethane-hexane (v:v = 1:1) containing the PAHs. These two fractions were concentrated by rotary evaporation and then were reduced to dryness under a gentle stream of nitrogen. At last the n-alkanes fraction was redissolved with n-hexane to approximately 100 µl, and PAH fraction was redissolved with dichloromethane-hexane (v:v = 1:1) to approximately 100 µl. Internal standard hexamethylbenzene was added at this point.

All fractions were separated into two parts and the one was analyzed by gas chromatography with mass spectrometry (Finnigan SSQ710). The chromatographic conditions were listed as follows: temperature program: 65ºC (5 min), 65-290ºC at a rate of 3ºC/min, 290ºC (20 min). The carrier gas was helium at a constant flow rate of 1.5 µl/min. A 1 ml sample was injected with a splitless model. Mass range m/z 50 and 500 was used for quantitative determinations. Quantification was performed from the gas chromatography profiles using the external standard method. The external standard we used contained 16 PAH compounds. Average response factors were calculated for each compound. All quantifications were based on the compounds area derived from the ion fragment. The other part of fractions was selected for stable carbon isotope analysis. Carbon isotopic compositions of individual molecular compounds of PAHs were measured by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS). GC-C-IRMS chromatograms of PAHs are shown in Fig. 2.

Analytical Quality Control

Field blanks, which accompanied samples to the sampling sites, were used to determine any background contaminations. Method blanks (solvent) and spiked blanks (standards spiked into solvent) were analyzed. PAHs were not detected. These contaminants did not interfere with the recognition or quantification of the compounds of interest. In addition, surrogate standards were added to all samples (including QA samples) to monitor procedural performance and matrix effects. The mean recoveries (%) of surrogates in samples were 84% for Acenaphthene-D_{10}, 43% for Naphthalene-D_8, 93% for Perylene-D_{12}, 93% for Phenanthrene-D_{10}, 92% for Phenanthrene-D_{12}, and 85% for 1,4-Dichloro- benzene-D_4. The average recoveries of 16 PAHs in six matrix spikes varied from 40.15% (naphthalene) to 93.06% (benzo[g,h,i]perylene). PAH concentrations were corrected for recovery efficiency during extraction.

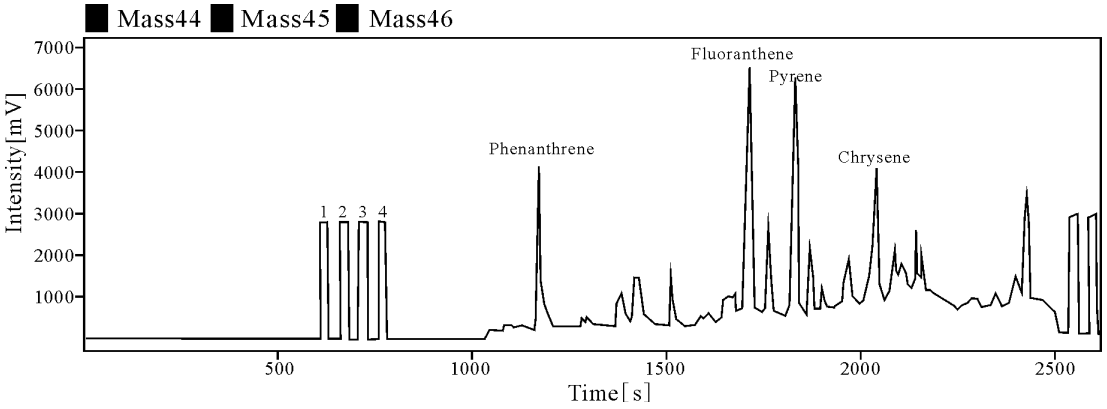

Fig. 2. GC/C/IRMS chromatogram of PAHs.

Results and Discussion

Characteristics of ∑PAHs

PAH concentrations in different seasons in PM_{10} in rural areas of Beijing were shown in Table 1. ∑16PAH concentrations ranged from 153.23 to 867.41 ng·m^{-3} in January, from 21.53 to 527.42 ng·m^{-3} in April, from 1.84 to 32.02 ng·m^{-3} in July, and from 14.86 to 114.81 ng·m^{-3} in November. The concentration of PAHs was highest in winter, followed by spring, and the concentration was lowest in summer. The result is the same as other reports in Seoul, Hongkong, and other cities in China that PAH concentrations in winter were higher than in summer [7, 9, 10, 17]. Due to the need for space heating, energy consumption in the residential sector was generally higher in the winter than during other seasons [17, 18]. The highest PAH concentrations are associated with burning coal for heating in January in Beijing.

In samples, some PAHs, including fluoranthene, phenanthrene, pyrene, and benzo[b+k]fluoranthene, are the major components. Naphthalene, acenaphthene,

Table 1. PAH concentrations in PM_{10} of different seasons in rural areas of Beijing (ng·m^{-3}).

		January		April		July		November	
Compound name	N	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
Naphthalene	12	0.32	0.28	0.23	0.18	0.15	0.08	0.32	0.30
Acenaphthylene	12	1.29	0.98	0.53	1.23	0.03	0.04	0.13	0.13
Acenaphthene	12	0.15	0.11	0.95	3.17	0.04	0.10	0.08	0.08
Fluorene	12	1.79	1.13	0.37	0.48	0.05	0.05	0.48	0.49
Phenanthrene	12	27.08	19.06	3.68	4.02	0.43	0.36	3.69	4.54
Antracene	12	7.05	6.65	0.80	1.33	0.13	0.12	1.13	1.65
Fluoranthene	12	58.84	39.18	13.70	21.09	1.25	0.96	6.62	4.00
Pyrene	12	74.23	56.94	12.91	20.24	1.33	1.02	6.45	4.16
Benzo[a]anthracene	12	46.88	33.11	13.59	22.91	0.78	0.79	5.40	4.84
Chrysene	12	42.74	26.80	12.60	17.66	1.16	0.72	6.20	4.67
Benzo[b+k]fluoranthene	12	59.77	36.49	13.79	13.48	2.70	2.30	9.61	4.22
Benzo[e]pyrene	12	29.69	21.95	12.63	17.00	2.45	2.04	6.19	4.29
Benzo[a]pyrene	12	27.81	20.63	10.45	15.37	1.19	1.01	4.01	2.49
Indeno[1,2,3-c,d]pyrene	12	24.69	23.27	6.88	6.49	2.73	3.62	5.24	3.94
Dibenzo[a,h]anthracene	12	4.85	5.62	1.52	1.12	0.73	1.38	0.99	1.30
Benzo[g,h,i]perylene	12	31.89	21.77	8.02	4.90	1.57	1.88	8.31	6.66
∑16PAHs	12	439.08	259.49	112.66	141.37	16.73	11.23	64.84	29.25

N - number of cases, Std. - standard deviation

Table 2. The CPI and C_{max} in samples.

	January	April	July	November
CPI	1.16	3.32	1.75	1.23
C_{max}	21	26	24	29

and dibenzo[a,h]anthracene are the minor components. This result is also similar to other studies [19-21]. The dominance of these chemical compounds may be explained by their high water solubility [22], higher emission rates, and lower reactivity in the atmosphere [23].

Determination of PAH Potential Emission Sources

The Distribution of Normal Alkanes

Although normal alkane (n-alkanes) mass is undoubtedly a minor fraction of the total organic matter of atmospheric aerosols, their features of relatively low reactivity and low volatility entitle them to be worth monitoring as tracers of both atmospheric transport and particle origin [24]. The carbon number preference index (CPI), carbon number maximum (C_{max}), and unresolved complex mixture (UCM) were often used to identify the origin source of particle matter of atmosphere [25, 26]. C_{max} is the carbon number for which maximum concentration was detected, which is an indicator of relative source input [27]. The equation used to estimate CPI values for our samples is:

$$CPI = \frac{C15 + C17 + C19 + C21 + C23 + C25 + C27 + C29 + C31 + C33 + C35}{C14 + C16 + C18 + C20 + C22 + C24 + C26 + C28 + C30 + C32 + C34} \quad (1)$$

According to the simplified model [28], CPI>5 indicates natural sources, primarily cuticular waxes of higher plants, whereas CPI value closer to unity arises from petroleum-derived n-alkanes reflecting combustion emission sources [29]. UCM is an important parameter, indicating petrogenic hydrocarbon inputs related to unburned petroleum emissions from vehicular traffic [27].

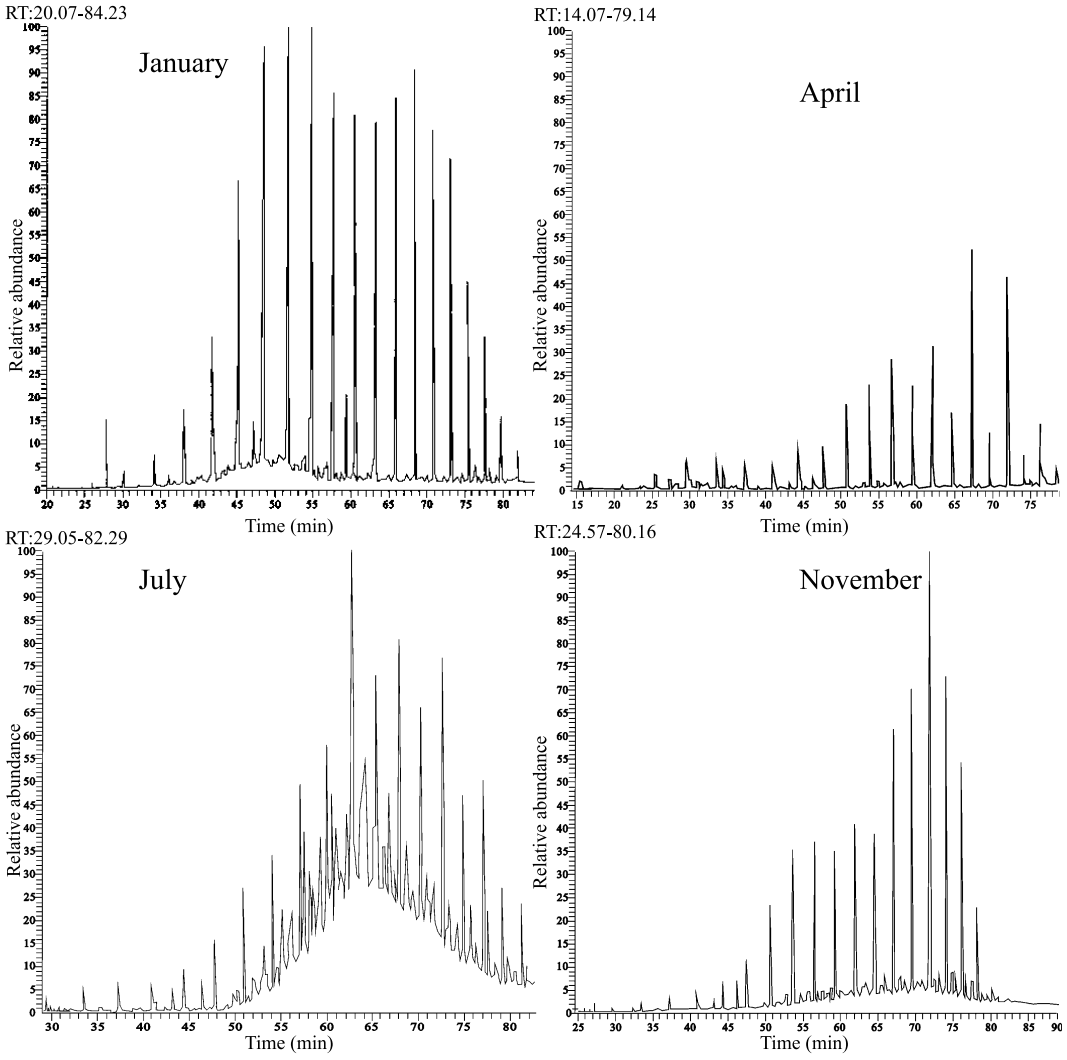

Fig. 3. Total ion chromatograms of n-alkanes.

The total ion chromatograms of n-alkanes were shown in Fig. 2 and the CPI and C_{max} in samples in different seasons were shown in Table 2. Fig. 3 reveals the distribution of *n*-alkanes in all samples showing remarkably no odd-to-even carbon number predominance as the C_{max} values vary between 21 and 29. The CPI values range from 1.16 to 3.32 (Table 2). In summer, autumn, and winter there is an unresolved complex mixture of aliphatic hydrocarbons. This shows a characteristic feature of the hydrocarbons presented in the sample and unburned petroleum emissions showed a variation as summer>autumn>winter>spring. All of these observations may imply that the main source of PAHs was fossil fuel.

Positive Matrix Factorization (PMF)

Positive matrix factorization (PMF) was utilized (USEPA PMF 3.0) to obtain quantitative information on potential sources based on the dataset of chemical species in the ambient PM_{10}. PMF is an advanced factor analysis technique based on the work of Paatero and Tapper [30] using realistic error estimates to weigh data values and impose non-negativity constraints in the factor computational process. This study investigated 48 pairs of PM_{10} samples with 16 PAHs (48×16 matrix). In the PMF model, PAH concentrations and uncertainties were used as input data and were run in a robust model to keep outliers from unduly influencing the model results [31]. The random seed mode with 25 as the random starting number was selected, and 3 to 8 as the number of factors were examined. The tentative calculation showed that the optimum number of sources was four and all the runs converged, finding the minimum Q_{robust}, and Q_{robust} was equal to the Q_{true}, indicating no outliers impacting the Q_{value}; most of the residuals were between +2 and -2 and were normally distributed, suggesting that the 16 PAHs were accurately modelled. With the bootstrapping technique, no factors were unmapped, indicating a stable result [32].

Four factors were identified by the PMF model. As shown in Fig. 4. Factor 1 was heavily loaded on phenanthrene and

Table 3. Seasonal variations of source contributions to the PAHs.

		Factor 1	Factor 2	Factor 3	Factor 4
Winter	mean	30.45%	22.76%	21.57%	20.20%
	standard deviation	23.77%	24.06%	22.26%	31.18%
Spring	mean	7.87%	34.79%	20.18%	23.16%
	standard deviation	11.43%	21.04%	19.57%	17.47%
Summer	mean	4.10%	23.34%	59.08%	13.49%
	standard deviation	5.03%	24.67%	36.56%	16.49%
Autumn	mean	10.26%	28.69%	48.19%	12.86%
	standard deviation	13.86%	22.58%	32.58%	18.61%
Total	mean	12.96%	28.25%	38.63%	20.16%
	standard deviation	17.70%	22.78%	31.43%	22.39%

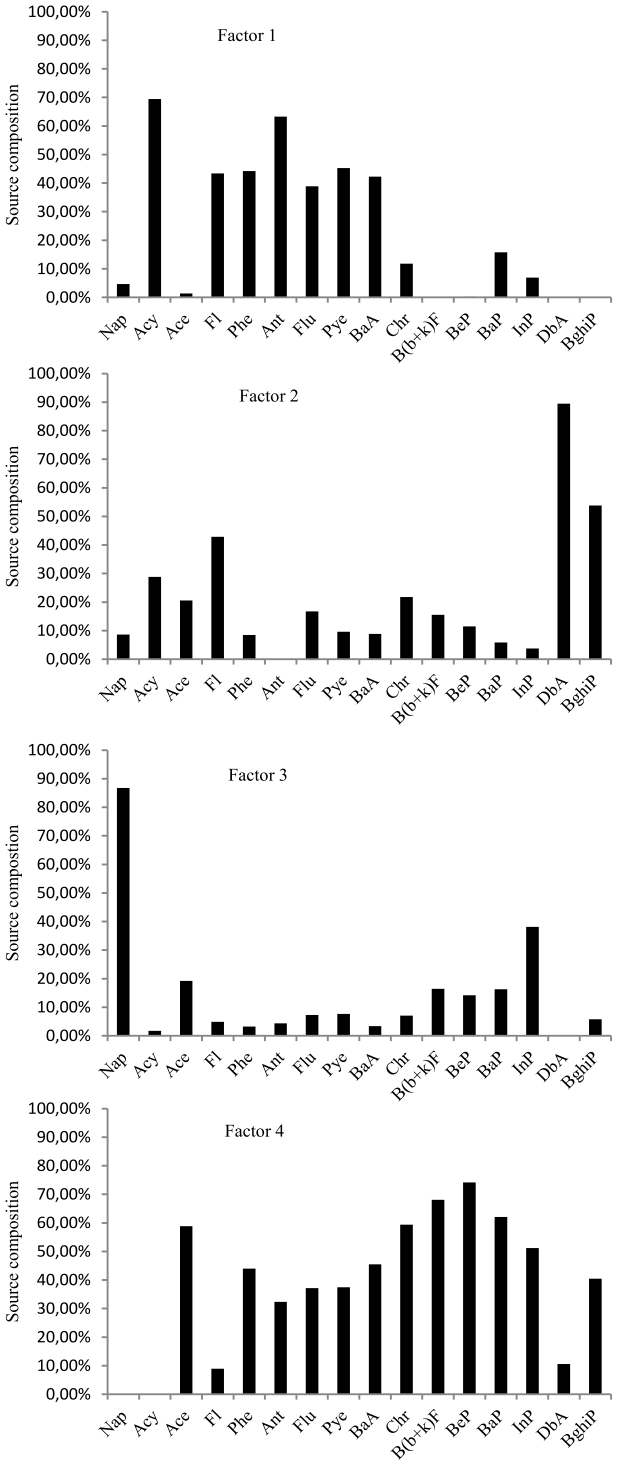

Fig. 4. Source profiles obtained from the PMF model
Note: Nap Naphthalene, Acy Acenaphthylene, Ace Acenaphthene, Fl Fluorene, Phe Phenanthrene, Ant Antracene, Flu Fluoranthene, Pye Pyrene, BaA Benzo[a]anthracene, Chr Chrysene, B(b+k)F Benzo[b+k]fluoranthene, BeP Benzo[e] pyrene, BaP Benzo[a]pyrene, InP Indeno[1,2,3-c,d]pyrene, DbA Dibenzo[a,h]anthracene, BghiP Benzo[g,h,i]perylene.

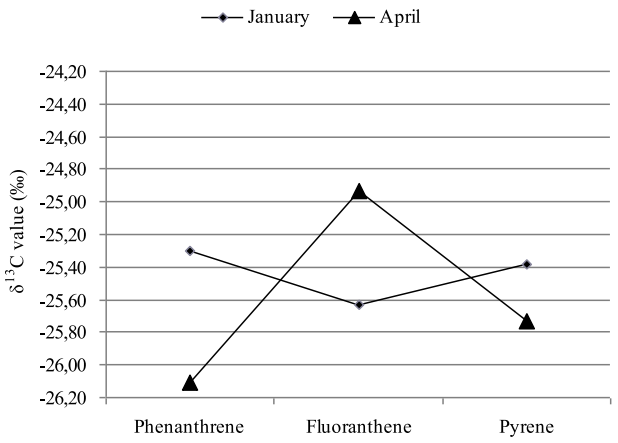

Fig. 5. Compound-specific δ13C values of PAHs.

antracene, and also got high acenaphthylene, fluoranthene, pyrene, benzo[a]anthracene and fluorene emissions from coal burning for heating [33-35]. Factor 2 heavily was weighted by benzo[g,h,i]perylene, dibenzo[a,h] anthracene, and moderate weighing of fluorine, chrysene, acenaphthylene, acenaphthene benzo[k]fluoranthene, benzo[e]pyrene, and fluoranthene was more similar to a gasoline-powered source [36]. Factor 3 was heavily loaded on naphthalene. This was believed to be indicative of volatilization from creosote or coal tar, of which naphthalene was a characteristic marker [37]. This factor was identified as a petroleum source. Factor 4 was heavily weighed by benzo[e]pyrene, benzo[b+k]fluoranthene, benzo[a]pyrene, acenaphthlene, indeno[1,2,3,c,d]pyrene, benzo[g,h,i] perylene, chrysene, and benzo[a]anthracene which were used to trace diesel combustion [37-39].

Seasonal contributions are shown in Table 3. Vehicular emissions (including diesel and gasoline-powered) was the major contributor, and it explained about 48.41% PAH source contribution. The petroleum source was also a major PAH source contributor, explaining 59.08% and 48.19% of PAHs for summer and autumn, individually, and the petroleum sources variation was similar to the UCM variation in the distribution of *n*-alkanes. Coal combustion was another main PAH contribution, and it occupied 30.45% contribution of PAHs in winter.

Compound-Specific Stable Carbon Isotope Analysis

Fig. 5 shows compound-specific $\delta^{13}C$ values of PAHs in samples in January and April. Okuda et al. [8] reported that soot PAHs extracted from gasoline and diesel vehicles show heavy isotopic signatures with a large inter-species $\delta^{13}C$ variation of -12.9‰ to -26.6‰, compared to soot PAHs extracted from wood burning smoke, which are isotopically light and have a small inter-species $\delta^{13}C$ variation of -26.8‰ to -31.6‰. According to McRae et al. [40], the PAHs obtained from fluidized-bed coal combustion particles had a small inter-species $\delta^{13}C$ variation of -25‰ to -31‰ and became more depleted in $\delta^{13}C$ with increasing PAH molecular weight. $\delta^{13}C$ values of PAHs in study ranged from -25.30‰ to -25.63‰ in January, and become more depleted in $\delta^{13}C$ with increasing PAH molecular weight. So PAHs in Beijing in January may be from burning coal. $\delta^{13}C$ values of PAHs ranged from -24.93‰ to -26.11‰ in April and become more depleted than $\delta^{13}C$ values of PAHs in January. The influence of coal is less in April than in January in Beijing rural areas.

Conclusion

PAH concentrations in PM_{10} in Beijing show seasonal variations. The concentration of PAHs was highest in winter, followed by in spring, and the concentration was lowest in summer. PAH emission sources were determined by using n-alkanes distribution analysis, positive matrix factorization analysis, and compound-specific stable carbon isotope analysis of PAHs. The results revealed that fossil fuel use-especially vehicular emission, coal burning for heating, and petroleum sources-were the main emission sources in rural Beijing.

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