



## Study on the Seasonal Variation and Source Apportionment of PM<sub>10</sub> in Harbin, China

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### ABSTRACT

The atmospheric respirable particulate matter (PM<sub>10</sub>) from four typical districts of Harbin was collected in four seasons. By analyzing the samples, we got the spatial distribution and seasonal variation of 20 elements. Besides, the sources of PM<sub>10</sub> were identified by means of enrichment factor (EF) analysis and chemical mass balance (CMB) receptor model. The results indicated that Cu, Pb, S, Zn, As, and Cd came mainly from anthropogenic sources, which varied evidently with season and space; Al, Ba, Ca, Cr, K, Mg, Mn, V, and Sr came mainly from natural sources, but we can not rule out the possibility of contamination from anthropogenic sources; Ti, Na, and Si were attributed mainly from natural sources. Results from CMB receptor model indicated that major sources in Harbin were traffic dusts, road dusts, coal burning dusts and dusts from petrochemical plants. Among these sources, the traffic dusts contributed the highest ratio in all seasons, road dusts ranked the second in spring, dusts from petrochemical plants ranked the second in summer and coal burning dusts ranked the second in winter.

**Keywords:** Atmospheric particles; Seasonal variation; Enrichment factor; Source apportionment.

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### INTRODUCTION

Harbin is located at the north region of China. With the rapid development of economic in these years, the scale of urban region is expanding, which thus influences the ambient air quality to some extent. According to the data of Environmental Monitoring Station in Harbin, particulate matter has become major air pollutant in Harbin. Consequently, it is highly required to reduce particulate matter concentrations in Harbin to improve atmospheric visibility, protect human health, and reduce ecological damage. However, in order to improve the ambient air quality effectively, we have to know the emission sources and their apportionments of atmospheric particulate matter. Thus, we can control the particle emission from the sources. Source apportionment which links emission sources to receptor is critical for the development of effective and efficient air pollution control measures.

Several major cities in China have been investigated for their characteristics and source apportionment of atmospheric particulate matter (Yao *et al.*, 2002; Lu *et al.*,

2006; Yang *et al.*, 2001); however, no detailed investigation was conducted in Harbin so far. There might be different air quality characteristics between Harbin and other cities due to high-latitude characteristics and cold climate in Harbin. Accordingly, it is very important to investigate the characteristics of particulate matter in Harbin. In order to investigate the seasonal variation and source apportionment of atmospheric particulate matter, we collected atmospheric respirable particulate matter (PM<sub>10</sub>) of Harbin in 2006 and 2007 to analyze the metallic element of PM<sub>10</sub> and further apportion their main sources by using enrichment factor (EF) analysis and chemical mass balance (CMB) receptor model.

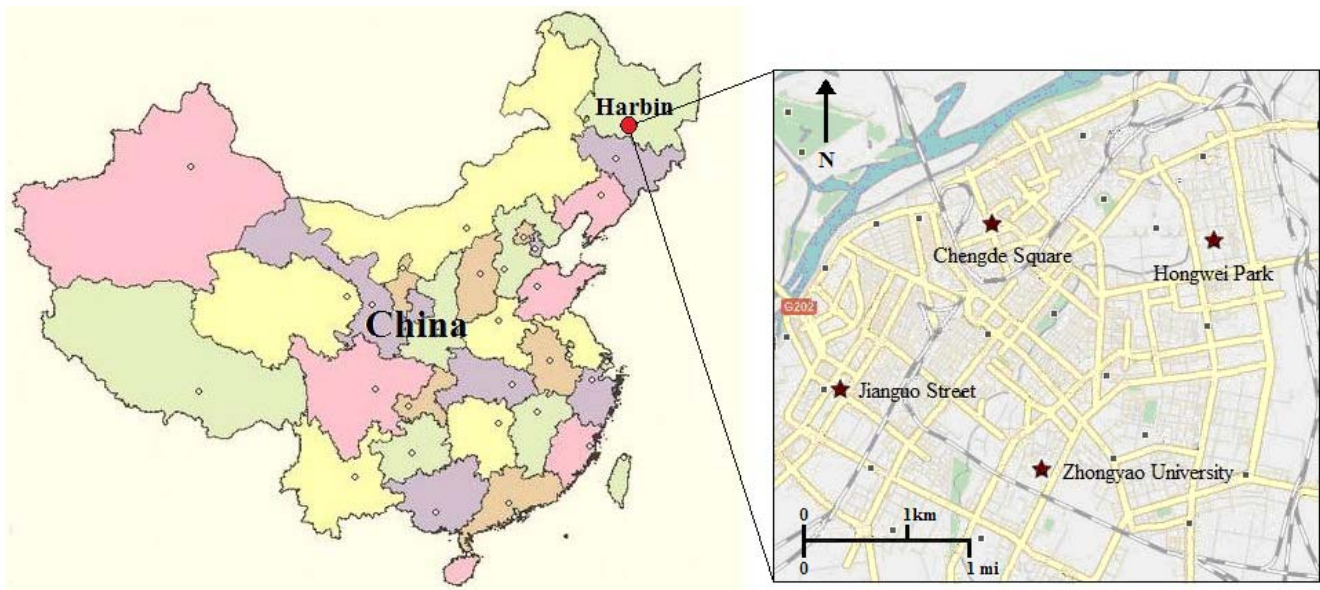
### SAMPLING AND ANALYTICAL METHODS

#### Sample Collection

In this study, four representative sampling sites, Chengde Square, Jiangguo Street, Hongwei Park and Zhongyao University, were selected to collect PM<sub>10</sub> from March 2006 to March 2007. The location of the sampling sites is shown in Fig. 1. Field sampling of PM<sub>10</sub> at four sampling sites in Harbin was simultaneously conducted three days per month. At each sampling site, an automatic sampler was used to collect PM<sub>10</sub> and automatically record the overall sampling volume and sampling duration. The sampling apparatus used for PM<sub>10</sub> sampling was medium

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**Fig. 1.** The locations of four sampling sites in Harbin, China

flow total suspended particulate sampler (TH-150 type) with  $PM_{10}$  selector which was made of Wuhan Tianhong Intelligent Instrument Factory. The sampling flow rate of the sampler was 100 L/min and the filters used in this study were 80 mm quartz filter. In order to investigate the seasonal characteristics and spatial differences of  $PM_{10}$  pollution in Harbin, a parallel sampling at four sites was consecutively conducted for twenty-four hours (from 8:00 am to 8:00 am) in each sampling period.

#### **Chemical Analysis**

After sampling, the filter samples were cut into 8 identical parts, one part of which was used for the analysis of metallic element. The filter sample was soaked by 15 mL mixed acid ( $HNO_3:HClO_4 = 3:7$ ) and put on a heating electric panel at 150–200°C for 2 hrs or more until the mix solution was boiled and clarified, and then diluted to 50 mL with distilled-de-ionized water. After conducting the above steps, metallic contents were digested by the mixed acid and further measured with inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkins Elmer, Model 400) (Yuan *et al.*, 2004). The element contents of  $PM_{10}$  analyzed in this study included Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, Sr, Ti, V, and Zn. The detection limit and analytical wavelength of each metallic element by ICP-AES are shown in Table 1.

#### **Source Apportionment**

This study applied enrichment factor (EF) analysis and chemical mass balance (CMB) receptor model to analyze the sources of  $PM_{10}$  in Harbin.

#### **Enrichment Factor (EF) Analysis**

In order to investigate the source of  $PM_{10}$  in Harbin, enrichment factor (EF) analysis was used to apportion the natural and anthropogenic sources of  $PM_{10}$  and their contribution ratios.

Enrichment factor is defined as below,

$$EF_{crust} = \frac{(Tr/Ref)_{PM}}{(Tr/Ref)_{crust}} \quad (1)$$

where  $Tr$  is the trace elements;  $Ref$  is the reference elements (e.g. Al, Fe, and Si *et al.*);  $(Tr/Ref)_{PM}$  is the concentration ratio of trace elements to reference elements in the suspended particles;  $(Tr/Ref)_{crust}$  is the concentration ratio of trace elements to reference elements in the crustal materials. For this particular study, Fe was selected as the reference element.

It is believed that the element should be enriched as if the EF of each element is greater than 10, indicating that atmospheric particulate matters come mainly from human activities. The greater value of enrichment factor shows the greater possibility of air pollution from anthropogenic sources. As the EF of an element is close to 1, it suggests that atmospheric particulate matters come mainly from soil or weathered rocks.

#### **Chemical Mass Balanced (CMB) Receptor model**

In this study, the software CMB8 (USEPA, 1997) based on CMB was used to estimate the contribution of emission sources by determining the best-fit combination of emission source and chemical composition profiles based on reconstructing the chemical composition of ambient samples. The basic calculation principle of model is as follow,

$$C_i = F_{i1} S_1 + F_{i2} S_2 + \dots + F_{ij} S_j + \dots + F_{iJ} S_J \quad (i = 1 \dots I; j = 1 \dots J) \quad (2)$$

Where  $C_i$  is the concentration of element  $i$  measured at the receptor site of atmospheric particulate matter ( $\mu g/m^3$ );  $F_{ij}$  is the concentration of elements  $i$  measured at the

**Table 1.** The detection limits and analytical wavelengths of elements by ICP-AES.

Element	Wavelength (nm)	Detection limit	Element	Wavelength	Detection limit
Al	396.15	0.050	Mn	257.61	0.016
As	193.70	0.014	Na	589.59	0.030
Ba	233.53	0.002	Ni	231.60	0.004
Ca	317.93	0.028	Pb	220.35	0.030
Cd	228.80	0.002	S	181.98	9.000
Cr	267.71	0.007	Si	251.61	1.500
Cu	327.39	0.007	Sr	407.77	0.010
Fe	238.20	0.009	Ti	334.94	0.009
K	766.49	0.050	V	290.88	0.200
Mg	285.21	0.029	Zn	213.86	0.004

source  $j$  of emitted particulate matter ( $\mu\text{g}/\text{m}^3$ );  $S_j$  is the contribution ratio of particulate matter emitted from source  $j$ ;  $I$  is the number of elements;  $J$  is the number of emission sources. The contribution ratio of the source  $j$  is defined as  $S_j/C \times 100\%$

When  $I \geq J$ , a group of results can be obtained by using the equation based on the effective variance and the least squares, which results in the contribution ratio of each source. The model needs the data from the chemical profile of emission sources and the elements concentrations of receptor samples. Based on these data the model can calculate the apportionment of each source. (Marcazzan *et al.*, 2003)

## RESULTS AND DISCUSSION

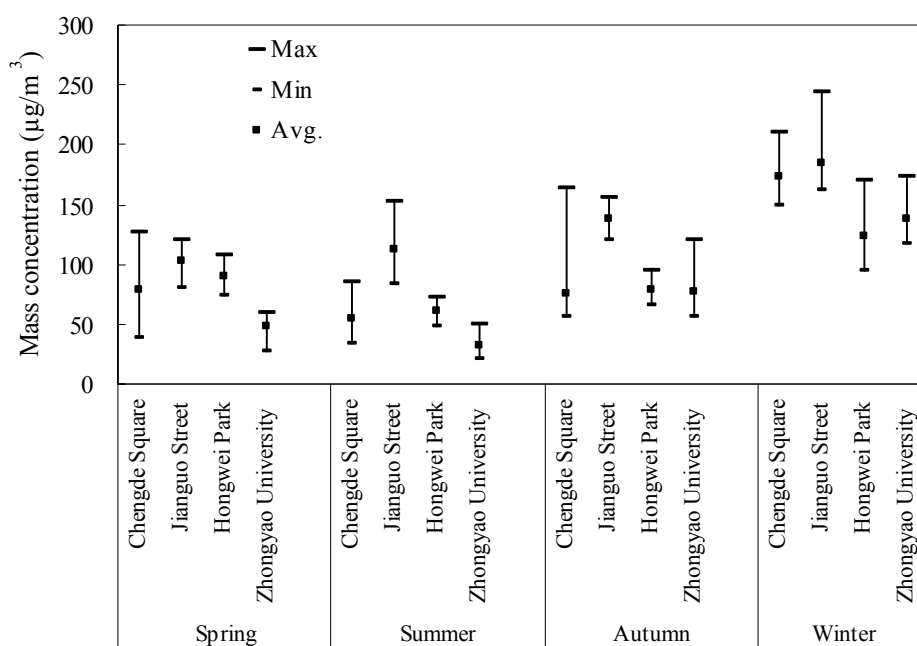
### Seasonal Variation of $\text{PM}_{10}$ Concentration

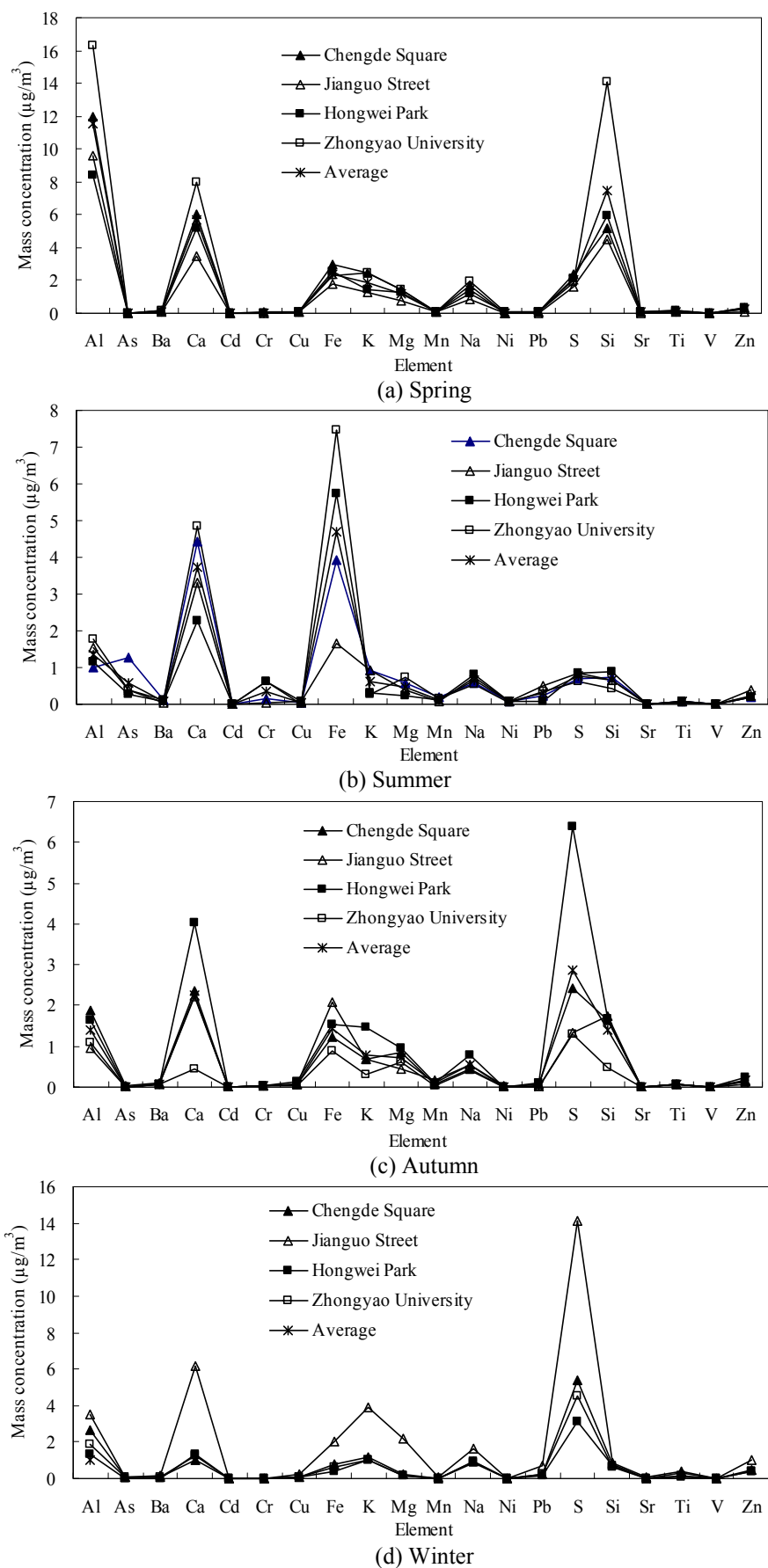
As shown in Fig. 2, the seasonal variation of  $\text{PM}_{10}$  concentration at each sampling site was observed with the lowest average concentration ( $65.0 \mu\text{g}/\text{m}^3$ ) in summer and

the highest average concentration ( $155.1 \mu\text{g}/\text{m}^3$ ) in the winter. Additionally, there was no obvious variation between the average concentration of  $\text{PM}_{10}$  in spring ( $83.1 \mu\text{g}/\text{m}^3$ ) and that in autumn ( $90.3 \mu\text{g}/\text{m}^3$ ). Space heating is a major pollution source during the winter in Harbin. Compared to other sampling sites, Jianguo Street showed a higher  $\text{PM}_{10}$  concentration in four seasons, mainly because it is located at the residential area, resulting in higher  $\text{PM}_{10}$  concentration from human activities. The concentrations of  $\text{PM}_{10}$  at Zhongyao University in the four seasons were quite different with a lower value in spring and summer, mainly because it is at upwind direction of industrial pollution sources, and a higher value in winter, mainly because it was near the heating region.

### Seasonal Variation of the Mass Concentration of Elements

Fig. 3 shows the seasonal variation of 20 elements of  $\text{PM}_{10}$  sampled at four sampling sites. The elemental concentration was the highest in winter and spring due to

**Fig. 2.** Mass concentrations of  $\text{PM}_{10}$  at four sites for four seasons in Harbin, China.



**Fig. 3.** Elemental concentrations of  $\text{PM}_{10}$  at four sites during four seasons in Harbin, China.

space heating. Al, Ca, Fe, S, Si, K, Na, and Mg accounted for 94% of total elements approximately. Other elements including trace elements had lower content and were mainly composed of Pb, Mn, Zn, and so on. Compared to other seasons, in Harbin, the road dusts in spring were very serious with a great contribution of about 30% to PM<sub>10</sub>. In addition, Al and Si are the main crustal elements, so the concentrations of Al and Si had high levels at all sites during the spring, which indicated that PM<sub>10</sub> in Harbin is mainly influenced by soil dusts in this season. The concentration of S was the highest in winter, and the lowest in summer. Seasonal variation of Pb, Mn, As, Cr was not obvious, but due to the regular inversion of temperature in winter, Pb, S, As and other pollution elements increased in varying degree. (Marcazzan *et al.*, 2002; Lin, 2002)

#### Source Apportionment by EF

From Table 2 and Table 3, the elements with EF less than 1 were Ti, Na, and Si which came mainly from natural sources; Al, Ba, Ca, Cr, K, Mg, Mn, V, and Sr with EF between 1 and 10 were mainly from natural sources but we can not ignore the influences of human activities; the elements with EF higher than 10 were Cu, Pb, S, Zn, As, Cd. From the views of Lautz et al, we consider the elements are enriched as their EF increase to  $10^{-1} \times 10^4$  (Tannera *et al.*, 2001). The higher air pollution, and the higher influence from human activities. Among these elements, the EF of Pb, S, As, and Cd were higher than 100 in winter, which showed that Pb, S, As, Cd pollution were more serious.

In addition, we observed significant seasonal variation of elements in four regions. The pollution levels were higher in spring and winter, which strongly correlated with space heating period. Autumn ranked the second and summer commonly had lower pollution levels. Among the elements, As, Pb, S, Cd, and Zn showed higher pollution levels in all seasons. In summer, the elements (As and Pb) pollution levels were much higher than those in spring, which were mainly affected by the importation of foreign sources or high impact of human activities. The EF of Pb in Jianguo Street varied obviously in all seasons, which showed that the concentration of Pb was mainly impacted by seasonal change. In Hongwei Park, the pollution levels in winter were significantly higher than other seasons, and the concentrations of S, Zn, Pb, As, Cd, Cu were 4.07, 5.98, 8.37, 2.13, 3.13, and 3.11 times higher than other seasons, respectively. For typical space heating period in December, these six elements mostly came from coal-fired power plants and man-made pollution in winter was more serious than other seasons.

Previous investigators have studied extraordinarily high concentration of some elements (Gao *et al.*, 2002). His study shows that the enrichment factor values of Pb and Zn in PM<sub>2.5</sub> at the control sites are significantly higher than those at polluted sites; however, there are no any severe pollution sources in the study thesis. This phenomenon may be affected by weather or other factors, which requires further study in the future.

#### Source Apportionment by CMB

Results from EF analysis indicated that particulate

**Table 2.** Elemental enrichment factors of PM<sub>10</sub> at each site during spring and summer in Harbin, China

Element	Spring				Summer			
	Chengde Square	Jianguo Street	Hongwei Park	Zhongyao University	Chengde Square	Jianguo Street	Hongwei Park	Zhongyao University
Al	9.68	12.73	8.04	16.74	0.603	2.25	0.49	0.56
As	133.64	293.09	507.96	328.27	8635.09	6446.58	1279.74	1371.97
Ba	5.17	5.62	4.26	8.84	3.1	3.65	1.29	1.86
Ca	2.81	2.63	2.86	4.71	1.56	2.76	0.55	0.89
Cd	261.35	429.87	307.86	166.02	98.87	705.6	67.52	51.73
Cr	12.34	5.56	3.98	2.58	17.39	13.08	52.3	40.19
Cu	17.82	39.42	26.78	24.20	13.25	39.26	9.21	0.89
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
K	1.60	1.33	1.09	2.03	0.46	1.09	0.1	0.06
Mg	1.15	0.97	1.22	1.46	0.35	0.55	0.09	0.23
Mn	1.74	1.64	1.59	1.63	2.61	2.82	1.05	0.99
Na	1.02	0.80	0.82	1.48	0.25	0.77	0.25	0.13
Ni	385.94	6.30	21.76	12.60	12.95	36.5	9.2	4.28
Pb	119.41	63.00	112.79	94.46	201.99	995.54	53.55	156.72
S	156.11	170.29	160.77	156.31	33.93	99.9	29.05	16.08
Si	0.38	0.54	0.51	1.30	0.04	0.09	0.03	0.01
Sr	2.49	2.75	2.12	4.10	0.56	1.18	0.38	0.21
Ti	0.55	0.43	0.62	0.46	0.17	0.53	0.17	0.08
V	1.25	1.03	1.03	1.11	0.47	0.9	0.26	0.2
Zn	72.66	38.51	103.79	76.37	37.26	166.41	23.2	18.99

**Table 3.** Elemental enrichment factors of PM<sub>10</sub> at each site during autumn and winter in Harbin, China

Element	Autumn				Winter			
	Chengde Square	Jiangguo Street	Hongwei Park	Zhongyao University	Chengde Square	Jiangguo Street	Hongwei Park	Zhongyao University
Al	3.70	1.09	2.56	2.88	7.76	4.06	7.58	6.53
As	519.05	125.90	294.28	3499.6	1843.84	970.28	1611.47	1211.35
Ba	10.04	3.71	6.49	9.24	15.73	8.03	9.49	10.32
Ca	2.68	1.46	3.64	0.69	1.70	4.11	4.40	2.37
Cd	951.60	369.31	1523.31	4277.29	2372.19	1685.23	1890.79	1921.21
Cr	8.61	4.54	7.22	14.38	7.98	4.60	1.22	2.35
Cu	40.27	27.35	71.63	19.11	75.85	103.46	155.59	112.53
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
K	1.10	0.63	1.85	0.66	2.78	3.62	4.80	2.89
Mg	1.64	0.52	1.52	1.67	0.58	2.49	0.92	1.20
Mn	2.98	3.95	3.15	1.81	2.20	2.68	3.47	2.36
Na	0.63	0.47	0.89	0.80	1.99	1.37	4.18	1.46
Ni	3.83	13.05	2.19	4.43	13.09	5.17	37.49	18.56
Pb	196.88	3.18	240.75	36.87	1116.56	1091.20	1198.04	1123.12
S	383.51	127.10	806.73	275.49	1279.85	1314.34	1461.82	1241.35
Si	0.29	0.18	0.24	1.12	0.20	0.09	0.35	0.12
Sr	1.19	0.35	1.03	9.36	4.00	2.63	5.61	2.30
Ti	0.76	0.42	0.52	0.75	3.89	1.96	2.14	2.25
V	2.73	0.88	0.97	0.41	4.54	3.05	4.53	3.56
Zn	89.65	48.44	119.60	64.79	414.55	343.48	716.03	412.12

matter (PM<sub>10</sub>) in Harbin was mainly attributed from anthropogenic sources. Thus, it is highly required to further conduct apportionment of emission sources. In this study, we applied CMB8 receptor model and source profile from Europe, the United States and Taiwan to analyze their sources (Yuan *et al.*, 2004). The results of analysis are shown in Table 4 and Fig. 4.

As shown in Fig. 4, the major sources of PM<sub>10</sub> were traffic dusts, road dusts, coal burning dusts and dusts from petrochemical industry in Harbin. Among them, traffic dusts were the highest contributor (103.59  $\mu\text{g}/\text{m}^3$ ), followed by road dusts (27.19  $\mu\text{g}/\text{m}^3$ ), while the lowest was the dusts from petrochemical industry (16.51  $\mu\text{g}/\text{m}^3$ ). There was obvious seasonal variation for the contribution ratio of these sources to PM<sub>10</sub>. The highest contribution to PM<sub>10</sub> was road dusts (50.64  $\mu\text{g}/\text{m}^3$ ) in the spring, sharing rate of 26%, which associated with strong windy sands in spring in Harbin. The lowest contribution of road dusts was in summer (8.76  $\mu\text{g}/\text{m}^3$ ), sharing rate of 7%, which was mainly because of high rainfall in summer. In addition, the contribution of petrochemical industry was particularly high in summer (45.96  $\mu\text{g}/\text{m}^3$ ), sharing rate of 36%, a little bite lower than that of traffic dusts (37%). It was mainly because of prevailing southerly or south easterly winds in summer in Harbin and the petrochemical industrial area was located at the upper wind of sampling sites. The contribution of traffic dusts was higher in all seasons, which indicated that traffic dusts were the major source of PM<sub>10</sub> pollution in Harbin. The contribution of coal burning dusts in winter (60.76  $\mu\text{g}/\text{m}^3$ ) with sharing rate of 25%, was significantly higher than those in other seasons, which

was related to space heating in winter (Balachandran, *et al.*, 2000).

## CONCLUSIONS

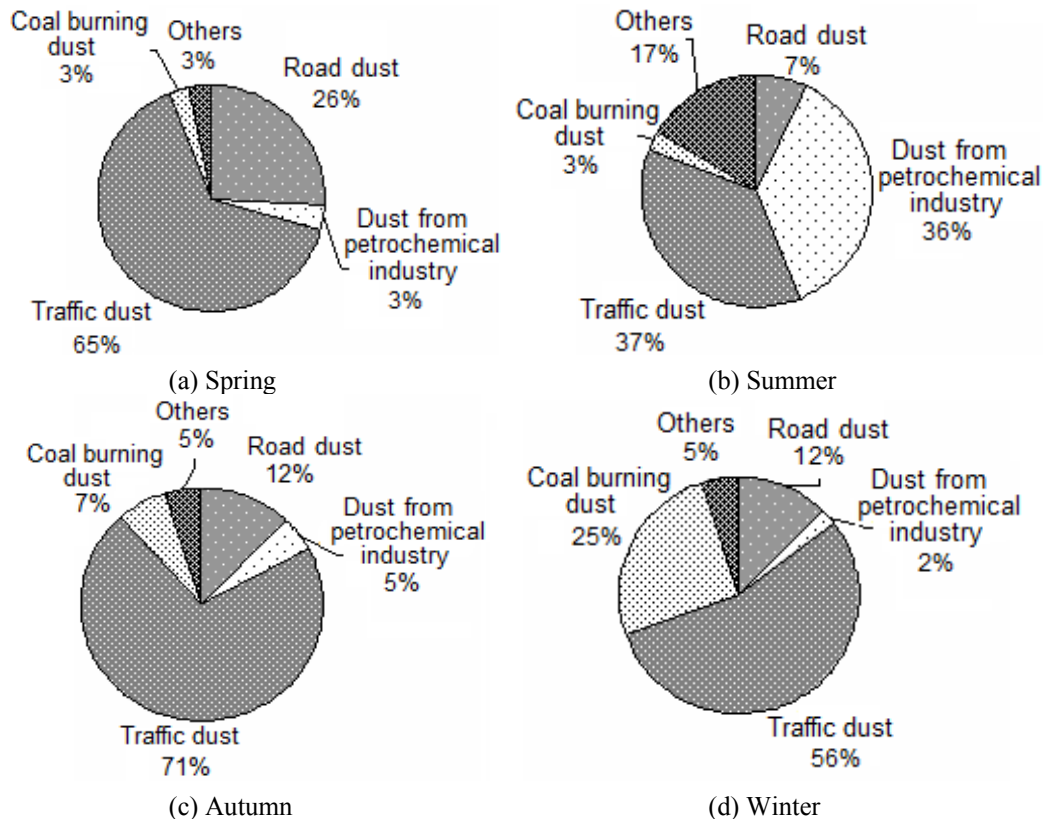
(1) The results of PM<sub>10</sub> concentration showed that the elemental concentration was the highest in winter and spring due to space heating; Al, Ca, Fe, S, Si, K, Na, and Mg accounted for 94% of total elements approximately; the concentration of S was the highest in winter, and the lowest in summer; seasonal variation of Pb, Mn, As, Cr was not obvious, but due to the regular inversion of temperature in winter, Pb, S, As and other pollution elements increased in varying degree.

(2) The EF analysis indicated that Ti, Na, and Si came mainly from natural sources; Al, Ba, Ca, Cr, K, Mg, Mn, V, and Sr were mainly from natural sources, but we can not ignore the influences of human activities; Cu, Pb, S, Zn, As, Cd came mainly from anthropogenic sources. Among these elements, the EF of Pb, S, As, and Cd were higher than 100 in winter, which showed that Pb, S, As, Cd pollution were more serious.

(3) The calculated results by CMB receptor model showed that the main sources of PM<sub>10</sub> were traffic dusts, road dusts, dusts from petrochemical industry and coal burning dusts in Harbin; Among these sources, the traffic dusts contributed the highest ratio in all seasons, road dusts ranked the second in spring, dusts from petrochemical plants ranked the second in summer and coal burning dusts ranked the second in winter.

**Table 4.** Mass concentrations of major sources of PM<sub>10</sub> for four seasons in Harbin, China ( $\mu\text{g}/\text{m}^3$ ).

Source	Spring	Summer	Autumn	Winter	Annual mean value
Road dust	50.64	8.76	19.29	30.05	27.19
Dust from Petrochemical industry	6.70	45.96	7.76	5.63	16.51
Traffic dust	125.85	45.79	109.99	132.73	103.59
Coal burning dust	6.27	3.45	10.21	60.76	20.17

**Fig. 4.** The contribution ratios of four sources to PM<sub>10</sub> during four seasons in Harbin, China.

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