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Chemical Elements and their Source Apportionment of PM_{10} in Beijing Urban Atmosphere

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Abstract Monitoring of Beijing PM_{10} was undertaken, data collected in a period of one year showed seasonal variation of the mass level of Beijing PM_{10} being highest in winter and spring, lower in summer and lowest in autumn. PIXE was used to investigate the chemical elements in PM_{10}. Results showed the chemical concentration also varied seasonally. Percentage of the masses of the crustal elements such as Al, Si, Mg, K, Ca, Fe, Mn and Ti, reached highest in spring and S, Cl, Pb, As, Cu, Ni and Zn which originated from anthropogenic sources reached highest in winter. The monitoring data showed gradual increase of the abundance of the elements from spring to winter in Beijing air and especially strong correlation of Si, Ca, Al, Fe, Mg and Ti from the factor analysis indicating these elements coming from the earth crust or soil, S, Zn and Pb probably from industrial pollution and Cl and As from combustion.

Keywords Beijing PM_{10} · Chemical elements · PIXE (Proton Induced X-ray Emission analysis) · Factor analysis

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1 Introduction

The study of health and air pollution related problems is extensive. Many researches demonstrated strong links exist between PM_{10} (aerodynamic diameter of particulate matter less than 10 μm) pollution and morbidity and mortality (Chapman et al. 1997; Richards 2003). Several parameters of ambient particles (such as particle size, chemical composition, microscopic composition, and solubility) have been found to play an important role in the development adverse health effects from air pollution. For example, Donaldson et al. (1997) testified free radicals generated from heavy metals contributing to oxidative damage induced by PM_{10}. Richard et al. (1989) have identified that it is the soluble Zinc that causes pulmonary damage. In addition, adverse health effects are also associated with the exposure to certain trace and heavy metals in air pollution. Therefore, 10 metal compounds (As, Be, Cd, Cr^{+6}, Co, Pb, Mn, Hg, Ni, and Se) are listed among the 188 hazardous air pollutant substances (HAPS) defined under the Clean Air Act Amendments of 1990 in United States (Utaunomiya et al. 2004). While in China, to ensure public health national standard of air quality have been enforced for control of air pollution. In order to study the respiratory sickness related to air pollution, monitoring of PM_{10} in Beijing has been undertaken at many institutes. It was found that the mass concentration of Beijing PM_{10} is always higher than the national standard (class-two is less than 150 μg m^{-3}) on account of the city locality and

fast economic growth. To welcome the coming 2008 Olympic game, air quality of Beijing is of greater concern than ever. To identify sources of Beijing PM_{10} and to find ways to remedy the polluted air, researches were carried out. There were a number of papers on the study of Beijing PM_{10}. Okuda et al. (2004) reported that the major primary sources of the aerosol of Beijing were soil dust and coal combustion by using CMB (Chemical Mass Balance) receptor model. Zhang et al. (2003) claimed that crustal matters, anthropogenic emission, and oil combustion contributed to Beijing aerosol level based on factor analysis during Beijing spring duststorm episode. Cao et al. (2004) analyzed the sources of Beijing coarse and fine airborne particles by positive matrix factorization (PMF) and reported that there were two area types and four source types, like soil, limestone quarry, crop burning and mixture of residue motor and coal burning in Beijing aerosol. In addition, the chemical composition of Beijing PM_{10} has been also reported in many literatures (Chang et al. 2000; Guo et al. 2004; Winchester and Bi 1984; Winchester et al. 1981; Yang et al. 2002). Up to this date, papers based on long term monitoring of PM_{10} are scarce. Since the chemical composition of PM_{10} can vary from day to day, monitoring of PM_{10} for a long period of time is necessary.

In this work on a period of one year monitoring of Beijing PM_{10} was undertaken by the authors in the northwestern area of Beijing city from April, 2002 to March, 2003. To provide supplementary information for the study of Beijing PM_{10}, Chemical elements analysis was performed using PIXE (Proton Induced X-ray Emission analysis) method.

2 PM_{10} Collection

The collection site was located in northwestern Beijing, about 1 km from the fourth ring road of Beijing city. Around the collection site, there were no visible pollution sources. The samplers were mounted on the fifth floor of the main building in China University of Mining and Technology (18.5 m above the ground level), 100 m west from the Xueyuan Road (a major road in Beijing). A Negretti selective head (UK) connected to a high-volume air sampler (Laoshan electronic co., China) running at a flow rate of 30 l min^{-1} using a flow meter (CT Playton Ltd. UK) during the collection. The particulate matters were collected onto polycarbonate filters (Millipore, UK, pore size 0.6 μm). 12-h PM_{10} were collected continuously in 7 days/month from April, 2002 to March, 2003. 168 samples were obtained in this study. During sample collection, temperature, humidity, wind speed and direction were also recorded. In each month one sample was randomly selected from the collecting samples. Another two samples in April and May were selected, respectively, to testify the PIXE results. The total number of chosen samples was 14. The detailed information of the 14 samples was listed in Table 1.

The polycarbonate filters were weighted before and after collection with a 0.01 mg precision microbalance after preconditioning for 48 h at constant humidity (40–42%) and temperature (20–22°C).

3 Experimental

The samples were cut into strips (width×length=6×33 mm^2) and sticked parallel on a plastic frame. About 1 mm was left blank between two samples, a blank about 10 mm was left in front of the first sample leaving this position to paste fluorescent paper for instrumental adjustment.

The collected samples were analyzed by PIXE (General Ionex Corporation USA) in the Institute of Low Energy Nuclear Physics, Beijing Normal University. This PIXE analyzer has been verified to be reliable by international standard inter comparison (Zhu and Wang 1998, 2000). For each sample, concentrations of 20 elements were determined, which included Mg, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, and Pb. One blank filter for corrections of multi-element concentration was also analyzed.

4 Results and Discussion

4.1 The variation of PM_{10} mass concentration

The monitoring data revealed that average mass concentrations of PM_{10} at the urban site fall into 71~319 μg m^{-3} (1 week/month) (Fig. 1). The mass

Table 1 Samples and sampling condition for PIXE analysis

Season		Date	Place	Tem./ °C	Hum./ %	Wind speed/ ($m \times h^{-1}$),	Flux (l/m^3)	Time (min)	Accumulative flux (m^3)	Mass concentration ($\mu g\ m^{-3}$)
Spring	SZB39	2002-04-11	CUMTB	9~16	19~35	4/N	30	717	21.51	368.64
	SZB40	2002-04-12	CUMTB	9~16	19~34	4/NW	30	715	19.44	389.37
	02D05-08	2002-05-20	CUMTB	22~28	19~32	6/SE	30	711	21.33	248.99
	02d05-09	2002-05-21	CUMTB	23~27	14~31	1~3	30	720	19.3	174.84
Summer	02D06-08	2002-06-14	CUMTB	23~29	18~33	1~3	30	720	21.6	57.14
	TEF28	2002-07-24	CUMTB	19~30	55~65	1~3	30	706	21.18	175.56
	02D06-19	2002-08-24	CUMTB	28~31	41~52	1~3	30	720	21.6	89.09
Autumn	PC-07	2002-09-25	CUMTB	23~24	32~33	1~3	25	720	18	123.88
	PC-24	2002-10-28	CUMTB	6~8	24~25	1~3	29	629	18.24	93.32
Winter	PC-34	2002-11-26	CUMTB	2~1	24~30	0	25	714	17.85	280.17
	TEF50	2002-12-29	CUMTB	−10~−6	25	0	30	715	21.45	138.47
	PC03-8	2003-01-21	CUMTB	−3~2	30~32	1~3	30	710	21.3	54.93
	PC03-19	2003-02-19	CUMTB	3~8	22~24	1~3	29	715	20.74	240.43
	PC03-68	200303-25	CUMTB	7~16	27~37	1~3	25	60	1.5	253

CUMTB: China University of Mining and Technology(Beijing campus)

levels of PM_{10} showed a seasonal variation, with much higher values in winter and spring, lower values in summer, and the lowest in autumn.

The maximum average mass concentration per week was 319 $\mu g\ m^{-3}$ which was caused by severe pollution happened in April 2002, while the minimum of PM_{10} mass concentration amounted to 71 $\mu g\ m^{-3}$. The relatively lower mass concentration of Beijing aerosol occurred in October which is regarded as the best season in Beijing during the whole year. From the analyzed data, PM_{10} mass concentration in Beijing air from April 2002 to April 2003 (except September and October) stayed much higher than the Class II National Air Quality Standard of China for PM_{10} (150 $\mu g\ m^{-3}$, GB3095-1996). This air pollution was very serious in Beijing urban area. However, compared with the Shi's results gotten at the same place in 2001(Shi et al. 2003), the mass concentration has decreased since a series of air pollution control measures taken by the Beijing municipal government had been effective.

The mass concentration levels of PM_{10} showed a seasonal variation in Beijing urban area. The mass levels of Beijing PM_{10} declined from spring to fall, and kept a relatively high level in winter (Fig. 1). Our results supported the arguments of Wang et al. (2002). The cause of the high mass concentration in spring and winter probably was drier climate than the other two seasons. In addition, frequency of duststorm occurrence in spring (Zhang et al. 2003) and coal combustion for heating purposes (Shi et al. 2003) in winter also contributed to the high level concentration of Beijing PM_{10}. On the contrary, PM_{10} concentration was relatively lower in summer and autumn.

4.2 Chemical elemental characteristic of Beijing PM_{10}

Different elements in Beijing PM_{10} had different mass concentration according to the PIXE analysis results (Fig. 2). The total of chemical element mass concentration were 23.77, 10.52, 6.7 and 13.89 $\mu g\ m^{-3}$ in spring, summer, autumn and winter, respectively. Maximum mass concentration of chemical elements was found in spring samples, while the minimum mass concentration existed in autumn samples. There were positive correlation between chemical elements level in Beijing aerosol and Beijing PM_{10} mass concentration. The major chemical elements in Beijing PM_{10} were Si, S, Ca, K, Al, Fe, Mg, Cl, Zn, their value were 14.98, 10.00, 7.26, 5.11, 4.59, 4.26, 2.84, 2.57, 1.07 $\mu g\ m^{-3}$, respectively. These nine elements in Beijing PM_{10} accounted to more than 96% of the total elements while percentage of the other 11 elements in PM_{10} was less than 4%. Individually Si was the richest element throughout

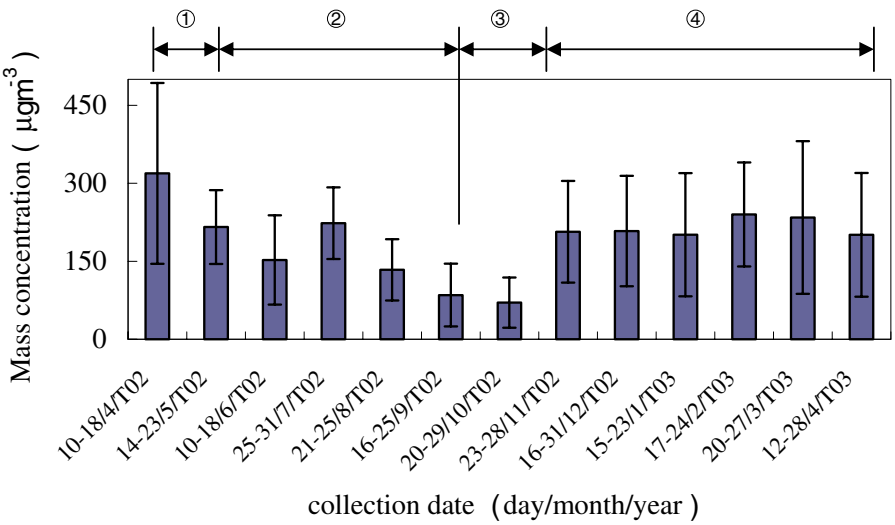

Fig. 1 Average 1 week/month mass concentrations of PM_{10} collected at the urban site from 2002 to 2003. Note: *error bars* represent the standard deviation, ①-spring; ②-summer; ③-autumn; ④-winter

all year round except in winter. Percentage of Silicon in the spring sample reached 8.11 μg m^{-3}, taking 54% of the total element in weight. Other crustal elements, such as Mg, Al, K, Ca, Fe, also reached their highest value in spring season. S, as a typical pollutant was the richest among the 20 elements in winter. Mass concentration of S was 3.384 μg m^{-3}. Other pollutant elements including Cl, Zn and Pb were higher in winter sample than in other seasonal samples.

4.3 The Enrichment Factors (EFs)

The enrichment factor was calculated by :

$$EF = (C_x/C_{Al})_{aerosol} / (C_x/C_{Al})_{crust} \qquad (1-1)$$

Where C_X is the concentration of the element in aerosol and C_{Al} is the abundance of aluminum in crust. Crustal elements, such as Al, Si and Fe, are

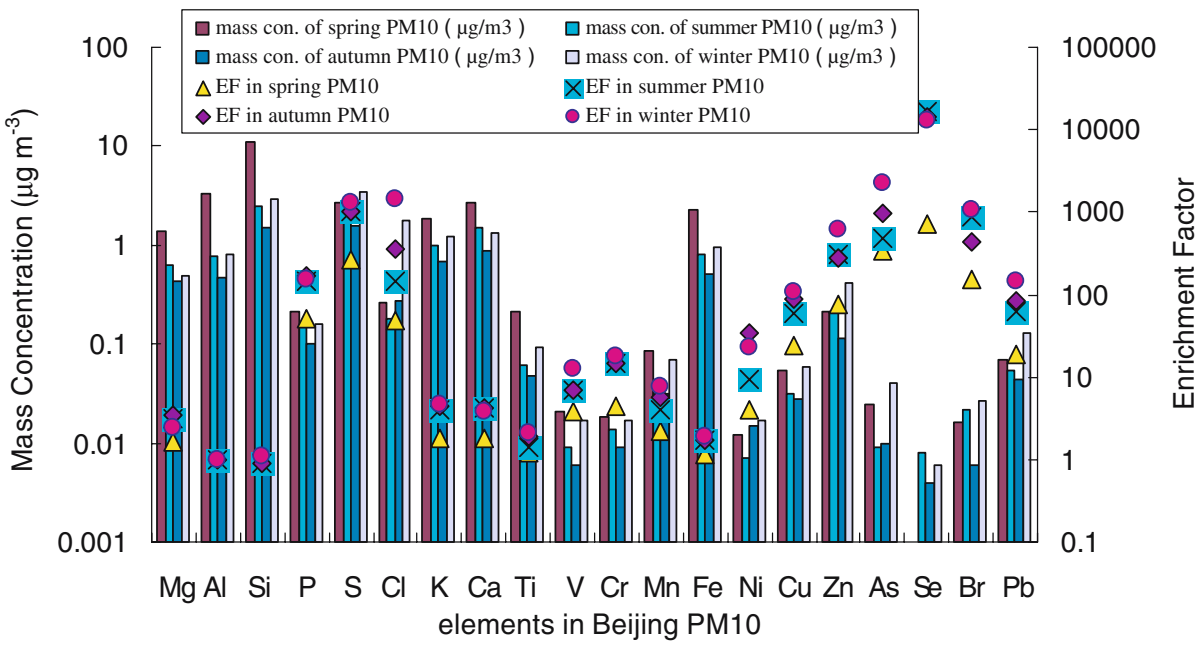

Fig. 2 Mass concentration of elements in PM_{10} and their EF

usually selected as reference material to calculate the enrichment factors of elements in aerosol. Here Al is selected as a reference material. Generally, if EF>10 (Tang 1990), the element X in aerosol is always regarded as coming from anthropogenic sources, or from crust. From Fig. 2, EFs of elements, such as Mg, Al, Si, K, Ca, Fe, and Si ranged from 0.9~5 in different seasons, which showed the seven elements mainly originated from natural dust. EFs of other nine elements, including Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Pb, were very high and varied greatly from spring to winter, with lowest in spring and highest in winter.

4.4 Factor analysis

Factor analysis is an important method for source distribution in the study of aerosols (Cao et al. 2004; Tang 1990). Its purpose is to find out the minimum factors that can explain the main variance of the system. Statistical analysis software SSPS10.0 was used for rotated component matrix factor analysis of element mass concentration in Beijing PM_{10} (Table 2).

The data reflected the factor loading matrix derived from the varimax rotation which could provide significant information about their origins. The first factor is 52.4%, the second 25.6%, the third 11.2%. It is sufficient to retain the three factors to explain 89.17% of the total variance. The first factor had strong relationship among the elements Si, Ca, Al, Fe, Mg and Ti, justifying the face that these elements coming from geological resources (Moreno et al. 2004). The second factor was relative with S、Zn、Pb、indicating that their major sources were from industrial emissions (Zhang et al. 2003), while the third factor had correlation with Cl and As, suggesting them mainly originated from coal combustion (Wang et al. 1999).

Table 2 Rotated component matrix of element mass concentration in PM_{10}

Elements	Factor1	Factor2	Factor3
Mg	0.977	9.160E-02	0.134
Al	0.968	−0.110	0.218
Si	0.969	−0.107	0.211
P	0.826	0.363	0.283
S	1.148E-02	0.924	0.292
Cl	−0.131	0.469	0.804
K	0.933	0.166	0.290
Ca	0.936	0.263	0.172
Ti	0.966	−8.412E-02	0.229
V	0.920	0.273	0.203
Cr	0.834	0.502	0.132
Mn	0.897	0.356	0.231
Fe	0.972	−3.876E-02	0.223
Ni	0.490	0.517	−0.151
Cu	0.868	0.260	0.382
Zn	0.121	0.864	0.384
As	0.501	−9.447E-02	0.814
Se	0.493	0.308	1.828E-02
Br	2.940E-02	0.782	−0.155
Pb	5.390E-02	0.963	6.307E-02

4.5 Discussion

One-year monitoring of Beijing PM_{10} indicated seasonal variation of mass concentration of PM_{10} and its chemical elements. Enrichment factors showed the elements, including Mg, Al, Si, K, Ca, Fe and Si in Beijing PM_{10} originated from crustal dust, while Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cl and Pb coming mainly from anthropogenic sources. Abundance of the anthropogenic pollutant elements increased gradually from spring to winter in Beijing air. Factor analysis testified that the major elements, Si, Ca, Al, Fe, Mg, and Ti in Beijing PM_{10} come from the same sources. The maximum values of these elements were all found in spring samples. This phenomenon probably caused by frequent windy days in spring season and making local dusts become fugitive in Beijing air. However, the anthropogenic elements, such as S, Zn, Pb, correlated strongly, indicating these three elements originated from the same source (Table 2). Mass concentration of sulfur reached its maximum (3.384 μg m^{-3}) in winter. It suggested that the sulfur is mainly originated from coal burning for resident heating. According to our survey, even if natural gas rather than coal has been used in Beijing central heating systems, coal is still widely used by Beijing residents especially in the rural areas. Our results agree with the conclusion by Wang et al. (1999) and Zinc in the airborne particles from industrial emission sources (Lin et al. 2005) which was considered most bioactive element in aerosol (Moreno et al. 2004; Lu 2003). In Beijing PM_{10}, Zn concentration did not vary much in all the seasons. Therefore, it was necessary to investigate the origination of this element in order to decrease its harm to health. Pb was found in Beijing PM_{10}, the major source is automobile exhaust

(Swietlicki et al. 1996). Although use of unloaded gasoline has been promoted, Pb is still another harmful element in Beijing PM_{10}.

Although As and Cl concentration were much less than the other elements in Beijing PM_{10}, the two are complex in composition in the Beijing PM_{10}. The As and Cl concentration (1.788 μg m^{-3}) reached maximum in winter. Cl originated from bio-material combustion (Liu et al. 2002) and also is a marker of coal burning, and As also comes from coal combustion. The cause of As and Cl is industrial combustion.

5 Conclusion

Conclusions are as following:

1. The mass levels of PM_{10} showed a seasonal variation, with much higher values in winter and spring, lower values in summer, and the lowest in autumn.
2. Mass concentrations of elements varied in PM_{10} collected in different seasons, with the highest percentage in spring PM_{10} and lowest in autumn. Mass concentration of crustal elements, such as Al, Si, Mg, Ca, Fe, reached maximum in spring season, while anthropogenic element, including S, Cl, Zn approached to higher in winter.
3. EFs of elements in Beijing PM_{10} suggested anthropogenic pollutant elements, including Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cl and Pb, increased gradually from spring to winter in Beijing air. Factor analysis indicated strong correlation of the elements Si, Ca, Al, Fe, Mg and Ti, which meant these elements coming from the earth crust or soil. S, Zn and Pb were associated with industry pollution. Cl and As might result from industrial combustion.

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