Journal of Environmental Sciences Vol.14, No.1, pp.7—11, 2002

ISSN 1001—0742
CN11-2629/X

Article ID: 1001-0742(2002)01-0007-05 **CLC number**: X131.1 **Document code**: A

Chemical composition of aerosols in winter/spring in Beijing

ZHANG Ren-jian, WANG Ming-xing, XIA Xiang-ao

(State Key Laboratory of Atmospheric Boundary Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China. E-mail: zrj@mail.iap.ac.cn)

Abstract: In 1999 aerosol samples were collected by cascade at Meteorological Tower in Beijing. The 12 group aerosol samples obtained were analyzed using PIXE method, which resulted in 20 elemental concentrations and size distribution of elemental concentrations. From the observation, the elemental concentrations, size distribution of elemental concentrations and their variations are analyzed. It shows that concentrations of the most elements in aerosols increase greatly compared with those in the past except that the concentrations of V, K, Sr, and the source of aerosols has changed greatly in the past decade. Fine mode aerosols increase more rapidly in the past decade, which may be due to the contribution of coal combustion and automobile exhaust. Pb content in aerosol is much higher than that at the beginning of 1980s, and has a decreasing trend in recent years because of using non-leaded gasoline.

Keywords: aerosol; PIXE; size distribution of elemental concentrations

Introduction

Aerosol plays an important role in radiative forcing and environment (Wang, 2000). Aerosols are the main pollution in north China, especially in urban areas because of human activities (Zhao, 1991).

The aerosol pollution in Beijing belonged to the type of coal combustion. As the number of automobile increases sharply with the development of economy, air pollution in Beijing has become more and more seriously. The "black pot" which often covers over Beijing in recent years especially in winter is neither SO_2 from coal burning nor NOx from emission gas of automobiles, but is fine particles, a mixture of the above mentioned two substances through physical and chemical transformation. The fine particles, which distribute from surface to 800 meters high not only has strong scattering effect on sunlight but also can bring bacterium and virus which can be absorbed into the lung and do harm to human being directly. So, it is very important to investigate the various elemental concentrations and particle size distributions of atmospheric aerosols.

At the beginning of 1980s, some research have been conducted on the chemical composition of atmospheric aerosol in Beijing (Ren, 1982; Wang, 1990) with PIXE method, but little research has been done since 1990s. With the progress of analysis technologies, individual particles of aerosol samples can be analyzed now (Wang, 1996a; 1996b; Zhang, 1996; 1998). In this paper, through the 6d experiments in February and March, 1999, the elemental concentrations of aerosols in Beijing and their change in recent years are investigated and discussed.

1 Observation

1.1 Sampler

The aerosol samples were obtained using instrument of cascade with 8 level of <0.25, $0.25-0.5$, $0.5-1$, $1-2$, $2-4$, $4-8$, $8-16$ and >16 μm. Samples are taken at 47m high level of in the Meteorological Tower during February 23 – 25, and at the top of a two-floor building nearby (6m high) during March 9 – 12 in the Institute of Atmospheric Physics, Beijing. The observation time is from 8:30 a.m. to 5:30 p.m. in the daytime and 5:30 p.m. – 8:30 a.m. in the nighttime of the next day. The flow rates at the beginning and the end of each sampling time were recorded, and the average of the two

Foundation item: NKBRSF Project (G1999043400) and Knowledge Innovation Project (KZCX2-204) of the Chinese Academy of Sciences

flow rates was used as the sample flow rate for the sample. In this study, 12 group samples for 6 days are obtained.

1.2 Analysis of the samples

The collected samples were analyzed by PIXE in Beijing Normal University. The PIXE analyses were carried out by using 2.5 MeV proton bombardments with a beam of 30 – 40 nA. Elemental concentrations and particle size distribution for 20 elements were determined, which are Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr and Pb.

2 Result and discussion

2.1 Elemental concentration

Table 1 gives the elemental concentrations for 20 elements from the experiment. Total elemental concentrations of most at 47m are higher than those at 6m, the elements are Al, Si, K, Ca, Ti, V, Cr, Fe, Ni, Cu, As, Se, Br and Pb. The ratio of the value is between 1 – 2.8. Concentrations of other elements such as P, Cl, Mn, Zn and Sr, at 47m are lower than those at 6m. The difference is less than 10%.

Table 1 Elemental concentration of aerosol (ng/m^3) in 1999

Elements	Fine mode			Coarse mode			Total concentration ratio (C_{47m}/C_{6m})
	47m 1999.2	6m 1999.3	Ratio (C_{47m}/C_{6m})	47m 1999.2	6m 1999.3	Ratio (C_{47m}/C_{6m})	
Al	3212.5	3386.5	0.95	10002.9	7922.7	1.26	1.17
Si	2883.3	2479.1	1.16	16492.7	12127.5	1.36	1.33
P	495.5	515.3	0.96	686.0	678.0	1.01	0.99
S	2194.9	3594.8	0.61	1095.6	1741.0	0.63	0.62
Cl	1130.5	1060.0	1.07	462.4	684.8	0.68	0.91
K	956.7	633.3	1.51	1240.7	986.7	1.26	1.36
Ca	845.9	634.8	1.33	6810.7	6700.9	1.02	1.04
Ti	67.2	47.2	1.42	440.2	341.6	1.29	1.31
V	1.2	0.7	1.71	8.2	5.0	1.64	1.65
Cr	12.3	9.3	1.32	15.7	12.2	1.29	1.30
Mn	52.6	77.6	0.68	124.0	103.8	1.19	0.97
Fe	828.3	574.8	1.44	4378.0	3317.8	1.32	1.34
Ni	21.1	13.9	1.52	83.9	51.7	1.62	1.60
Cu	25.1	35.7	0.70	73.0	53.5	1.36	1.10
Zn	155.9	165.4	0.94	126.0	125.7	1.00	0.97
As	27.5	24.1	1.14	40.8	29.1	1.40	1.28
Se	13.4	5.6	2.39	26.5	9.0	2.94	2.73
Br	34.9	22.7	1.54	28.4	11.0	2.58	1.88
Sr	5.9	8.2	0.72	46.4	49.5	0.94	0.91
Pb	117.6	143.0	0.82	122.4	62.5	1.96	1.17

Fig.1 gives the elemental concentrations of aerosol in 1983 and in 1999. Except Si, K, Ca, Ti, Sr and V, all elemental concentrations increase in various extent.

Among the coarse-mode aerosols, Al now is 0.9 times higher than that in 1983, while elemental concentrations of Si and Ti decrease. Concentration of As, which is the representative elements of coal combustion, is 3.8 times higher than that in 1983. This shows that the concentration of primary aerosols have a descendent trend, while the concentration of secondary aerosols have the increasing trend, dust removal arrangement does not offset the increase of aerosol emissions.

Among fine-mode aerosol, K concentration decreases by 60%. In 1983, the present sample site is a suburb area, and farmers used cordwood for warming, cooking and living, but now coal and natural gas are used. Cordwood has high K content. That is why K concentration decreases. V concentration decreases by 80%, this may be due to decrease of certain man-made emissions. P, Se, As and Cu are 3.6, 2.7, 3.7, and 4.1 times respectively higher than those in 1983. It shows that the fine mode aerosol increases quickly during the past decade, which may be due to the contribution of increase of coal combustion and automobile exhaust gas. In the present, the Pb concentration is about 1 times higher than that in 1983 but is lower than that in 1987 (Wang, 1990). This shows that Pb concentration has decreased in Beijing because of using clear gasoline recently. Presently, Pb in atmospheric aerosol maybe comes from local soil dust or remains in gasoline tank, which need to be investigated. It is estimated that the Pb concentration in aerosol in Beijing will continue to decrease in the following years.

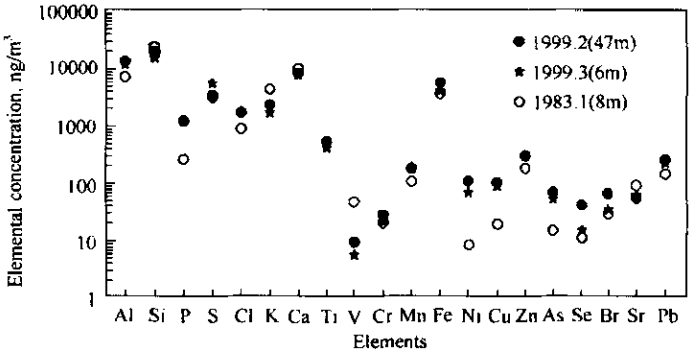

Fig.1 Elemental concentration of aerosol in Beijing in 1999 and 1983

2.2 Size distribution of elemental concentration

The size distribution of elemental concentration can reflect the sources of aerosols to some extent. Fig. 2 shows size distribution of Al, which is the single-peak, the concentration reaches maximum at 4 – 8 μm which is in the range of coarse mode. It shows that Al mainly comes from soil dust. The size distribution of Si, Ca, Ti, V, Fe and Ni are similar to Al. The concentrations of these elements at 47m are higher than that in 6m. It shows that the sources may come from elevated sources, concentrations of pollution emitted from chimneys at 30 – 40m altitude reach maximum at 40 – 50m, and are diffused to downwind with wind. Fig.3 are the size distribution of Mn and As which have two – peak appeared at 0.5 – 1 (or 0.25 – 0.5) μm and 4 – 8 μm. The size distribution of K is similar to that of Mn. The most of As is distributed in fine-mode in 1983 (Wang, 1983) but in coarse mode now. Cu has two-peak distribution in 1983 (Wang, 1986) but single-peak in 47m now, besides, its two-peak distribution in 6m is not distinct (Fig.4). Fig. 5 gives the size distribution of Pb, which is bi-mode in 47m and single-peak in 6m. S, Zn and Br have the similar distributions which means that they probably have the same sources.

Fig.6 are the size distribution of S at 47m and concentrations at 6m with different relative humidity during observed 3 days. The size distribution of S is bi-mode at 47m, but not bi-mode at 6m. The concentration at 6m is higher than that in 47m. At 6m, the elemental concentrations increase during the 3

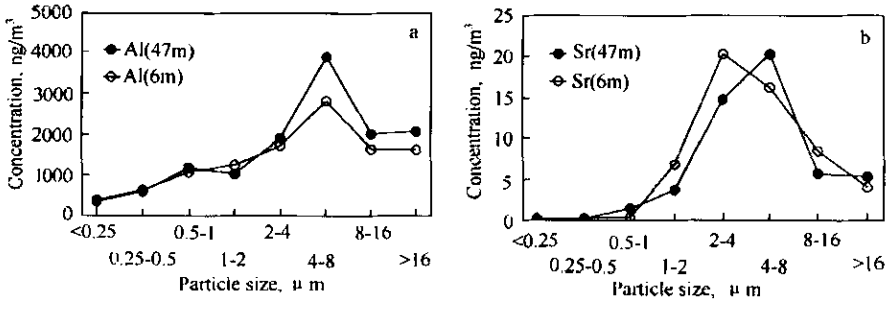

Fig.2 Elemental size distribution of Al and Sr

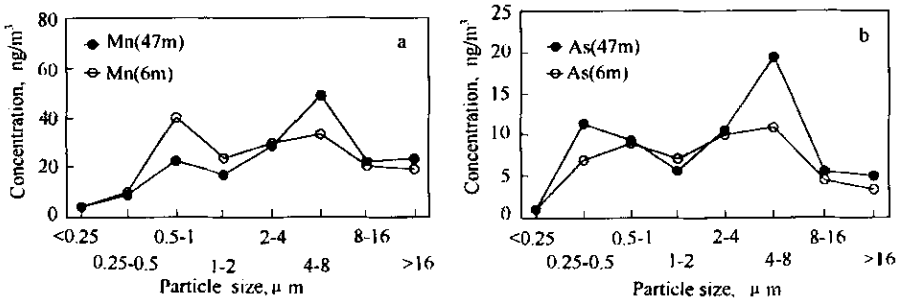

Fig.3 Elemental size distribution of Mn and As

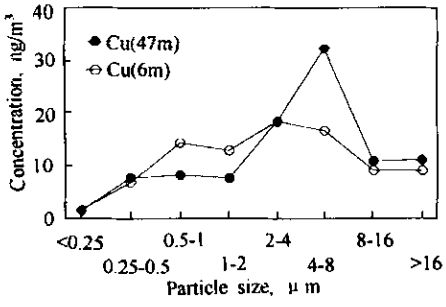

Fig.4 Elemental size distribution of Cu

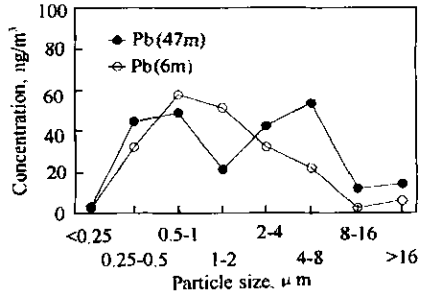

Fig.5 Elemental size distribution of Pb

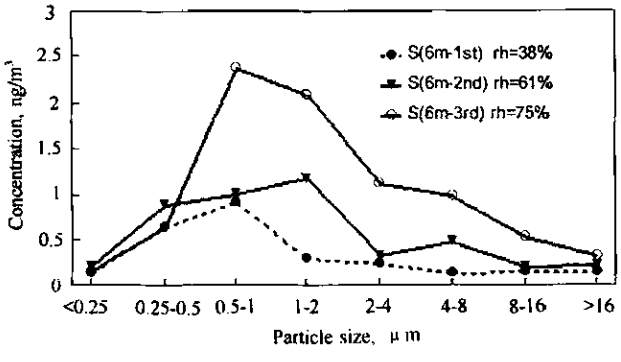

Fig.6 Elemental size distribution of S

days with the increasing of relative humidity, which is 38%, 61% and 75% respectively. Under the high relative humidity condition, SO_2 can be absorbed by aerosol or converted to SO_4^{2-} by multiphase reactions.

2.3 Enrichment factors analysis

The enrichment factors of elements in aerosol are defined as:

$$EF = (C_x/C_r)_a/(C_x/C_r)_r. \quad (1)$$

Where C_x is the concentration of elements x, C_r is a reference element, the subscript a refers to that in aerosol, while r to that in reference material. Usually, Al, Si and Fe are chosen as reference material, but Si is selected as reference element to calculate the enrichment factors of elements in aerosol in Beijing relative to crusted elements (Winchester, 1981). The enrichment factors of elements in aerosol in Beijing relative to crusted elements is also calculated using Si as reference material. The results are listed in Table 2.

Compared with those in 1983, enrichment factors of K and Sr decrease a bit while that of V decreases sharply. Enrichment factors of other elements increase distinctly. Enrichment factor of Cr in coarse mode now is 39 times higher than that in 1983. Enrichment factor of Ni in coarse mode now is 9 times higher than that in 1983 and 13 times higher in fine mode. Enrichment factor of Al in fine mode now is about 15 times higher than that in 1983. This shows that industry pollution sources have increased while natural dust has decreased. It is because of the rapid increase of coal burning and automobiles due to the urbanization in Beijing.

3 Results

From the research on elemental concentration of aerosol in Beijing, the following conclusions are drawn: (1) In the past decade, fine mode aerosols increase more rapidly, which may be due to the contribution of coal combustion and automobile exhaust gas. So more attention should be paid to small particles later. (2) Elevated source is one of the main sources of aerosol in Beijing. (3) Concentration of Pb now is lower than that at the beginning of 1990s because of using non-leaded gasoline, but is still higher than that in 1983, which may be due to resident Pb in soil dust and gasoline tank. It shows that the control on air pollution is effective. (4) With administration on the boiler reconstruction and using clear gasoline, the air condition is expected to be better, however, more research should be conducted to understand the sources and to provide scientific policy for pollution control.

Table 2 Enrichment factors in Beijing aerosol

Date	1999.2		1999.3		1983.1	
Element	Fine mode	Coarse mode	Fine mode	Coarse mode	Fine mode	Coarse mode
Al	3.76	2.05	4.61	2.20	0.22	1.24
S	805.25	70.26	1533.70	151.84	409.31	61.70
Cl	829.50	59.31	904.48	119.45	185.88	42.50
K	3.51	0.80	2.70	0.86	3.02	1.58
Ca	2.21	3.11	1.93	4.16	1.69	3.52
Ti	1.46	1.67	1.19	1.76	1.06	1.52
V	0.85	1.01	0.58	0.84	3.56	4.22
Cr	11.73	2.62	10.32	2.77	10.39	0.06
Mn	5.28	2.18	9.06	2.48	1.60	1.23
Fe	1.58	1.46	1.28	1.50	0.53	0.87
Ni	26.84	18.65	20.56	15.63	1.95	1.08
Cu	43.53	22.13	72.00	22.06	7.12	3.27
Zn	212.44	30.01	262.11	40.72	99.02	9.38
As	1457.30	377.94	1485.19	366.59	281.26	41.55
Se	25563.65	8837.08	12423.86	4081.63	6680.58	1312.65
Br	1331.60	189.41	1007.22	99.77	283.92	83.03
Sr	1.50	2.06	2.43	2.99	1.31	3.18
Pb	862.88	156.99	1220.20	109.02	391.44	42.03

Acknowledgement: The authors would like to express their thank to Prof. Zhang Wen for his help in the observation.

References:

Ren L X, Lu W X, Wang M X, 1982. A study of elemental concentrations in atmospheric aerosol from Beijing in late winter[J]. Scientia Atmospheric Sinica, 6(1):11—17.

Wang X F, Zhu G H, 1990. Elemental concentration and size distribution of atmospheric particles in the north urban area in winter/summer [J]. Scientia Atmospheric Sinica, 14(2):199— 206.

Wang A P, Yang S L, Sha Y, 1996a. Chemical characterization of individual aerosol particles in Beijing[J]. Chinese Journal of Environmental Chemistry, 15 (6): 488—495.

Wang A P, Yang S L, Sha Y, 1996b. Chemical characterization of individual fly ash particles from coal-fired power plant[J]. Chinese Journal of Environmental Chemistry, 15 (6): 496—504.

Wang M X, Ren L X, Lu W X, 1986. Elemental concentration and their size distribution of Beijing aerosol in January[J]. Atmospheric Sciences, 3(2): 199—207.

Wang M X, 2000. Aerosol in relation to climate change[J]. Climate and Environmental Research, 1—6.

Winchester J W *et al*., 1981. Fine and coarse aerosol composition from a rural area in northern China[J]. Atmospheric Environment, 15: 933—937.

Zhang D Z, 1996. Features of individual nitrate-containing particles in the urban atmosphere over Beijing[J]. Scientia Atmospheric Sinica, 20 (4): 408—413.

Zhang D Z, Zhao C S, Qin Y, 1998. Composition and morphology analyses of dust particles[J]. Acta Scientiae Circumstantiae, 18(5):449—456.

Zhao D S, Wang M X, 1991. Urban pollution atmospheric aerosol of coal combustion[M]. China Environmental Science Press. 404.

(Received for review November 17, 2000. Accepted February 12, 2001)