ELEMENTAL CONCENTRATIONS AND THEIR SIZE DISTRIBUTIONS OF BEIJING AEROSOL IN JANUARY

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ABSTRACT

Aerosol sampling was carried out at a city centre site and a suburb site in Beijing in January 1983. PIXE (Proton Induced X-ray Emission) compatible cascade impactors were employed. The samples were analysed for 20 elements by PIXE in Fudan University. It has been found that most of the elements have bi-mode size distributions with a gradual progression from mainly coarse mode Ca, Ti and Al to mainly fine mode Zn, As and Pb. Elements Cl, K, S and Si show most obvious bi-mode, of which Si and S are particularly interesting. The concentrations of coarse mode aerosol in the city centre are about 1.4 times as large as that in the suburb for most of the elements, while the concentrations of fine mode aerosol in the city centre differ greatly from that in the suburb and vary significantly among elements, indicating some industrial sources. The enrichment factors of elements indicate that the coal smoke has a large-scale influence in North China.

I. INTRODUCTION

Aerosol is a trace constituent of the atmosphere with very low concentration, which may be easily affected by human activities. Recent measurements have shown that aerosol mass loading in polluted cities may be 1000 times as high as that in remote clean air. The increase of aerosol particles will cause visibility degradation, affect weather, the radiation budget and the climate of the earth's atmosphere and may have hazard health effect on man. The deposition of aerosol particles may also affect the soil and water, causing secondary pollution. Aerosol particles may be absorbed by leaves of plant, which may then produce polluted food. Therefore, the particulate in the atmosphere has been a major concern of the environmental research.

The principal sources of aerosol particles in urban atmosphere are fossil fuel combustion, industrial activities, and traffic and wind-blown dust. The mass concentration of aerosol in coal-consuming cities may be very high, which may threaten our living environment. The aerosol in polluted atmosphere contains many toxic substances, which have various degrees of hazard depending on their size distributions. In order to define proper air quality standards and to make efficient and economic pollution control strategies, it is necessary to investigate the concentrations as well as particle size distributions of atmospheric aerosol.

Particles with a size less than about 10 μm may become a component of stable aerosol in the atmosphere, which have long atmospheric residence time and may be transported within a long distance to pollute the rural area under dry weather conditions. Coal smoke is one of the major air pollutants in Beijing. During winter, in particular, coal combustion for space heating emits large amounts of coal smoke, so that the particulate loading often exceeds the

national air quality standard[1]. In the early morning with a temperature inversion the mass concentration of TSP (Total Suspended Particulate) near the surface may be as high as 1 mg/m^3. It is noted that some toxic substances, e. g. As and polycylic aromatic hydrocarbons have very high concentrations in coal smoke. These substances are likely to be found in the fine mode, which has more serious health hazard. Thus, the investigation on the concentrations and particle size distributions of various elements in Beijing aerosol is of practical importance. Presented in this paper are the results obtained during a ten-day experiment in January 1983 at a site in the living and commercial zone of the city centre (in what follows we will call this site city centre) and a site at the edge of the city proper (in what follows we will call this site suburb). The characteristics of elemental concentrations and particle size distributions for both sites will be discussed. The enrichment factors of elements relative to the earth crust and background aerosol have been calculated, and the sources of aerosol are investigated.

II. EXPERIMENTAL

Aerosol sampling was carried out by using procedures compatible with elemental analysis by PIXE. Single orifice cascade impactors[2] were employed to collect 7 size fractions of aerosol particles with size cuts at 0.25, 0.5, 1, 2, 4, and 8 μmad[1]. The first size fraction, <0.25 μmad was collected by a backup nuclepore filter with 0.4 μm pore diameter and a thickness of 2 μm, the second size fraction was collected by a paraffin-coated Mylar film, and the rest by vaseline-coated Mylar films. The nuclepore filter and impaction slides have very low blank value for all the elements but Si, P, S, Cl, and Zn, which are abundant in urban aerosol. Thus for all the elements measured by PIXE the blank concentrations on collection slides are much lower than that in urban aerosol.

The experiment in January 1983 had two sampling sites. The city centre site was on the second floor of the Institute of Archaeology, Chinese Academy of Social Sciences, 5 meters above the ground, which is located in a residential area without heavy industry. The primary pollution sources are distributed to coal combustions for space heating, cooking and water boiling. The site was selected in such a way that had avoided the direct influence of plumes from nearby chimneys. Therefore, the samples collected here may reflect the general situation of the residential area in the city. The suburb site was on the first level of the Beijing 325-meter meteorological tower, 8 meters above the ground, which is located at the edge of the city proper. The samples collected here may represent the suburb air.

The sampling durations were about 9 and 14 hours for day (08—17 h) and night (18—08 h). These sampling durations were determined according to aerosol mass concentration with a criterion that the flow rate will not vary greatly during sampling. In fact, the flow rates at the beginning and the end of each sampling were recorded, and the average of the two was used as the sampling flow of that sample. In most cases, the two measured flow rates are very close, which indicates that the sampling durations are correct and the average flow rate may well represent the true sampling flow.

13 samples were collected for each site during the period of January 5—15, which was just in midwinter so that the results presented here may reflect the general characteristics of the winter air.

The samples were analysed by PIXE in Fudan University. Elemental concentrations

1) μmad=μm aerodynamic diameter.

and particle size distributions for 20 elements have been determined, The PIXE analyses were carried out by using 1.8 MeV proton bombardments with a beam current of 20 nA. A 660 μm thick Mylar X-ray absorber was used before the Si (Li) detector to enhance the sensitivity of heavy metals[3].

III. RESULTS AND DISCUSSIONS

1. *Particle Size Distributions of Elemental Concentration*

Fig. 1 shows particle size distributions of elemental concentration for 12 representive elements, in which solid dots represent the mean of 13 city centre samples, while small circles represent that of 13 suburb samples. It can be seen that most of the elements show bi-mode distributions that differ significantly from the results measured in nonurban area in North China[4]. This may indicate the complicacy of sources of urban aerosol which is a mixture of fine and coarse mode aerosols. An inspection of the size distributions reveals that they may be grouped into three categories depending on the relative contributions of fine to coarse mode. The size distributions of Ca, Ti, and Al show essentially a coarse mode with insignificant fine mode. Most material is found in the 2—4 and 4—8 μmad size fractions. This indicates an origin of soil dust and coal smoke for these elements. It is noted that particles emitted from small boilers without any dust collectors are large in size, and those from coal stoves are even larger, which are as large as soil dust particles. Zn, As, and Pb show a distribution with large fine mode but very small coarse mode, which indicates that these elements mainly come from the conversion of gas to particle, and the small coarse mode may be due to coal smoke as the soil contains little of these elements. Cl, K, Si, and S show comparable fine and coarse modes. The bi-mode distributions of Si and S are particularly noteworthy. They were about the first ever reported in the literature. Particulate S has been recognized as secondary pollutant that is generated from gas to particle conversion of gaseous SO_2. Most material of particulate S has been found in the size fraction of 0.5—1 μmad. The coarse mode S, peaked at 2—4 μmad size fraction in Beijing aerosol is as large as the fine mode. This large coarse mode S could not be originated from soil dust. Its possible sources are: 1) unburned coal particles from small boilers and stoves, 2) growth of finer particles generated from gas to particle conversion of gaseous SO_2 under favorable conditions, 3) SO_2 oxidation on the surface of pre-existed large particles. Si has been recognized as typical earth crustal element, but the ultra-fine Si observed in Beijing aerosol (<0.25 μmad) could not be generated from the soil. It may have a source of incomplete coal combustion which also produce high CO[5]. The bi-mode distribution of Pb further confirms our idea that the particulate Pb in Beijing has complex sources, e. g. coal smoke and automobile exhaust[6].

The major difference between the city centre and suburb samples is that the suburb aerosol has more significant coarse mode which peaks further towards to the coarsest size. This may be due to the larger ratio of surface wind-blown dust, which is coarser, to coal smoke in suburb aerosol.

2. *Elemental Concentrations of Aerosol*

Listed in Table 1 are elemental concentrations of fine and coarse aerosols in both city centre and suburb. It can be seen that the elemental concentrations of coarse aerosol in the city centre are about 1.4 times as high as that in the suburb for most of the elements. For

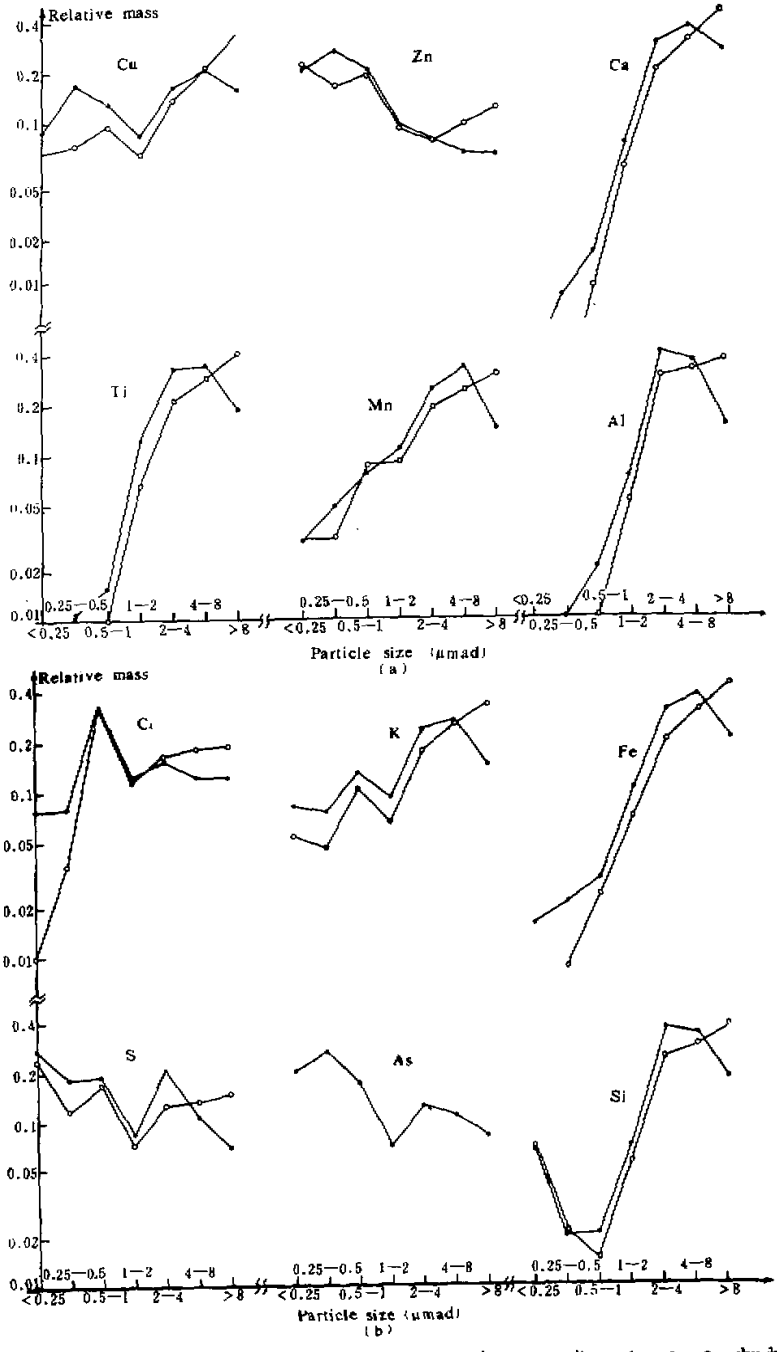

Fig. 1. Particle size distributions of elemental concentration. •—• city centre, o—o suburb.

the elements that are most abundant in the soil, e. g. Al, Si, and Ti, this ratio is about 1.3. As is a tracer element of coal smoke, and its concentration in coarse aerosol in the city centre is 1.5 times as high as that in the suburb. These results indicate that the coarse soil dust loading shows little difference between the two sampling sites, while the coal smoke is 50% higher in the city centre than in the suburb.

The elemental concentrations of fine aerosol in the city centre differ greatly from that in the suburb, and the differences are much more complicated. For the representive element of coal smoke As, the concentration in the city centre is 40% higher than that in the suburb. This may represent the spacial distribution of coal smoke. The concentrations of Cr, P, Pb, and Br in the city centre are much higher than that in the suburb, indicating industrial sources of these elements in the city centre. Pb and Br are major constituents of automobile exhaust. The very large difference of concentration between the city centre and suburb for Pb and Br, compared with that for As, 4 tims for Br and twice for Pb, indicates that the aerosol Pb in Beijing is partly from coal combustion and partly from automobile[6]. Smaller differences between city centre and suburb aerosols are found for the concentrations of Cl, K, S and V. This indicates that these elements in fine aerosol are generated from combustion processes that have rather uniform spacial distribution over a large area.

Table 1. Elemental Concentrations in City Centre and Suburb Aerosol

Element	Fine Mode (ng/m³)			Coarse Mode (ng/m³)		
	Centre	Suburb	Ratio	Centre	Suburb	Ratio
Al	518	350	1.48	8027	6303	1.30
Si	3703	5269	0.7	23583	18017	1.31
P	336	147	2.28	298	110.4	2.71
S	2525	2039	1.24	1215	1051	1.16
Cl	535	463	1.16	399	362	1.10
K	1732	1506	1.15	3451	2698	1.16
Ca	1067	1183	0.90	13828	8408	1.64
Ti	77.8	89.6	0.87	586	437.3	1.34
V	10.3	9.2	1.12	56.2	37.3	1.51
Cr	146.3	19.9	7.30	6.1	0.42	1.45
Mn	34.1	29.2	1.17	112.6	76.3	1.49
Fe	547	505.2	1.08	3760	2851	1.32
Ni	3.1	2.8	1.11	6.6	5.3	1.24
Cu	12.7	7.5	1.69	16.8	11.8	1.42
Zn	280.0	132.8	2.11	78.8	43.0	1.83
As	13.8	9.7	1.42	7.6	4.9	1.55
Pb	190.8	97.5	1.96	51.4	35.8	1.44
Se	12.4	6.4	1.94	5.9	4.3	1.37
Br	53.9	13.6	3.96	10.76	8.7	1.24
Sr	13.2	9.4	1.40	114.5	78.1	1.47

Table 2 gives a comparison between the elemental concentrations of aerosol in Beijing and other locations. Listed also in Table 2 are the background values for North China[7]. It can be seen that concentrations of Al, Si and Ca in the city centre of Beijing are higher than in the suburb and much higher than in Xinglong and in Washington. Ca, in particular, has a concentration in the city centre 60 % higher than in the suburb and 14 times higher

than in Xinglong. This indicates that much of the particulate Ca is from lime-cement dust of construction site rather than from soil dust[7]. The concentration of S in the city centre is only 20 % higher than in the suburb and 60 % higher than in Xinglong, indicating that particulate S is rather uniformly distributed over a large area in North China. It is noted that the concentration of particulate S is twice as high as that in Washington. For the other elements, except Pb and Br, concentrations in the city centre of Beijing are about 5—10 times higher than in Xinglong and Washington, indicating the gravity of pollution problem in Beijing. The concentrations of particulate Pb and Br in Beijing are much lower than in Washington, but 6 times higher than in Xinglong and 30 times higher than the background value of the region. This may further confirm that the particulate Pb in Beijing aerosol is partly from coal combustion and partly from automobile exhaust.

Table 2. Elemental Concentrations of Beijing Aerosol, Compared with Other Locations

Element	Concentrations (ng/m³)				
	Beijing City Centre	Beijing Suburb	Xinglong	Background	Washington[6]
Al	8546	6653	1552	602	1580
Si	27286	23286	3441	1741	3150
P	635	258	—	—	—
S	3739	3090	2329	358	1890
Cl	934	825	203	28.0	140.0
K	5184	4475	585	208	510
Ca	14894	9590	999	860	770
Ti	664	527	112	36.1	120
V	66.5	46.5	—	2.12	54
Cr	152.4	20.3	—	1.1	11
Mn	146.6	105.5	37	10.5	27
Fe	4308	3356	760	438	1260
Ni	9.7	8.1	2.3	0.8	27
Cu	29.5	19.3	2.8	0.7	13
Zn	358.5	175.8	30	8.9	150
As	21.4	14.6	2.6	0.63	5.7
Pb	242.9	133.3	30	7.3	1400
Se	18.3	10.6	1.3	<0.1	3.5
Br	64.6	22.3	3.2	0.64	190
Sr	127.7	87.5	18	4.3	3.2

3. *Enrichment Factors*

Aerosol particles collected near the ground have a surface origin, so that it is expected that the atmospheric aerosol near the surface in a clean atmosphere has a composition similar to that of the earth crust[8]. Therefore, it is a common practice to compare the measured aerosol composition with that of the earth crust for a quick estimation of pollution sources of various elements. This is carried out by calculating the enrichment factors of various elements in aerosol relative to the earth crust. The land surface of the earth, however, is very complicated in chemical compositions, which vary greatly from place to place. Furthermore, the atmosphere is a super fluid so that the aerosol particles generated from the

surface may be transported and mixed over the globe. Thus, it is usually difficult to decide whether the averaged earth crust or the local rock and soil should be used as the reference material. The ideal reference is the local background aerosol, but this is hardly obtained for polluted cities.

The enrichment factors of elements in aerosol are defined as

$$\mathrm{EF}=\frac{(C_x/C_r)_a}{(C_x/C_r)_r}\ , \qquad (1)$$

where C_x is the concentration of element x, C_r is that of a reference element, the subscript a refers to that in aerosol, while r to that in reference material. Those elements that are abundant in natural aerosol but have fewer pollution sources are chosen as references. Fe has been widely used as a reference element. However, a significant amount of Fe in Beijing aerosol is generated from coal combustion, so that it is not a good reference for this study. It can be shown that Al may serve as a better reference for our purpose here[10]. Using Al as the reference, the enrichment factors of elements in Beijing aerosol relative to averaged earth crust and background aerosol of North China have been calculated. The results are listed in Tables 3 and 4 respectively.

Table 3. Enrichment Factors of Various Elements in Beijing Aerosol Relative to Averaged Earth Crust

Element	Fine Mode			Coarse Mode		
	Beijing Centre	Beijing Suburb	Coal Smoke	Beijing Centre	Beijing Suburb	Coal Smoke
Al	1	1	1	1	1	1
Si	2.12	5.26	0.32	0.87	0.85	1.46
P	—	—	—	—	—	—
S	1523	82	—	47.3	52	74
Cl	645.3	36.7	75	31.1	22.5	11.5
K	10.44	13.88	0.39	1.34	1.47	0.02
Ca	4.58	2.36	0.40	3.82	1.82	0.34
Ti	2.78	4.3	0.55	1.35	1.28	3.6
V	11.69	10.1	1.75	4.12	3.48	0.75
Cr	235.3	51.7	1.46	0.63	0.04	0.49
Mn	5.48	5.2	0.70	1.17	1.01	1.27
Fe	1.73	2.0	0.97	0.75	0.74	0.46
Ni	6.50	8.9	9.7	0.89	0.91	0.14
Cu	36.58	19.5	5.3	3.12	2.79	3.93
Zn	628.4	88	6.1	11.4	7.9	0.77
As	1211	1260	420	43.04	35.3	24.8
Pb	2302	96	—	40.02	35.5	17.5
Se	4×10^4	3×10^4	240	1225	1×10^3	900
Br	3356	1253	112	43.2	44	20.6
Sr	5.54	3.8	1.51	3.1	1.54	0.47

It can be seen from Table 3 that in coarse mode aerosol those elements that were enriched in coal smoke have high enrichment factors for both city centre and suburb sites with one exception of Ca. The enrichment factor of Ca is low in coal smoke, but high in suburb

coarse aerosol, and even higher in city centre coarse aerosol. These indicate that the coarse mode aerosol in Beijing has three sources, i. e. soil dust, coal smoke, and construction dust. The first two sources have a similar strength for the city centre and suburb sites, while the third is stronger in the city centre than in the suburb. As discussed earlier, Pb in Beijing aerosol has a distinct size distribution with a significant coarse mode. The enrichment factor of Pb in coarse aerosol in Beijing is high, and is about the same in the city centre as in the suburb. This indicates that the coarse mode Pb is originated from coal combustion.

Table 4. Enrichment Factors of Various Elements in Beijing Aerosol Relative to Background Aerosol

Element	Fine Mode		Coarse Mode	
	City Centre	Suburb	City Centre	Suburb
Al	1	1	1	1
Si	2.50	5.26	1.03	1.0
P	—	—	—	—
S	68.6	82	2.13	2.35
Cl	28.7	36.7	1.38	1.6
K	10.8	13.9	1.39	1.5
Ca	1.44	2.4	1.2	0.93
Ti	2.5	4.3	1.21	1.2
V	7.7	10.1	2.69	2.3
Cr	257	51.7	0.09	0.05
Mn	4.1	5.2	0.88	0.76
Fe	1.5	2.0	0.64	0.64
Ni	6.7	8.9	0.91	0.93
Cu	22.3	19.5	1.90	1.1
Zn	126	88	2.28	1.6
As	266	770	9.5	5.6
Pb	127	96	2.2	2.0
Se	2×10^3	1200	74	50
Br	520	138	4.8	4.9
Sr	3.6	3.8	2.01	1.0

The enrichment factors in fine mode aerosol are much more complicated. Many elements, e.g. K, Ca, V, Cr, and Mn, that were not enriched in coal smoke have high enrichment factors in fine mode aerosol. Cu, Zn, As, Se, and Br have much higher enrichment factors in fine mode aerosol than in coal smoke. These indicate that the above mentioned elements in fine mode aerosol have other industrial sources in addition to coal combustion. A special case is element Si that has higher enrichment factors in the suburb than in the city centre. This may indicate a source of steel plant, which is closer to our suburb sampling site. The enrichment factor of Pb in fine mode aerosol is 20 times higher in the city centre than in the suburb, which is much higher than in coal smoke. This may indicate that the fine mode Pb is originated from automobile exhaust and other industrial processes rather than coal combustion, in contrast to the coarse mode.

The enrichment factors of elements in aerosol relative to local background aerosol listed in Table 4 are better indicators of air pollution problem. The high enrichment factor

of an element may definitely indicate a pollution source of that element. It can be seen that the enrichment factors in the coarse mode are generally low for all the elements but As, Se, and Br, and they are about the same in the city centre as in the suburb. This indicates that the coarse coal smoke and soil dust are rather uniformly distributed in this study region. The air pollution problem is clearly reflected in fine mode aerosol, which has very high enrichment factors for many elements. It is these fine particles that are hazard for human health.

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