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Preliminary study of airborne particulate matter in a Beijing sampling station by instrumental neutron activation analysis

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Abstract

A long-term study on airborne particulate matter (APM) and air pollution trend in Beijing has been undertaken supported by International Atomic Energy Agency (IAEA) and National Natural Science Foundation of China. Sampling was carried out using Gent stacked filter unit sampler at a sampling station (traffic representative) in Beijing city. Two hundred and ten samples were collected during 1999 and 2000 in two size fractions of PM10 (coarse) and PM2.5 (fine). About 45 elements were determined for most of the samples by instrumental neutron activation analysis. Enrichment factor analysis and Factor Analysis were performed based on data determined. Possible sources of the APM were preliminarily identified. Some interesting correlation was observed between sandstorm episode and the variation of relevant element concentrations. In general, during the sandstorm episodes the concentrations of crust elements with natural origin increase dramatically and the increase of fine fraction is usually higher than that of coarse fraction. On the contrary, the pollution elements of local origin decrease during sandstorm episodes.

Keywords: INAA; Fine fraction; Coarse fraction; Sandstorm; Source apportionment

1. Introduction

The study of airborne particulate matter (APM), especially the distribution and multielement composition of PM2.5 (fine particles with diameter $<2.5\,\mu m$) and PM10 (coarse particle with diameter between 2.5 and $10\,\mu m$), is gaining worldwide attention because of its severe health effects (Pope et al., 1992; Dockey et al., 1989; Dockey and Pope, 1994) such as respiratory and cardiovascular disease (Dockey et al., 1993), as well as visibility effects and transboundary transportation. Among the methods for multielemental determination in APM, neutron activation analysis (NAA) has unique features including high-precision, non-destruction and multielemental capability (Tian, 2000; IAEA, 1992). Based on data obtained by NAA (or other nuclear and non-nuclear methods) receptor modeling (Hopke, 1985, 1991) has been used to study the aforementioned issue (Hopke, 1994). In our work, more than 40 elements were determined in most of the APM samples. Based on nearly two years continuous sampling and analysis, a picture of seasonal variation of multielement concentrations was depicted that enable us to gather enough information for the study of pollution trends, source impact and Asia sandstorm. Some interesting correlation was found between sandstorm episode and elements concentrations variation. Enrichment factor analysis and factor analysis were also performed to identify possible sources in Beijing urban area with the data measured in the study.

2. Experimental

2.1. Sampling, sample handing and standard preparation

The sampling site is located at CheGongZhuang, northwest of Beijing (representative of heavy traffic). A

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Gent stacked filter unit (SFU) sampler (Maenhaut et al., 1993) consisting of two nuclepore filters with 0.4 and 8 μm pore sizes was used for collecting PM10 and 2.5 APM at a general frequency of twice a week. Altogether 210 samples were obtained from 11 December 1998 to 28 September 2000.

Constant humidity ($50 \pm 5\%$, rel) has been maintained when samples were weighed before and after APM collection using Mettler Toledo GmbH Microbalance (readability 1 μg). One blank filter for every 20 samples was analyzed for corrections of multielement concentrations in APM samples. Chemical standard solutions were made by high-purity metals or compounds of elements to be determined. Standards were prepared by quantitatively dispensing the solution onto ashless filter paper, drying under infrared lamp, and packing in PE bag (for short irradiation) or Al foil (for long irradiation). Weighed Fe wire and 25 μm Zr foil were used for comparator and neutron flux ratio monitors, respectively, in k_0-NAA.

NIST SRM 1632a (coal powder) and GBW 07312 (stream sediment) were concurrently analyzed for quality control.

2.2. Irradiation and counting

Samples were packed in clean capacitor paper for short irradiation. After counting and decay for one week (or longer), they were repacked in Al foil for long irradiation.

All irradiation was carried out at a 15 MW heavy water research reactor in China Institute of Atomic Energy. For short irradiation, a rabbit system was used with neutron flux of $1 \times 10^{13}\,\mathrm{n\,cm^{-2}\,s^{-1}}$ at irradiation position. For long irradiation, arbitrary heavy water reflector channels were used with neutron fluxes of (3–$6 \times 10^{13}\,\mathrm{n\,cm^{-2}\,s^{-1}}$. A typical irradiation-counting scheme is shown in Table 1.

All countings were performed at an automated HPGe spectrometer system (Canberra 35%, 2.1 KeV). Software SPAN was used for peak analysis and a hybrid k_0-relative software ADVNAA (Ni, 1997) for elemental concentration calculations. It is noteworthy that S, an element commonly not considered to be determinable by NAA in APM samples, has been determined in 25–30% fine APM samples using our 35% efficiency HPGe detector. By using an HPGe with much higher efficiency (say, 60% or higher), S could be very well determined in most fine APM samples.

3. Results and discussion

Forty to forty-seven elements were determined in the 210 coarse and fine APM samples so far analyzed. Internal consistency and quality control were achieved by comparisons between results from k_0 and relative NAA, and analytical results and certified values of the elements of interest in SRMs/CRMs. In general, the elemental concentrations of the APM collected from December 1998 to September 2000 (two winter seasons and two summer seasons) show the characteristic seasonal variation in Beijing city. For example, in the wintertime the fine and coarse concentrations of Br, Co, Ga, As can reach high values, while in summer they drop down dramatically, as shown in Fig. 1. Two of the reasons may be the coal burning for heating and the sandstorm episodes during winter and early spring in Beijing city.

It is important to choose reference element when calculating EF values. The elements of Al and Sc are the optimal choices. When one is chosen, the other can be used as verifying element in such a way that its EF value should be close to one. Enrichment factors of 45 elements for an average of 210 APM samples are presented in Fig. 2. All EF values are calculated with respect to earth crust average from Meason (Al is

Table 1
A typical irradiation-counting scheme for APM analysis

Counting #	Neutron flux, n ($\mathrm{cm^{-2}\,s^{-1}}$)	T_i	T_d	T_c (s)	Elements determined
1	1×10^{13}	300 s	300 s	300	Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Cu, Br, Sr, In, I, Ba, Dy
2	1×10^{13}	300 s	1 h	500	Na, K, Sr, In, Ba, Dy, Mn
3	1×10^{13}	300 s	10 h	1000	Na, K
4	3×10^{13}	16 h	4 d	1500	Na, Ca, Ga, As, Br, Mo, Cd, Sb, Ba, La, Nd, Sm, Yb, Lu, W, Au, U
5	3×10^{13}	16 h	15 d	4000	Sc, Cr, Fe, Co, Ni, Zn, Se, Rb, Sr, Zr, Ag, Cs, Ce, Nd, Eu, Tb, Lu, Hf, Ta, Hg, Th

Note: $T_i T_d, T_c$ refer to irradiation time, decay time, and counting time, respectively.

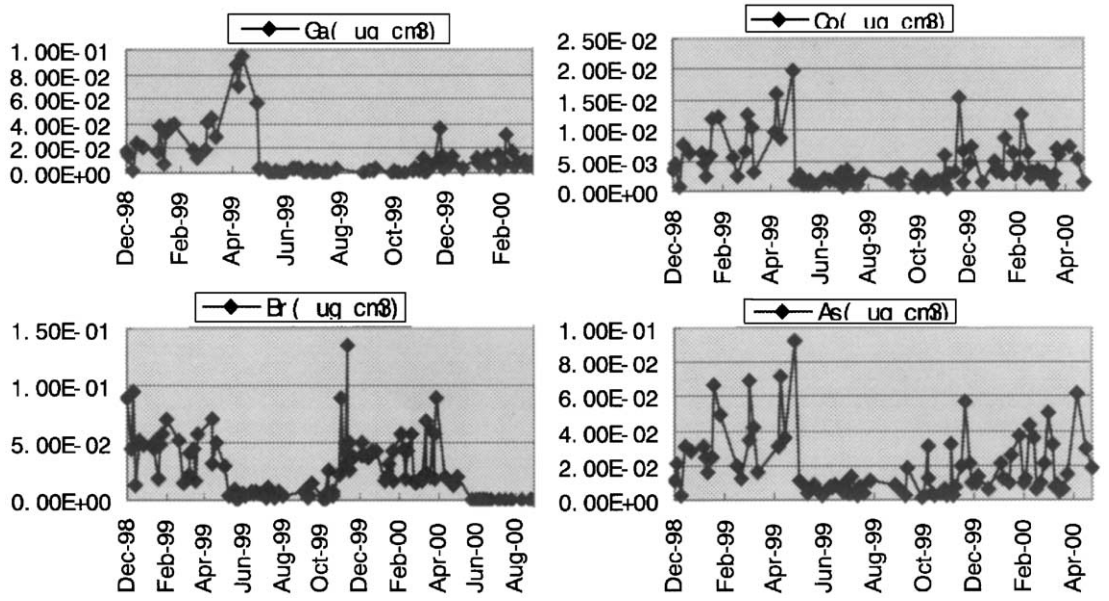

Fig. 1. The concentrations of Br, Co, Ga, As in fine fraction from December 1998 to September 2000.

reference element), The following can be observed based in Fig. 2:

(a) The EF of Sc is close to one, confirming the suitability of Al as a reference element.
(b) The fine particles usually have larger EFs than coarse ones for pollution elements.
(c) EF values of Al, Ba, Ca, Ce, Mg, Dy, La, Lu, Sm, Tb, Yb, Ta, V, Th, Hf, Sc, Fe, Mg, Ti are close to one, indicating their dust and soil origin. The same conclusion can be drawn from the factor analysis, as described below.
(d) The elements having prominently high EFs such as As, Br, Cd, Hg, I, In, Se, Sb, S, Zn, etc., clearly indicate their anthropogenic pollution origin.

Factor analysis based on 90 fine APM samples (98–12 to 00–05) for 36 elements have been made. The rotated

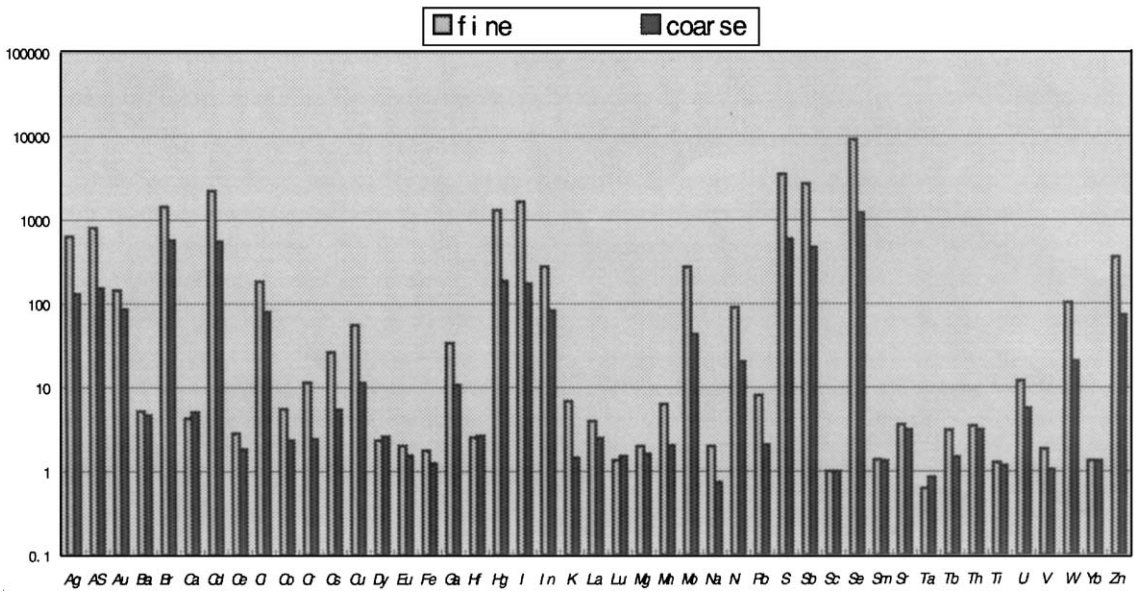

Fig. 2. Enrichment factors of 45 elements for fine and coarse particles, in logarithm.

Table 2
Rotated factor loadings for 36 elements in fine APM

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Communality
Ag	−0.18	0.09	0.12	0.11	−0.03	**0.87**	0.04	0.83
Al	**0.89**	0.02	0.06	0.02	0.06	0.01	−0.15	0.83
As	0.05	**0.52**	**0.73**	0.16	0.13	−0.04	0.24	0.91
Au	0.02	−0.15	0.12	**0.60**	−0.02	0.32	0.22	0.55
Ba	**0.85**	0.09	0.24	0.19	0.08	−0.12	0.04	0.84
Br	0.24	0.17	**0.64**	0.36	0.33	0.13	−0.05	0.75
Ca	**0.78**	0.24	−0.02	0.03	−0.05	0.00	0.15	0.69
Cd	−0.03	0.02	−0.03	−0.04	**0.79**	0.08	−0.19	0.67
Ce	**0.83**	−0.04	−0.08	−0.05	0.01	0.03	0.37	0.83
Cl	0.09	0.07	0.11	**0.89**	−0.02	−0.04	−0.02	0.81
Co	0.34	0.17	**0.81**	0.29	−0.02	−0.08	0.05	0.90
Cs	0.18	**0.88**	0.26	−0.08	−0.04	0.10	0.02	0.90
Cu	0.25	0.11	0.30	0.38	−0.10	0.15	**0.64**	0.75
Eu	**0.78**	−0.01	0.13	0.22	−0.17	0.00	0.16	0.73
Fe	**0.92**	0.30	0.02	0.02	−0.02	0.07	0.07	0.95
Ga	**0.54**	0.27	**0.69**	0.21	−0.03	0.02	0.06	0.89
Hf	**0.88**	−0.01	0.14	0.10	−0.06	−0.02	−0.11	0.82
I	−0.11	**0.52**	−0.03	−0.06	**0.43**	0.09	**0.51**	0.74
In	−0.06	0.16	0.10	0.01	**0.70**	−0.09	0.26	0.60
K	0.29	**0.82**	−0.04	0.09	−0.02	0.01	−0.01	0.78
La	**0.82**	0.10	0.02	0.01	0.03	0.01	0.43	0.87
Mg	**0.89**	0.30	0.03	0.08	−0.07	−0.06	0.08	0.90
Mn	0.45	0.46	0.10	0.01	0.20	**0.65**	0.09	0.90
Na	0.38	0.32	0.43	**0.67**	−0.05	−0.07	0.08	0.90
Rb	0.43	**0.83**	0.17	−0.02	0.09	0.04	−0.12	0.92
S	−0.35	0.30	−0.14	−0.37	−0.34	−0.01	0.14	0.51
Sb	0.02	**0.63**	**0.61**	0.10	0.05	0.05	0.27	0.85
Sc	**0.96**	0.12	0.22	0.09	0.00	−0.01	−0.07	0.99
Se	−0.13	**0.66**	**0.63**	0.05	0.02	−0.02	0.06	0.85
Sm	**0.93**	0.03	0.25	0.11	0.06	0.00	−0.16	0.97
Th	**0.96**	0.07	0.21	0.08	0.03	0.00	−0.04	0.97
Ti	**0.94**	0.02	0.00	0.02	0.04	0.04	−0.08	0.90
U	0.30	0.00	**0.85**	0.15	0.00	0.10	−0.09	0.86
V	**0.83**	0.23	**0.46**	0.12	0.01	−0.02	−0.05	0.97
W	−0.07	0.06	**0.53**	−0.25	−0.07	0.28	0.04	0.44
Zn	0.05	**0.78**	0.36	0.07	0.27	0.15	0.14	0.86

Note: Bold data indicate elements with highest scores in the factor.

factor-loading matrix is shown in Table 2. Seven factors are identified. The total communalities for 31 of the 36 elements are >70%, meaning that they are largely accounted for. From the major elements in each factor, the following is implied.

In factor 1, elements with the highest scores include Al, Ba, Ca, Ce, Eu, Fe, Ga, Hf, La, Mg, Sc, Sm, Th, Ti, and V, clearly indicating the soil and fly ash origin. In factor 2, elements with the highest scores include As, Cs, I, K, Rb, Sb, Se, and Zn, and at a less extent, Ca, indicating a mixture of refuse incineration and limestone, originating from large and small refuse incineration sites and numerous construction working sites in Beijing. In factor 3, elements with the highest scores include As, Br, Co, Ga, Sb, Se, U, V, and W, indicating, among other origins, the motor vehicle exhaust and coal burning origins. In factor 4, elements with the highest scores include Au, Cl, and Na, indicating a sea spray origin. The origin of Au is to be investigated. In factor 5, elements with the highest scores include Cd, I, and In, probably having a refuse incineration (e.g. used battery, etc.) and/or paint pigment origin. In factors 6 and 7, elements with the highest scores are Ag, Mn and Cu, I, respectively. They may have an origin of non-ferrous metal research institutes or factories.

The sandstorm, which originates from Mongolia across north China (inner Mongolia, Beijing, Hebei, Tianjin) to the east of Korea and Japan, has become a very important regional environmental event. Two samples were collected on 4 and 9 April 2000 when the fifth and sixth sandstorm of this year occurred in Beijing. During sandstorm episodes, volume concentrations of most elements of natural origin, such as Al, Ce, Cr, Cs, Eu, Fe, Hf, Lu, Sc, Sm, Th, Ti and V were much

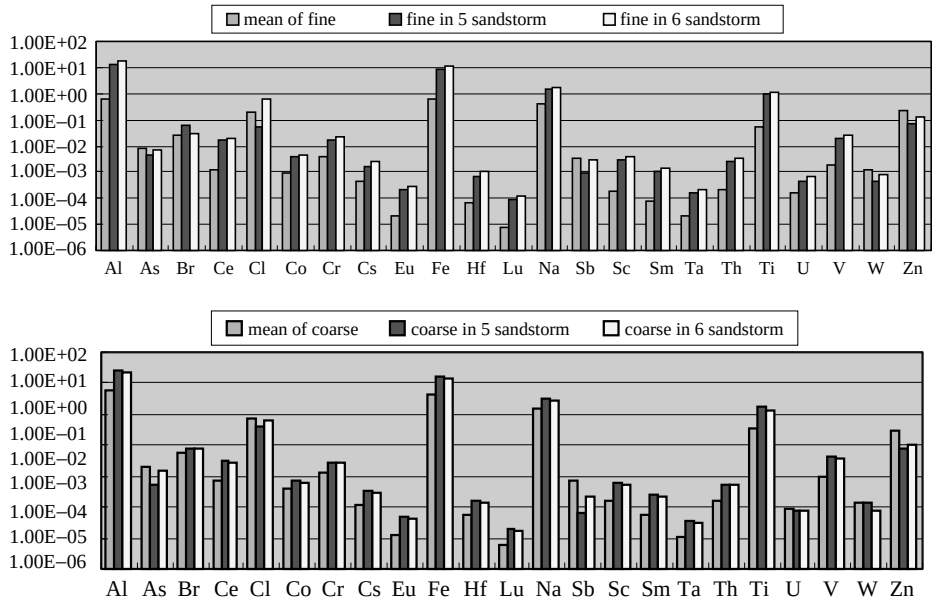

Fig. 3. Comparison of fine and coarse concentration between mean of usual time and fifth, sixth sandstorm. In logarithm ($\mu g\,cm^3$).

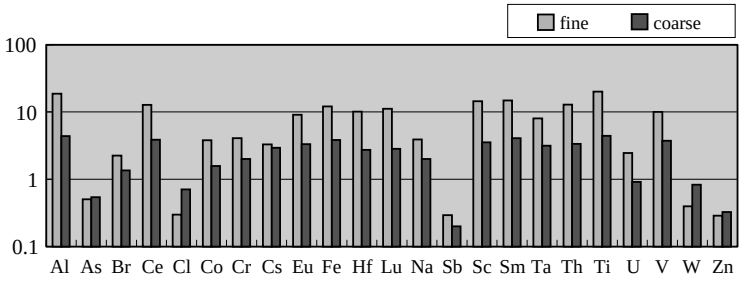

Fig. 4. The concentration increase of fine and coarse APM during sandstorm, in logarithm.

higher than usual time, as shown in Fig. 3. Furthermore, it can be seen from Fig. 4 that this increase for fine fraction is usually higher than that for coarse one, which shows the two characteristics of fine particles, i.e. long-distance transportation and long-time residence. It was also interesting to find from both Figs. 3 and 4 that, instead of increase, the concentrations of pollution elements such as As, Cl, Sb, W, Zn decrease compared to those at usual time. It indicates that these elements were not transported by the storm, but had local origin and dispersed and diluted by the storm.

4. Conclusion

Taking the advantages of high-precision and multi-element capability of INAA, the elemental composition and concentrations were obtained in both fine and coarse fractions of APM samples collected during past two years in Beijing, China. The origins of some important anthropogenic pollution elements, such as As, Br, Hg, I, In, S, Sb, Se can be identified by EF analysis, factor analysis and analysis of the concentrations variation during sandstorm episodes. The major sources of atmospheric pollution are preliminarily recognized to be wind-driven soil, industry, and coal burning, vehicle exhaust, waste incineration, etc., through factor analysis. It is interesting to find that the increase of fine fraction is usually higher than that of coarse one, while the pollution elements decrease during sandstorm episode. In-depth studies are expected to be done after more information is collected in the near future.

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