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Status of air pollution in Beijing*

Wu Jin[1], Wang Anpu[1], Huang Yanchu[1], Ma ciguang[1],
Y. Iida[2], S. Daishima[2], K. Furuya[3], T. Kikuchi[3],
H. Matsushita[4] and K. Tanabe[4]

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Abstract—A study has been made on elements organic constituents, TSP, SO_2, NO_2, of atmospheric pollutants in Beijing. 17 elements, and some PAHs, e. g. B(a)P, B(b, j, k)P, and B(g, h, i)P, in airborne particles by X-ray fluorescence spectroscopy and HPLC, GC/MS, have been determined respectively. It has been shown that the elements Pb, Zn, S and Cu were more enriched in fine particles and different valence states of sulfur at various sites. It was found that the concentrations of S^{6+} and S^{2-} were more than 85% and less than 15% of the total sulfur respectively. Concentrations of major PAHs and sulfur-containing compounds increased in winter and in urban area. High values for Pb and Zn in city, Fe and Mn at industrial area and Cu, Al rural sites were obtained respectively. This implies the functions of different elemental sources of various sites. Thus, elements can be from distingushed anthropogenic and natural sources.

The main contribution of SO_2 was found of to have same seasonal variation as the anthropogenic elements, while that of NO_2 varied only with emission from vehicles.

Keywords: air pollution; particles; elements; PAHs.

INTRODUCTION

Coal combustion is a major source of air pollution in China. In Beijing, coal amounts to about 70% of total energy consumed in the area and this percentage is increasing by the year. Oil is also used as fuel in many industries.

Consumption of coal for domestic heating in Beijing in the four months starting from mid November to mid March next year accounts for 50% of the whole year. Desulfurization

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*This is a Chinese-Japanese cooperative study—a project of Center for Asian and Pacific Studies, Seikei University (1981–1984)

[1]Research Center for Eco-Environmental Sciences (former Institute of Environmental Chemistry), Academia Sinica.
[2]Faculty of Engineering, Seikei University, Tokyo, Japan.
[3]Faculty of Science, University of Tokyo, Tokyo, Japan.
[4]Department of Regional Environmental Health, National Institute of Public Health, Tokyo, Japan.

technique of heavy oil and coal is still insufficient. Emission is released through short chimneys under unfavorable meteorological conditions, and air pollution is serious. Before 1983, Beijing had no automatic air monitoring stations, and weekly interval sampling was adopted.

This research is intended to elucidate seasonal variations of atmospheric pollutants and characteristics of airborne particles in the Beijing area. The research was a Chinese-Japanese cooperative study: a project of the Center for Asian and Pacific Studies, Seikei University Japanese site and the Research Center for Eco-Environmental Sciences, Academia Sinica (Oct. 1981-March 1984).

EXPERIMENTS

Three representative sites were selected for sampling: an urban site (Dongdan) in the city center, an industrial site (Beixinan) and a rural site (Huairou).

SO_2 was collected by fritted bubbler and analyzed by P-Rosaniline colorimetric method. NO_2 was absorbed by a filter badge (Tokyo Roshi Co.) and exposed in air for 24 hours. Saltzman method was applied to determine concentration of NO_2.

Airborne particulates were collected with a high volume air sampler once a week from June, 1982 to December, 1983 with a quartz filter (Whatman QM-A). The filter sheet with particles was determined by X-ray fluorescence spectroscopy (XRF, Philips PW 1400) to have 9–17 inorganic elements. The concentrations of S were compared and calibrated with XRF and infrared absorption method (Cui F. H., et al., 1983). These were carried out by the Chinese group. Organic hydrocarbon compounds in particles were supersonically extracted with benzene-ethanol to take neutral components, which were fractionated into hydrocarbons+PAHs, nitroarenes and others. They were analyzed by HPLC with a fluorescence detector and/or GC/MS (Finnigan-MAT 4530) (Daishima, S. et al., 1983; Matsushita, H. et al., 1981). The measurements were carried out with positive and/or negative ion chemical ionization (PCI and/or NCI). (Matsushita, 1981, 1983; Hunt, 1976). These analyses were carried out by the Japanese group from Seikei University and National Institute of Public Health.

A Hi-Volume cascade impactor (Shibata AH 600) fitted with organic filter (perchloroethylene) was used to measure the size distribution of elements, which were analyzed by ICP (Jarrell-Ash 1155V). Chemical states of sulfur in particles were identified by ESCA (XPS, KRATOS AEI ES 300) (Jiang, 1982) and a high resolution double crystal X-ray spectrometer (Toshiba AFV-701). The experiments were carried out by the Chinese group and Science University of Tokyo.

RESULTS AND DISCUSSION

Variation in concentration of SO_2, NO_2 and total suspended particles (TSP).

Similar behavior of seasonal variation of SO_2 and TSP was observed at three sampling sites. These are shown in Fig. 1 and 2.

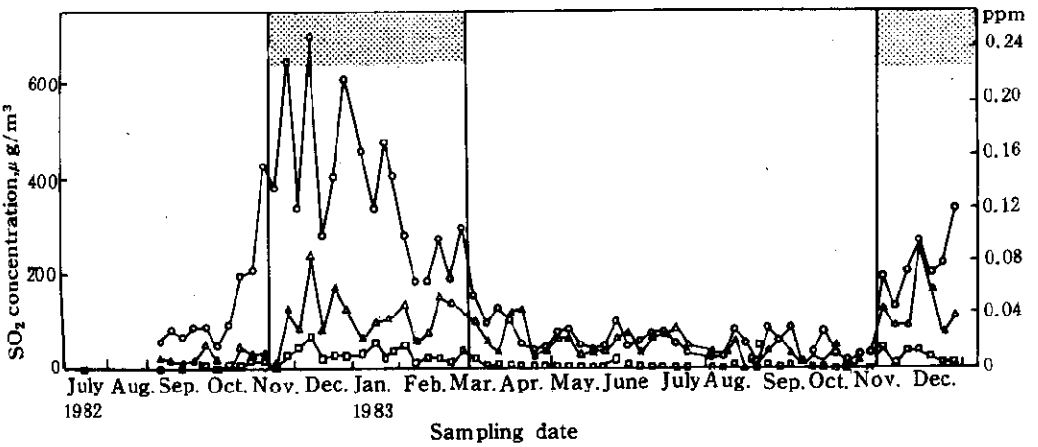

Fig. 1 Seasonal variation of SO_2 concentrations at three sampling sites
○: Urban ▲:Industrial □:Rural ▨:Heating period

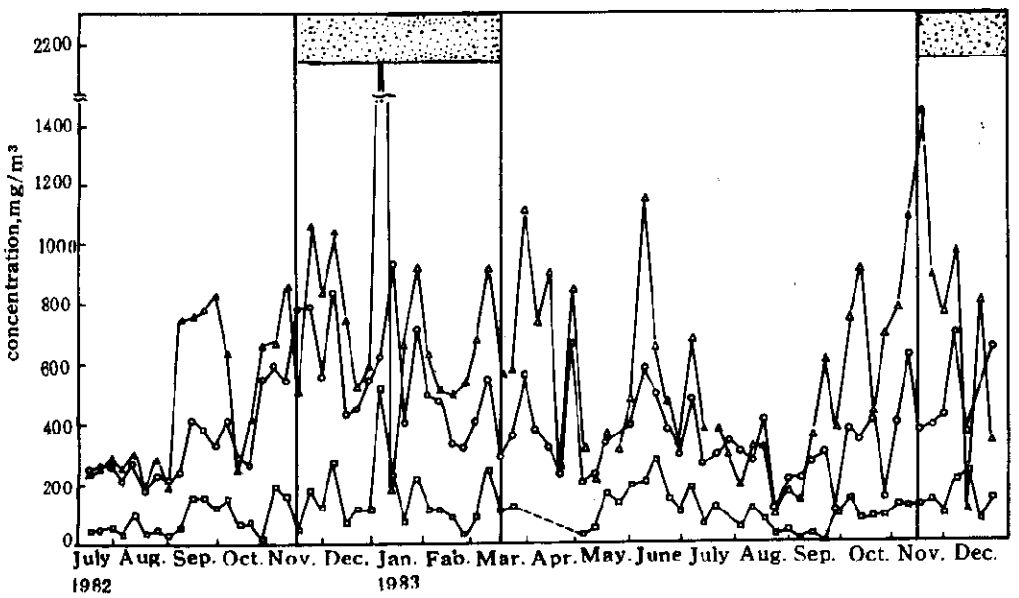

Fig. 2 Seasonal variation of airborne particulate concentrations at three sampling sites
○: Urban ▲:Industrial □:Rural ▨:Heating period

SO_2 concentrations during the heating period went up 2 to 10 times higher than those during the non-heating periods. The difference of SO_2 concentrations between the heating and non-heating periods at industrial site was almost doubled and the seasonal variation was small. At the rural site, a low concentration through out the year was observed and it was lower than

the other sites. Because all stocks were used by large industrial plants, so relatively lower SO_2 concentrations were observed at industrial area.

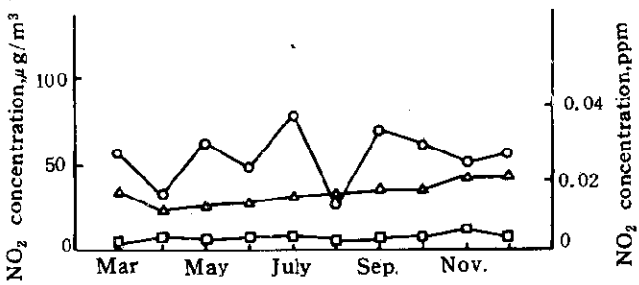

Fig. 3 Seasonal variation of NO_2 concentrations at three sampling sites
o: Urban ▲:Industrial □:Rural

Fig. 3 shows that the degree of NO_2 concentration was in the order: urban, industrial and rural, and that there were little seasonal variations at all sites. The average NO_2 concentrations were 0.54$\mu g/m^3$, 0.41 $\mu g/m^3$ and less than 0.14$\mu g/m^3$, at the urban, industrial and rural sites respectively. It is likely that NO_2 mostly was affected by automobile exhast.

Behavior of inorganic compositions in particulates

Fig.4–6 shows the monthly average of some elements which were selected from the analyzed 12 elements. The following characteristics were observed:

Most elemental concentration levels at the industrial sites were slightly higher than those at the urban site, and far lower values were observed at rural site. In winter generally, the concentration tended to increase at all three sites, but their patterns of variation were not similar for each site.

All elements may be classified into three groups. They were high concentration elements: Ca, Fe, Al, K; medium concentration element: Mg; and low concentration elements: Zn, Mn Pb, Cu and so on.

The average of these elements were expressed in weight percentage of particulates are shown in Table 1.

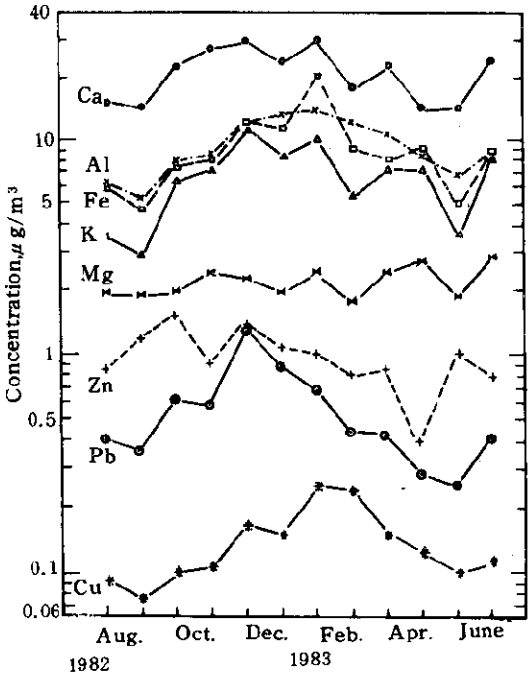

Fig. 4 Concentrations of inorganic elements in airborne particulates at urban site in Beijing

Table 1 Concentrations of elements in particulates at three sampling sites (wt %)

	Element									
Site	Fe	Mn	Pb	Zn	Cu	Ca	Mg	K	Al	S
Urban	2.14	0.07	0.13	0.26	0.03	5.20	0.57	1.55	2.24	1.89
Industrial	3.55	0.12	0.08	0.15	0.02	5.26	0.53	1.93	1.79	1.14
Rural	1.95	0.06	0.08	0.21	0.07	4.63	0.76	2.03	2.89	3.40

High values were obtained in Pb and Zn at the urban, while Fe, Mn at the industrial and Cu, Al at the rural site, respectively. It implies the different functions of the sites and the different elemental sources.

There are two types of elemental sources: natural and anthropogenic. According to enrichement factor (EF) of elements (Dams, R., 1976), we chose Al as a reference element and the results are shown in Table 2.

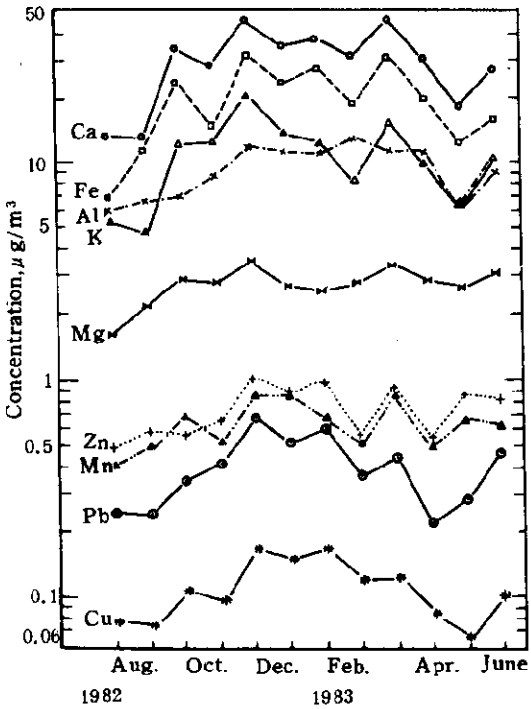

Fig. 5 Concentrations of inorganic elements in airborne particulates at industrial site in Beijing

Table 2 Enrichment factors of elements in airborne particulates at three sampling sites (Al=1.00)

Site	Elements									
	Fe	Mn	Pb	Zn	Cu	Ca	Mg	K	Al	S
Urban	1.6	2.5	365	131	21	5.3	1.0	2.2	1.00	124
Industrial	3.4	6.0	273	95	18	7.0	1.2	3.6	1.00	110
Rural	1.1	1.8	297	86	39	3.7	1.0	2.2	1.00	195

In Table 2 the *EF* values of elements Pb, Zn, Cu were higher and indicated that they were contributions by anthropogenic sources. An extraordinary high value of *EF* of Pb at the urban site shows that automobile pollution existed. *EF* of Fe and Mn at the industrial site was greater than others, because the iron and steel plants in operation emitted them in a form of

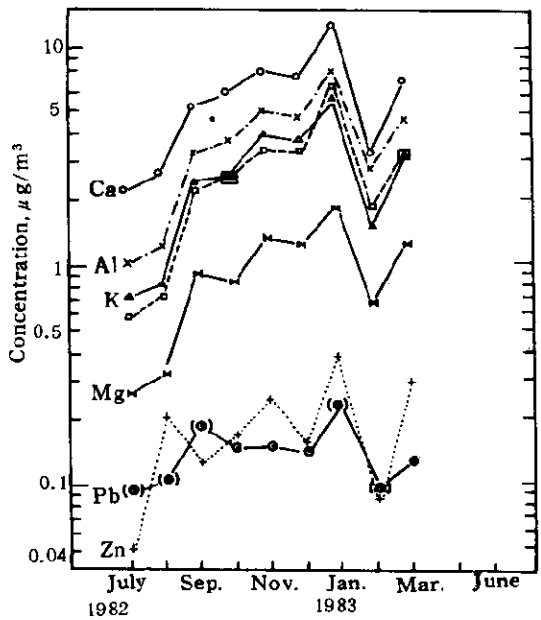

Fig. 6 Concentration of inorganic elements in airborne particulates at rural site in Beijing

ore dust plume.

The *EF* of S exceeded 100, which shows considerable contamination by human activities.

Chemical states of sulfur in airborne particulates

The value of sulfur concentration at the urban site during domestic heating period are 1.5 times as high as that during non-heating period.

We have found four different valence states of sulfur (S^0, S^{2-}, S^{4+}, S^{6+}) present in the particulates by ESCA (Jiang, 1982), and quantitatively determined the amount of S^{6+} and S^{2-} by a high resolution double crystal X-rays spectrometer (Yutaka, 1985).

The S^{6+} concentrations amounted to more than 85% of the total S in the particulates at each site. There were similar seasonal trends in the case of total sulfur. The S^{2-} concentration was less than 15% of the total sulfur. Seasonal variation of S^{2-} showed a different trend from the total sulfur and S^{6+}. During the non-heating periods, the values at the urban and industrial sites were almost at the same level. But during the heating period, they went up 2.6 times at the urban site, and 1.4 times at the industrial site. At the rural site, values were always small and did not increase during the heating period. In view of this, the trend was much more similar to SO_2 in the ambient air than the total S or particulate.

The effect of space heating was especially remarkable for the increase of S^{2-} at the urban site. It may be caused by incomplete coal combustion in households. At the industrial site the highest S^{6+} percentage suggests the effect of efficient industrial furnaces. Seasonal variations

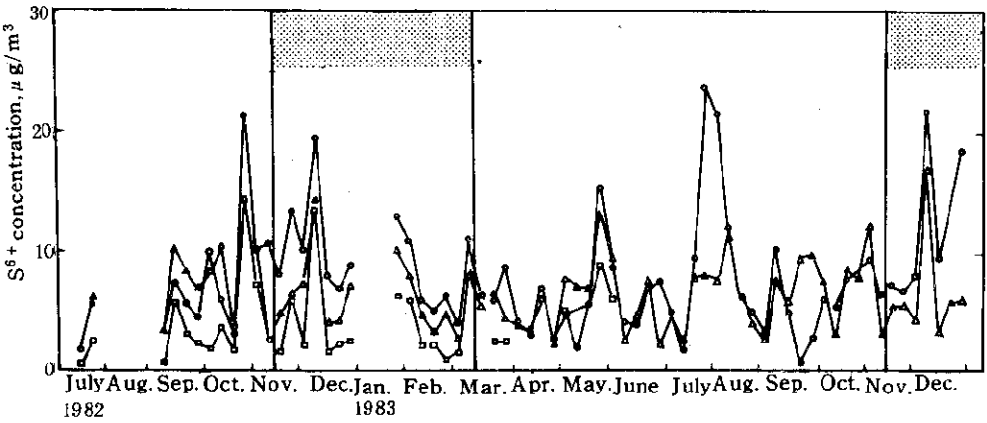

Fig. 7 Seasonal variation of S^{6+} concentrations in particulate at three sampling sites in Beijing

○: Urban ▲:Industrial □:Rural ▨:Heating period

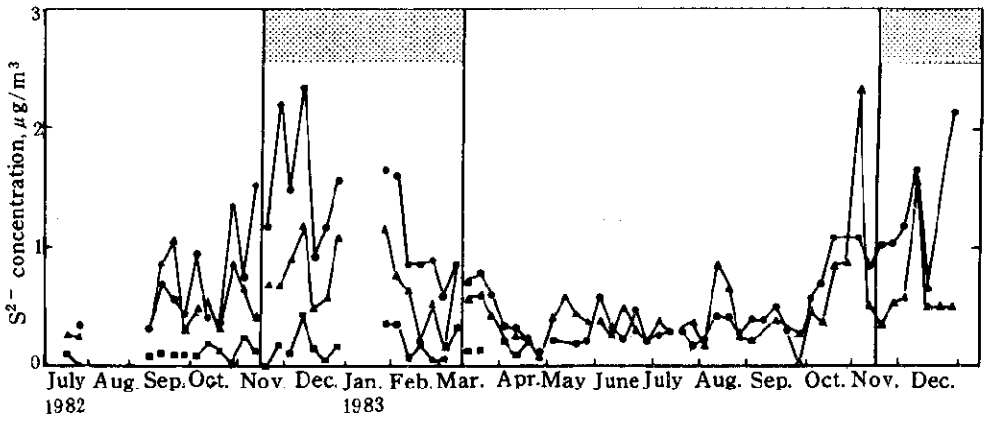

Fig. 8 Seasonal variation of S^{2-} concentrations in particulate at three sampling sites in Beijing

○: Urban ▲:Industrial □:Rural ▨:Heating period

of S^{6+} and S^{2-} were shown in Fig. 7 and Fig. 8.

Behavior of organic constituents in particulates and their behavior

Toxic organic constituents were determined by NCI and PCI methods at the three sites in Beijing and an urban site in Tokyo both in summer and winter. The chromatograms were shown in Fig. 9–12.

The major components were fluoranthene, benzo(a)pyrene, benzofluoranthenes (sum of b, j,

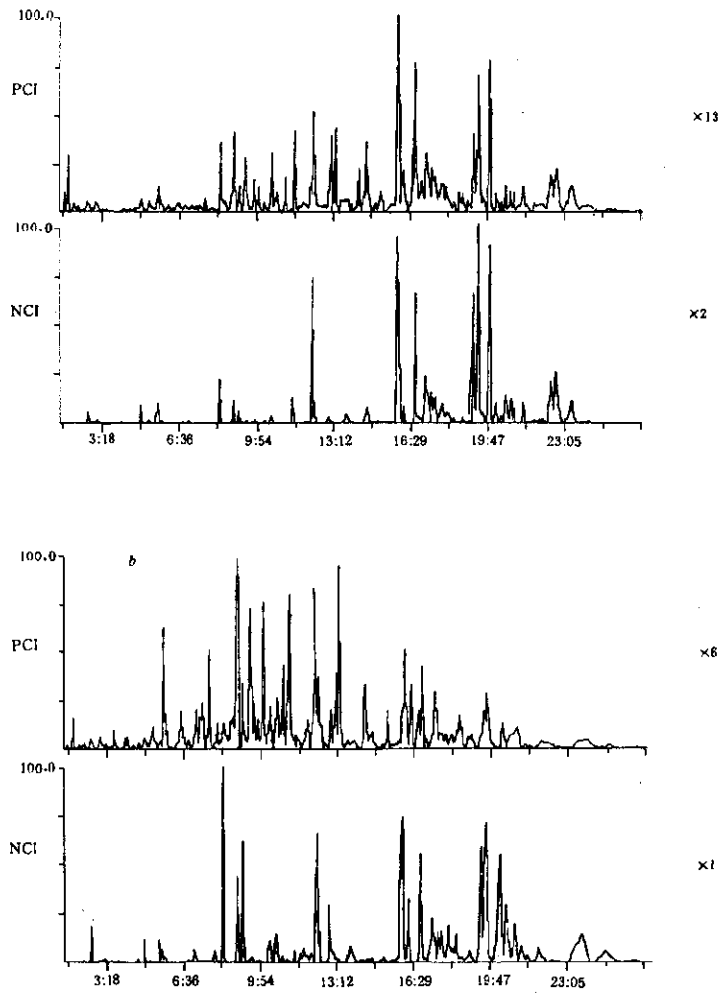

Fig. 9 Total ion chromatograms (m/z 70–400) of airborne particulate at urban site in Beijing. (a) Summer, (b) Winter

k isomers), indeno (1, 2, 3–c, d) pyrene, benzo (g, h, i) perylene and dibenzo (a, e) pyrene. The chlorine and sulfur compounds also were found at the three sites. These results are evaluated as follows:

The order of concentrations was generally the industrial, urban and rural sites, and the concentrations in winter was 2–5 times high than in summer.

Seasonal variation could be classified into three groups; group A with large seasonal variations (fluoranthene, bozo(a) pyrene; except in the rural site); group B with medium seasonal

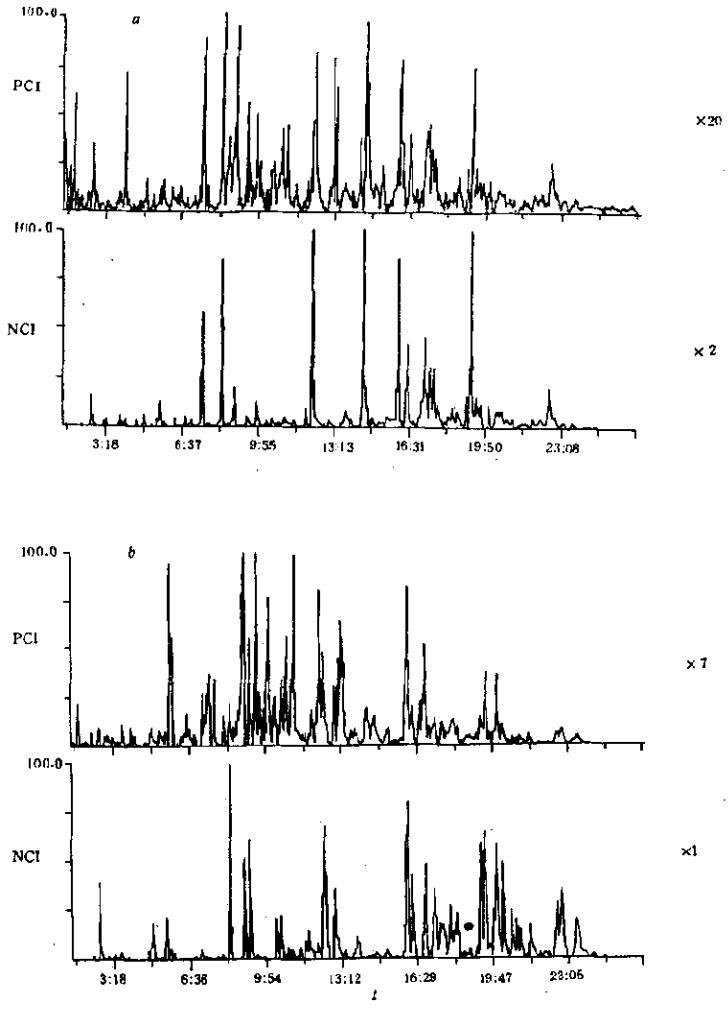

Fig. 10 Total ion chromatograms (m/z 70-400) of airborne particulate at site industrial in Beijing (a) Summer (b) Winter

variations (benzofluoranthene, benzo (g, h, i) perylene), and the group C with small seasonal variations indeno (1, 2, 3-c, d) pyrene and dibenzo (a, c) pyrene). The organic components group A decreased down to less than 20 μg/g in May to September, and increased during the heating period. The chlorine and sulfur compounds had similar trend, and they might be influenced by coal combustion. The group B was rather stable at concentration level (20–60μg/g during the heating period and <100 μg/g during the non-heating period). These components might be attributed to other kinds of emission sources, such as industrial plumes and diesel

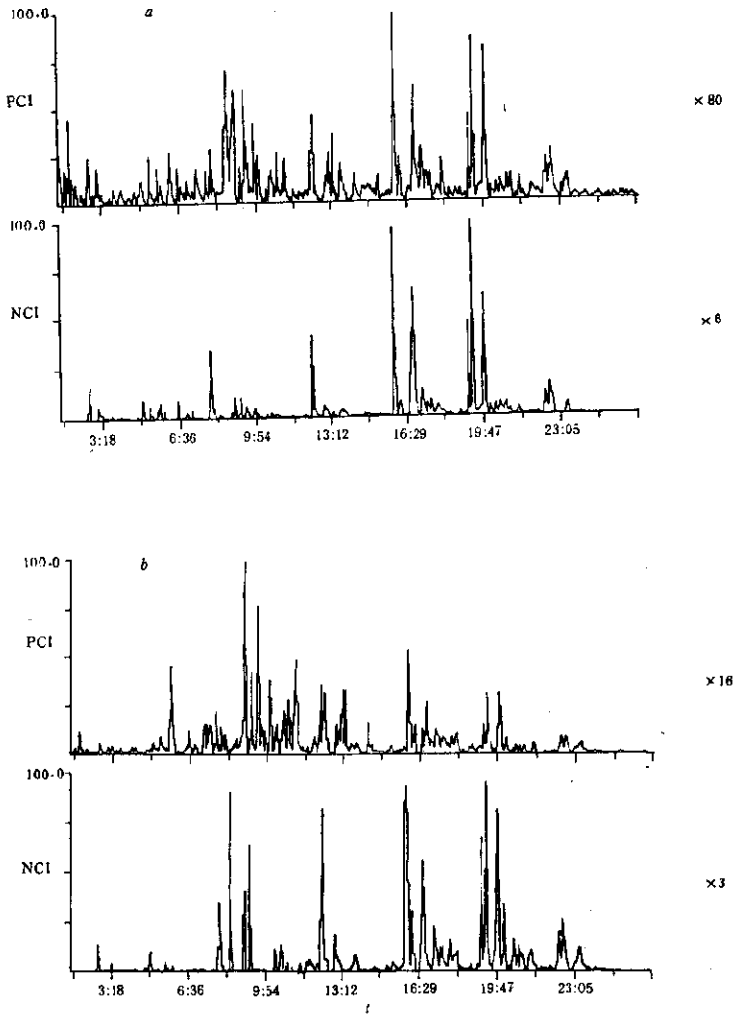

Fig. 11 Total ion chromatograms (m/z 70-400) of airborne particulate at rural site in Beijing (a) Summer (b) Winter

exhaust.

The concentration of B(a)P and B(g, h, i)P in ambient air in Tokyo (urban site) was slightly lower than those at the rural sites in Beijing and as low as 1/5 to 1/10 of those at the urban site in Beijing.

The main nitroarenes were 2-nitrofluorene, 9-nitroanthracene, nitrofluoranthene isomer and 1-nitropyrene. The concentration of nitroarenes was as low as one to several percent of those PAHs, and was slightly higher at the industrial and urban sites than at the rural site.

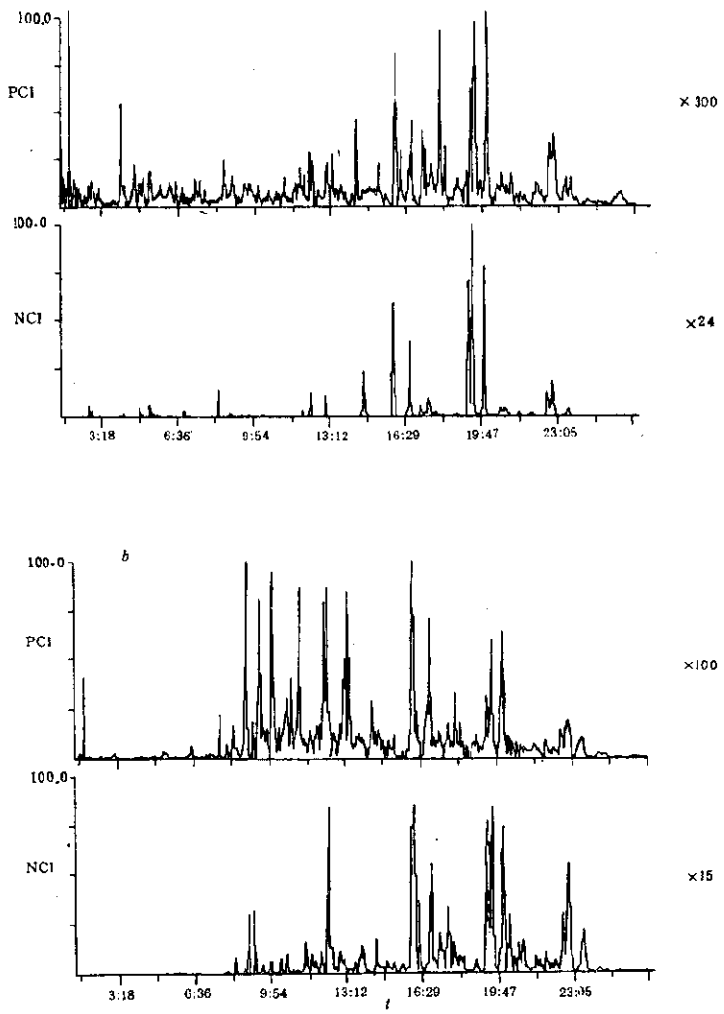

Fig. 12 Total ion chromatograms (m/z 70-400) of airborne particulate in Tokyo (Musashino). (a) Summer, (b) Winter

The overall behaviors of 1-nitropyrene exhibited a small difference between sites and a small seasonal variation. These were different from PAHs and it suggests a possibility of sources coming from diesel exhaust and industrial emission.

The concentration of elements was measured in five sizes. The size distributions of elements were different for different sites. It seemed that most of lithophilic elements (e. g. Ca, Mg, Fe, K, Na etc.) were enriched in coarse particle (>2μm). The elements Pb, Zn, Cu, Mn and Cr are usually enriched in the fine particle (< 2μm) sizes. The general features of size distributions of

soil dust elements are significantly different from those of the anthropogenic elements.

From the average concentration ratio of coarse particles to total particle, it was estimated that the environmental impact from soil dust was about 50% of the total particle in Beijing, particularly in winter.

CONCLUSION

This investigation has demonstrated that SO_2, TSP, and some elements and organic constituents had similar patterns in seasonal concentration variations in Beijing. NO_2 concentration did not vary with seasons. Elements Pb, Zn, S and Cu were more enriched in fine particles. Concentrations of S^{6+} and S^{2-} were more than 85% and less than 15% of the total sulfur respectively. Concentrations of major PAHs and sulfur-containing compounds increased in winter and particularly in urban areas. Nitroarenes were largely affected by anthropogenic sources. The percentage contribution of soil to TSP was about 50%.

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