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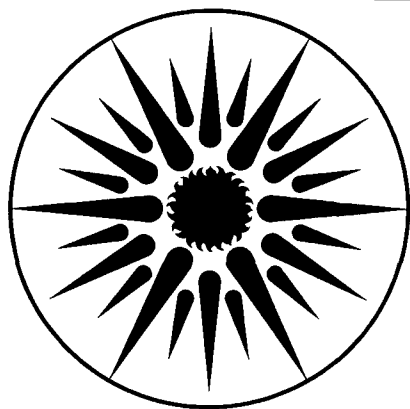W. Su, Q. Zhang, and W. Song

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SULFATE AND CARBONACEOUS AEROSOLS IN BEIJING, CHINA†

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Abstract

Results of our aerosol study, performed during 1983-1984 in Beijing, demonstrate that ambient carbonaceous aerosols are derived principally from coal combustion. Different SO_2 oxidation processes have been observed in summer and winter. The winter sulfate appears to be produced locally and associated with products of incomplete combustion.

Introduction

This paper describes the results of an aerosol chemistry study performed in Beijing, China, during 1983-1984. Beijing air pollution is due principally to coal combustion with a relatively minor contribution from automotive sources. Coal is burned in a large number of individual furnaces and stoves as well as in a number of industrial plants. Because of the low height and large number of chimneys and stacks, the Beijing atmosphere, especially during cold periods, is dominated by local sources. Therefore, studies of pollutant chemistry at such a location may lead to a better understanding of the relation between secondary species such as aerosol sulfate and primary source emissions. Large urban centers such as Beijing, because of the lack of sufficient environmental controls and inefficient combustion technology, may contribute to atmospheric pollution disproportionately more than their per-capita energy consumption may suggest. Chemical characterization of such source-dominated atmospheres may also be useful in assessing their potential impact on the global environment.

Only a few aerosol studies have been performed in Beijing to date (See, for example, Winchester and Bi, 1984, and references therein.). Winchester and Bi (1984) have determined the elemental composition of urban Beijing aerosols with emphasis on the sources of 18 trace elements and concluded that elements in the fine particle mode are principally derived from coal combustion. Here we report our results on carbonaceous and sulfate aerosols in the Beijing atmosphere as well as on other trace elements. The results demonstrate that the carbonaceous aerosol consists predominantly of soot derived from coal combustion. The data also show that different SO_2 oxidation processes occur in summer and in winter. The winter sulfate appears to be produced locally and associated with products of incomplete combustion.

Experimental

Filter samples of ambient aerosol particles were collected in a densely populated part of Beijing, using a sampler constructed at Lawrence Berkeley Laboratory. The

sampler provides for the simultaneous collection of two low-volume samples on 47-mm diameter filters. A Sierra Instruments Model 248 aerosol inlet, which restricts the collected particle size to less than 12-μm aerodynamic diameter at the operating flow rate, was used. This inlet has been shown to have a consistent cut-point independent of wind direction to velocities of approximately 20 km hr^{-1}(Wedding et al., 1977). Vacuum is applied to the two filter holders located in a mixing chamber through two rotameters by a single rotary vane pump. Flow rate through each filter is restricted to 6.5 liters min^{-1}. One filter was Pallflex 2500 QAO quartz fiber that had been fired at 800°C for 4 hours to remove the organic binder; the other fiber was Millipore RAWP cellulose ester. Flow impedance and loading characteristics of these filter media caused no difficulties in maintaining a constant flow rate.

Daily 24-hr aerosol samples were collected during 1983 and part of 1984. The sampling program was arranged to cover approximately three seasons -- spring, summer, and winter. The spring samples were collected from March through the beginning of May, 1983. Summer samples were gathered during July, 1983; the winter samples, from the end of October, 1983, through February, 1984.

SO_2 measurements were made for a period each morning near the aerosol sampling site using a ThermoElectron Series 43 pulsed fluorescence monitor. In the absence of 24-hr averages, these were taken as estimates of the daily average SO_2 concentration. Total carbon was determined on the quartz filters by a combustion technique (Hoffman, 1977). Temperature-programmed evolved gas analysis (EGA) was used to determine the primary carbon content (Dod and Novakov, 1982; Novakov, 1981). Particulate sulfur and other trace element concentrations were measured on the cellulose ester filters by energy-dispersive x-ray fluorescence (XRF) spectrometry (Giauque et al., 1979).

A subset composed of 20% of the samples was analyzed by ion chromatography. Pieces of known area were taken from the quartz filters and extracted in water with sonication for 10 min. The extract was filtered and analyzed for anions using a Dionex Sys-

tem 12 ion chromatograph.

The agreement between sulfur concentrations determined by XRF on Millipore filters and sulfate on quartz filters determined by ion chromatography is shown in Fig. 1. The slope of the line is not significantly different from unity with a correlation coefficient (r^2) of 0.98. This establishes not only that the sulfur in the aerosol particles is practically all in the form of sulfate but also that the parallel filter samples (on quartz and cellulose ester) do contain equivalent particle loadings and that artifact sulfate formation is not significant.

Results and Discussion

Figure 2a shows the 24-hr total particulate carbon concentrations in micrograms per cubic meter for each sampling day: it is evident that the total carbon concentrations are relatively low and approximately constant during spring and summer. The average concentrations during these periods were approximately 30 μg m^{-3}. Starting in October, however, much larger carbon concentrations are seen. The maximum 24-hr carbon concentration reached nearly 400 μg m^{-3} in the beginning of December. During the entire winter, carbon concentrations greater than 100 μg m^{-3} were frequently measured.

Representative samples from different months were also analyzed by EGA. The single most distinctive feature of all the EGA thermograms is the black carbon, composing typically 40-50% of the total carbon. Such a feature is characteristic of combustion-produced soot particles, as demonstrated previously (Novakov, 1981). (A small fraction, usually less than 15%, of total carbon was present as mineral carbonate.) Based on this evidence, we conclude that most of the particulate carbon is primary (i.e., soot) and therefore that the total carbon concentrations approximate the soot concentrations.

The average monthly minimum and maximum temperatures (compiled from international weather reports) are indicated in Fig. 2a. It is evident that the period of increased ambient soot concentrations corresponds to lower temperatures, suggesting that space heating is a significant source of ambient soot during cold periods. Stagnant

air conditions occurring during cold days would, of course, result in maximum soot concentrations.

Particulate sulfur (sulfate) concentrations for the entire set of samples are displayed in Fig. 2b. The sulfate concentrations, as well as the carbon concentrations, are relatively constant during April, May, and July. However, during cold periods, large sulfate concentration peaks are observed on many days. The maximum 24-hr average concentrations were about 18 μg m^{-3} of particulate sulfur (or 55 μg m^{-3} of sulfate). The average particulate sulfur concentrations are not very different for summer and winter periods, however, because of the greater variation in concentrations during winter.

Soot, a primary combustion-generated pollutant, can be used as a conservative tracer for the products of incomplete combustion (Novakov, 1981); and therefore the ratio of particulate sulfur (or sulfate) to soot can be used to study the relationship between sulfates and source emissions. This approach is illustrated in Fig. 2c, where the particulate sulfur to carbon ratios are shown. The most striking feature seen in this figure is the difference in these ratios for different periods of the year. During July, large scatter in these ratios is seen, while in the winter S/C ratios are nearly constant but lower than in summer. The values for spring are intermediate between summer and winter. The summer aerosol (and to a lesser degree, the spring aerosol) is therefore enriched in sulfate with respect to the soot tracer. In contrast, the winter sulfate is directly related to the soot emissions.

Fig. 3 illustrates a somewhat different way of presenting these conclusions, with particulate sulfur plotted against particulate carbon for summer (July) and winter (November, 1983, through February, 1984). It is obvious from this figure that an excellent sulfur-carbon correlation ($r^2 = 0.86$) exists during the winter. Such a correlation is virtually nonexistent during summer, however. The systematic seasonal variations in sulfur-to-carbon correlations are evident from Table I, where semimonthly sulfur-to-carbon correlation coefficients observed during different periods of the year are tabu-

lated.

The seasonal behavior of the S/C ratio is corroborated by the ratios of S to other tracer elements. (Complete elemental concentrations are presented in the Appendix, Table III.) Table II lists the semimonthly average S/C, S/As, S/V, C/Pb, C/V, C/As, and As/V concentration ratios. In the following analysis, it was assumed that As and V are tracer elements for coal and fuel oil, respectively (Gordon et al., 1981). The standard deviations for ratios to As and V are greater than those for the S/C and C/Pb ratios largely because of the greater analytical error in the determination of concentrations of these elements. Nevertheless, both the S/As and S/V ratios are significantly higher in July than in December. The values for these ratios in March are generally between those for July and December. One interpretation of the differences in these sulfur to tracer ratios could be the existence of at least two different SO_2 conversion processes, one being pronounced in the summer and the other in the winter.

Several tentative conclusions about the sources of particulate matter can be reached from examination of these ratios. C/As ratios are essentially the same for all three months, suggesting that the principal source of particulate carbon is coal combustion. C/V ratios are the same during March and July but noticeably higher in December. Such behavior would be expected if the fuel oil usage is approximately constant throughout the year. The higher C/V ratio in December reflects the increased coal use in December. A similar conclusion is suggested by the As/V ratios. The C/Pb ratio is about an order of magnitude higher than in Western countries, which have a much higher automotive source component. It has also been reported that gasoline in China has a low Pb content (Jiang et al., 1984). Because the absolute Pb concentrations are low and the C/Pb ratio is similar for all three seasons, we conclude that most of the atmospheric lead is derived from coal combustion.

From the results presented thus far, it is clear that aerosol pollution in Beijing is predominantly the result of coal combustion and that sulfur conversion chemistry

appears to be different at different seasons. We can furthermore conclude that winter sulfates are derived from local sources. This is evident from the excellent correlation with soot, which, because of its high concentration, is most likely of local origin. Further examination of the data from this location also suggests that the fraction of SO_2 oxidized to the winter sulfate is converted rapidly, a conclusion reached by examining periods of air stagnation that can last for several days. During such periods the residence time of pollutants in the air (and thus the available reaction time) increases from day to day. This should result in a systematically increasing ratio of sulfate to a primary particulate tracer; however, this was not observed. The sulfate-to-soot ratios, for example, remained approximately constant during the entire winter sampling period, including the stagnant periods.

The reasons and mechanisms responsible for this apparent rapid formation are not known at present. However, several processes potentially capable of explaining these wintertime observations can be identified. One obvious possibility is that local sulfates are primary, i.e., produced by SO_2 oxidation to SO_3 in flames. This explanation agrees with the observed correlations between sulfate and primary combustion-generated species. However, wintertime sulfate is estimated to average about 10% of total airborne sulfur, i.e., much higher than 1%, which is generally assumed for primary sulfate (Dietz and Wieser, 1983).

We have already indicated that sulfate behavior in summer is different from that in winter. The summertime sulfate formation mechanism is also more efficient, as evidenced by higher particulate to gaseous sulfur ratios (Table II). These differences could be interpreted as a result of photochemical SO_2 oxidation during summer, and a less efficient mechanism during winter. Nevertheless, the maximum absolute concentrations of sulfate are lower during the summer because the concentration of SO_2 available for oxidation is also low. Conversely, a relatively inefficient wintertime mechanism can produce high sulfate concentrations because the SO_2 concentrations are high.

An examination of supplementary meteorological information indicates that there may be a substantial increase in the S/C ratio when relative humidity exceeds 60%, suggesting that a heterogeneous aqueous process (or processes) is involved in the oxidation of SO_2. This finding is illustrated in Fig. 4, where the S/C ratios for the entire sampling period are plotted against the average 24-hr relative humidity. Qualitatively similar behavior has been observed in the United States by McMury and Wilson (1983).

In Beijing during 1983/84, the relative humidities were markedly higher during summer than in winter or spring. Because high S/C ratios were also observed during summer, we conclude that the summertime SO_2 conversion mechanism could involve liquid water droplets as the medium in which the oxidation reaction takes place. During winter, low ambient humidity will limit both the aqueous-phase reaction time and the liquid water content. Such an explanation, although speculative, could explain the "quasi-primary" wintertime sulfate behavior.

The question of the oxidants responsible for the SO_2 oxidation remains unanswered at this time. It is plausible, however, to assume that photochemically generated radicals and/or peroxides play a major role during the summer. During the winter, primary combustion-generated gaseous and particulate compounds are a distinct possibility. These oxidants oxidize SO_2 in aqueous media rapidly (Benner et al., 1985) and would therefore be consistent with the apparently rapid oxidation suggested by the field data.

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Figure Captions

Figure 1. Particulate sulfate (as sulfur) determined by ion chromatography vs. total particulate sulfur determined by x-ray fluorescence for a representative set of samples - Beijing 1983/84.

Figure 2. Daily concentrations of particulate carbon (a), sulfur (b), and particulate sulfur to carbon ratios (c). Mean maximum and minimum temperatures are also shown.

Figure 3. Seasonal differences in the correlation of particulate sulfur with particulate carbon.

Figure 4. Particulate sulfur to carbon ratios as a function of daily mean relative humidity.

Table I.

Sulfur:carbon correlation coefficients (r^2)

Period	March	Month July	December
First half	0.80	0.16	0.97
Second half	0.40	0.20	0.88
Entire month	0.70	0.23	0.94

Table II.

Semimonthly elemental ratios (±)

Ratio	March		July		December	
	1–15	16–31	1–15	16–31	1–15	16–31
S/C	0.10(0.03)	0.11(0.03)	0.15(0.07)	0.19(0.08)	0.06(0.01)	0.06(0.01)
S/As	246(162)	225(97)	287(199)	361(237)	151(42)	159(47)
S/V	67(39)	57(20)	104(55)	156(117)	97(50)	75(30)
C/Pb	214(74)	214(51)	210(49)	172(56)	234(46)	253(31)
C/V	636(240)	520(111)	701(196)	801(311)	1573(661)	1234(432)
C/As	2342(1185)	2030(682)	1881(882)	2024(1089)	2458(540)	2615(720)
As/V	0.34(0.23)	0.28(0.10)	0.47(0.21)	0.50(0.42)	0.77(0.23)	0.48(0.19)
$2S/SO_2$	~0.06	~0.07	~0.16	~0.15	~0.11	~0.07

Table III.

Average semi-monthly particulate
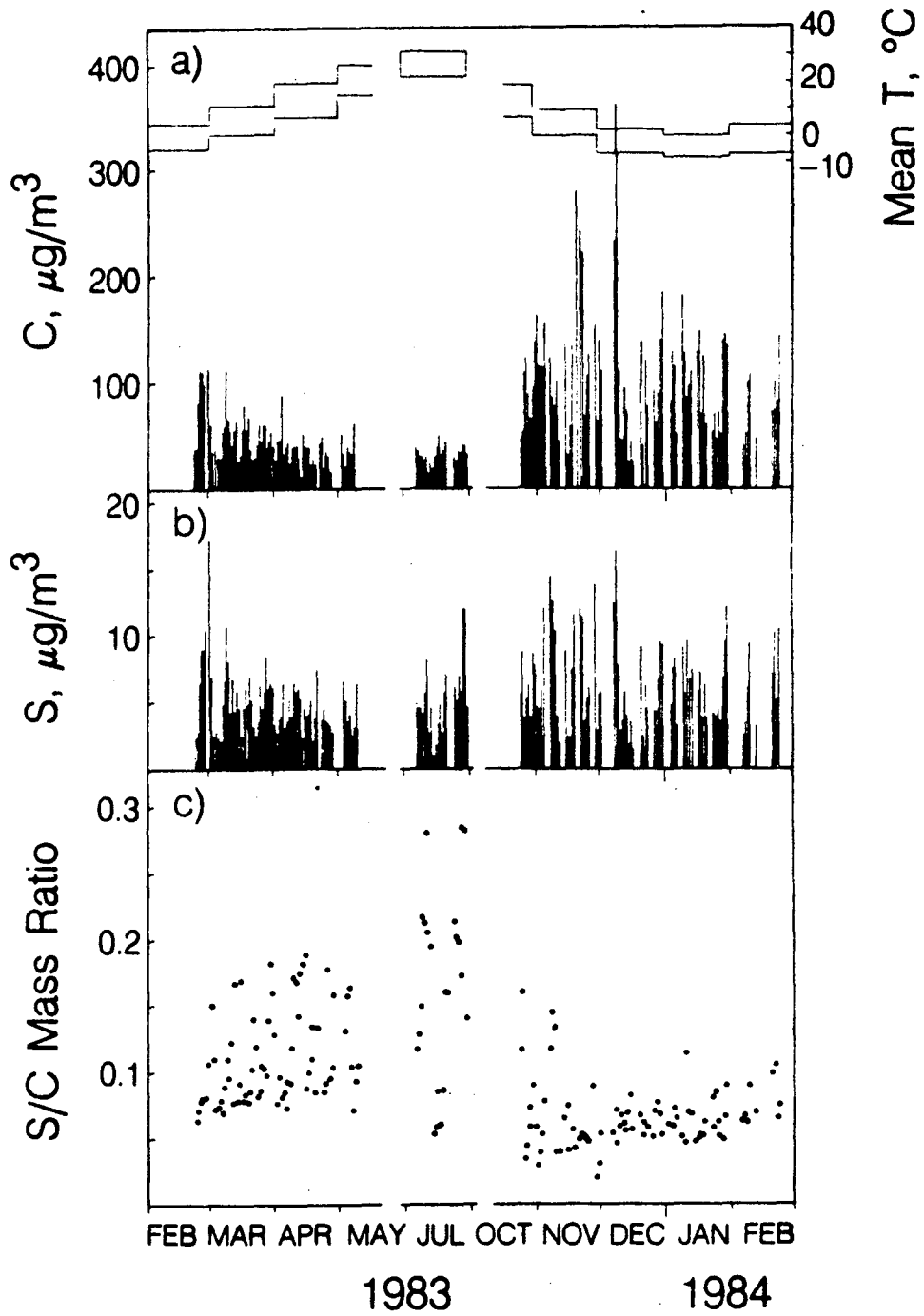elemental composition (ng m^{-3})

Element	March		July		December	
	1-15	16-31	1-15	16-31	1-15	16-31
C	55400	49500	27600	35800	115400	98000
S	6010	5390	4190	6370	6440	5910
K	3420	3470	2140	2730	3590	3120
Ca	10400	12500	7530	9400	7490	10800
Ti	903	749	432	547	850	991
V	94.4	96.8	44.3	49.2	71.4	85.4
Cr	75.8	66.5	32.5	39.8	156	35.8
Mn	205	216	166	165	175	226
Fe	7410	7040	4230	4950	5920	7170
Ni	30.8	30.7	16.9	17.6	24.8	29.4
Cu	24.0	28.0	27.9	30.7	112	48.8
Zn	511	476	338	344	1050	490
Ga	28.7	19.8	11.7	13.4	52.4	50.5
Hg	26.2	20.2	10.7	10.5	38.5	45.2
As	28.8	27.0	18.4	21.7	49.9	45.2
Pb	301	250	143	229	531	401
Se	15.8	14.1	10.3	12.3	40.7	27.9
Br	27.1	24.1	19.4	21.1	138	39.2
Rb	18.4	18.2	12.9	16.4	23.3	22.7
Sr	158	124	60.4	73.5	175	197
Si	22210	20560	10070	11750	16410	20910
Cl	843	866	34	26	2405	1512

$$[S]_{I.C.} = 1.03 \, [S]_{XRF} + 0.61$$

$$r^2 = 0.98$$

XBL 859-8982

Figure 1.

Figure 2.

XBL 859-8984

Figure 3.

Figure 4.

XBL 859-8983