



PERGAMON



Atmospheric Environment 36 (2002) 4189–4199

ATMOSPHERIC  
ENVIRONMENT

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# Characterization of Atmospheric Aerosol over XiAn in the South Margin of the Loess Plateau, China

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Received 4 January 2002; received in revised form 12 May 2002; accepted 23 May 2002

## Abstract

The mass concentrations of TSP, PM-10, several secondary aerosol species, and up to 20 elements were determined for bulk aerosol samples collected from four ground-based monitoring sites in XiAn, China. The samples were collected during four seasons from September 1996 to August 1997; and in July 1998. Daily concentrations of TSP, SO<sub>2</sub> and NO<sub>x</sub> from 1995 to 1997 were also obtained from the same sampling sites. Representative concentrations (annual averages) of TSP, SO<sub>2</sub> and NO<sub>x</sub> were 410, 39, 43 μg m<sup>-3</sup>, respectively. PM-10 accounted for about 60–70% of TSP in summer 1998. The most abundant elements in the samples were Si, Ca, Al, Fe, Cl, P, K and S. A fraction of the Ca, which is typically associated with dust, was from non-crustal sources, especially in coarse particles. In winter, the element with the highest concentration was S, and it was primarily in the form of sulfate. The seasonal mean sulfate concentrations, averaged over all sites, were 100, 340, 59 and 27 μg SO<sub>4</sub><sup>2-</sup> m<sup>-3</sup> for autumn, winter, spring and summer, respectively. The corresponding loadings of ammonium ion were 49, 140, 40 and 17 μg NH<sub>4</sub><sup>+</sup> m<sup>-3</sup> for the same seasons and those for nitrate were 22, 65, 33, 16 μg NO<sub>3</sub><sup>-</sup> m<sup>-3</sup>. Dispersed sources of coal-combustion (most likely residential heating), as opposed to stationary point sources, evidently play an important role in the large increases in TSP and three-fold increases in sulfate, nitrate and ammonium loading during XiAn's space-heating season.

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**Keywords:** TSP; PM-10; Elements; Sulfate; Nitrate; Ammonium products

## 1. Introduction

XiAn (33°29'–34°44'N, 107°40'–109°49'E, population 3.66 million), the largest city in northwestern China, lies within the Guanzhong Plain of a topographic basin surrounded by Qinling Mountains to the south and the Loess Plateau to the north (Fig. 1). The climate of XiAn is dominated by large variations in East Asian monsoon. During the winter half year, the northerly Asian winter

monsoonal winds prevail, and they are associated with the transport of Asian dust from Chinese deserts and nearby loess areas (Zhang et al., 1993, 1997). In summer, the monsoonal winds bring moisture to the region from the south.

XiAn has become a popular tourist attraction because of its historical sites and antiquities, and it is a gateway to western China. With the development of economic and agricultural activities and tourism, the city has unfortunately also become subject to high concentrations of atmospheric particulate matter, which often are immediately obvious as a dense haze over the city. XiAn

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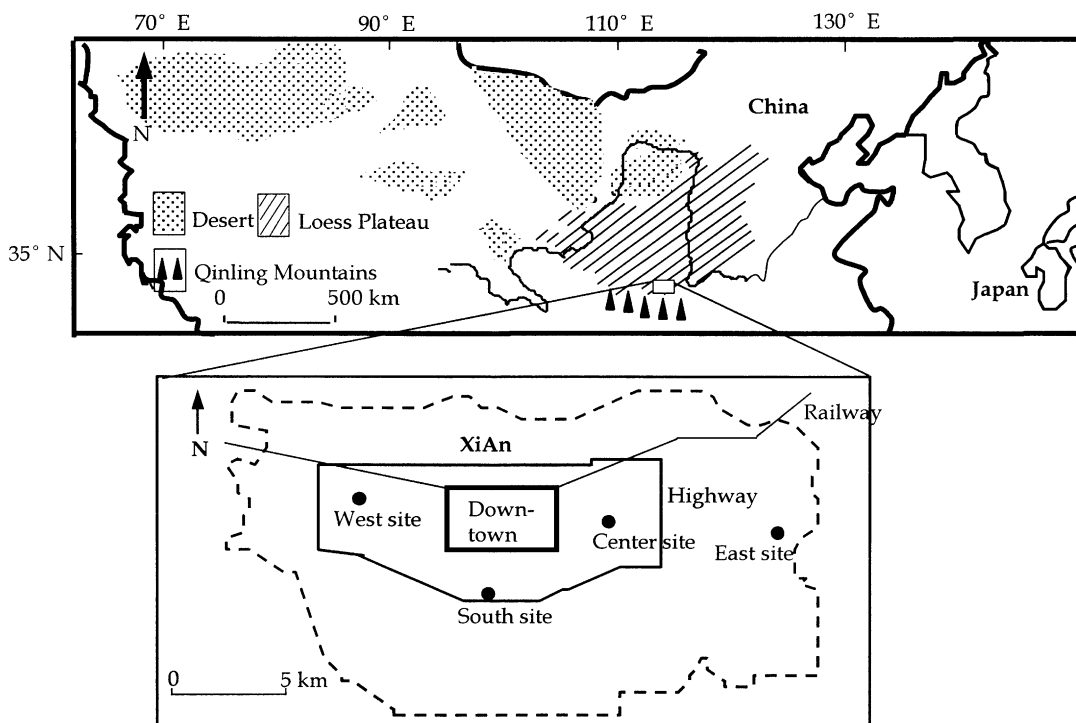


Fig. 1. Map of sampling site.

can be considered a typical city in north China with significant air pollution problems, and therefore it is a good place to investigate impacts on air quality from natural and anthropogenic sources.

We present here the results of an investigation of the composition and characteristics of ambient particulate matter in XiAn. The main objective for the study was to provide information on the spatial and temporal variations in aerosol mass, the concentrations of trace elements and selected secondary aerosol species, including sulfate, nitrate and ammonium ion, and in so doing, gain a better understanding of levels of TSP and PM-10 in a city near a major source for Asian dust. These data also are the basis for a subsequent paper dealing with the apportionment of sources and controls on air quality in the city.

## 2. Materials and methods

A total of 299 bulk aerosol samples were collected from four monitoring sites (West, Central, East and South) in XiAn, China during each of the four seasons from September 1996 to August 1997 (we refer to these as the 1997 samples). Additional sets of twenty-four PM-10 samples (particles  $< 10 \mu\text{m}$  aerodynamic equivalent diameter) and 24 bulk aerosol samples were collected from the southern monitoring site during July

1998 (the 1998 samples). In addition, the concentrations of TSP (total suspended particles),  $\text{SO}_2$ , and  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) were determined for 1230 daily samples collected from the same four sampling sites between 1995 and 1997.

These sampling sites represent the following environments: (1) a western heavy industrial area (near industrial plants involved with electronics, chemicals, paper products, plastics, sand/gravel, and cement); (2) an urban commercial and residential area (near the center of the city, especially middle-income housing); (3) a light industrial area (near textile mills) in the eastern suburbs; and (4) an urban cultural, residential and commercial area (near institutes, college, main line of transportation, retail stores and restaurants) in the southern part of the city. The four sites are part of Global Environmental Monitoring System (GEMS), and data from these sites are submitted weekly to the World Health Organization (WHO) database.

Single stage KB120 bulk aerosol samplers, and single stage PM-10 samplers (Laoshan Institute for Electronic Equipment, Qingdao, China) were used for TSP and PM-10 sampling with Whatman 41<sup>®</sup> filters (Whatman International Ltd., Maidstone, England) used as the collection substrates. Sampling intervals ranged from 1 to 24 h with flow rates of  $\sim 6 \text{ m}^{-3} \text{ h}^{-1}$ . The TSP and PM-10 mass loadings were determined gravimetrically, using a microbalance with a sensitivity of  $1 \mu\text{g}$ .

The elemental concentrations were analyzed directly by a proton induced X-ray emission (PIXE) method using the 2.5 MeV protons with a 50 nA beam current produced at the  $2 \times 1.7$  MV tandem accelerator in Beijing Normal University (BNU, for details see Zhang et al., 1993). Through the PIXE analyses we were able to determine the concentrations of 20 elements: Al, As, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, P, Pb, S, Se, Si, Sr, Ti, V, and Zn. The data were corrected for background filters, and the concentrations of the elements were also determined by PIXE in 8 aliquots of a standard reference material from the National Bureau of Chemical Exploration Analysis, China (GSS, 1984). The quality control and accuracy tests showed that both the precision ( $<10\%$ ) and accuracy ( $<15\%$ ) were satisfactory.  $\text{SO}_2$  and  $\text{NO}_x$  concentrations were determined via solution absorption and spectrophotometric analysis according to Chinese EPA's monitoring procedures (SEPB, 1991).

Of the 299 bulk samples, 97 were selected for determinations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and other ionic species, including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$  and  $\text{Cl}^-$ , as a means of evaluating the material balance for the particulate mass. The 24 PM-10 and 24 bulk 1998 aerosol samples were analyzed for all the ionic species. A portion of each aerosol-laden Whatman 41<sup>®</sup> filter was extracted with 25 ml of double-deionized water (DDI) using a  $75 \times 125$  mm clean-room Poly bag (Clean Room Products, Inc., Ronkonkoma, NY). The resulting extracts were analyzed for nitrate and sulfate by ion chromatography (Dionex 300 series) with a OmniPac Pax-500 column, 25 mM  $\text{H}_2\text{SO}_4$  autoregenerant, and gradient elution (from 5 to 28.75 mM  $\text{NaOH}/5\%$  methanol) at the Department of Oceanography, University of Hawaii. Ammonium ion analysis were performed isocratically with an IonPac CS-10 column, 20 mM  $\text{HCL}/2$  mM DL-2,3-diaminopropionic acid fluent and 0.1 M tetrabutylammonium hydroxide autoregenerant.

### 3. Results and discussion

#### 3.1. Characterization of TSP, $\text{SO}_2$ , $\text{NO}_x$ and PM-10

The arithmetic mean concentrations of TSP,  $\text{SO}_2$  and  $\text{NO}_x$  calculated for the samples collected from September 1996 to August 1997 were 410, 39 and  $43 \mu\text{g m}^{-3}$ , respectively (Fig. 2a–c). The spring and autumn TSP values (Fig. 2a) were comparable, with the values averaging  $\sim 400 \mu\text{g m}^{-3}$ ; are roughly twice the summertime levels ( $\sim 200 \mu\text{g m}^{-3}$ , Fig. 2a). The TSP loadings exhibited wintertime highs that were synchronous with high  $\text{SO}_2$  concentrations (Fig. 2a and b), suggesting an important influence of coal combustion on TSP, especially during the winter. This argument is supported

by the fact that the large increase of wintertime  $\text{SO}_2$  ( $\sim 200 \mu\text{g m}^{-3}$ ) relative to the other three seasons ( $\sim 30$ – $50 \mu\text{g m}^{-3}$ , Fig. 2b) was associated with a significant increase of TSP from typical levels of ( $\sim 200$ – $400 \mu\text{g m}^{-3}$ ) to higher wintertime values of  $\sim 800 \mu\text{g m}^{-3}$  (Fig. 2a).

The seasonality in  $\text{SO}_2$  coincides with the so-called “heating season” in XiAn as well as the most cities in northern China (November 15–March 15 each year) when the emissions of coal-related secondary sulfate and coal fly ash from residential heating to the atmosphere increase dramatically (Fig. 3). The moderately strong correlation between TSP and  $\text{SO}_2$  ( $r^2 = 0.47$ ) demonstrates that while coal-related pollutants are probably responsible for a large proportion of the TSP in winter, other pollutant sources and not just coal-combustion contribute to the particulate loadings in XiAn (Fig. 3). The apparent effects of the heating season also imply that emissions from dispersed area sources, as opposed to stationary point sources, are probably responsible for a major fraction of the pollution from coal-combustion in XiAn. This conclusion is based on the assumption that emissions from stationary point sources are maintained at relatively similar levels throughout the year.

Extensive meteorological analyses have not been conducted for this paper, but the role of meteorology in determining the concentrations of air pollutants should not be ignored. A variety of meteorological factors can affect pollutant concentrations of XiAn in winter. For example, low precipitation can pollute the air by reducing scavenging particles from the atmosphere. Temperature inversions can trap pollutants in the boundary layer, leading to the most severe pollution episodes in winter.

During the springtime, high levels of TSP (Fig. 2a) are associated with the occurrence of mineral aerosol transported long distances combined with particles resuspended by local activities. The large fluxes of mineral aerosol to the region during spring and late autumn have been well documented (see Zhang, 1984; Merrill et al., 1989; Zhang et al., 1993, 1996), and these dust fluxes are associated with winds driven by the northerly East Asian winter monsoon (An et al., 1990; Zhang et al., 1994).

A comparison between time series for TSP and visibility for September 1996 to August 1997 (Fig. 4) shows that these two variables generally were anticorrelated, suggesting that relatively fine particles, with long residence times and strong effects on scattering, were important components of the TSP. We also observed sporadic increases of  $\text{SO}_2$ ,  $\text{NO}_x$  throughout the study; these precursor gases can be converted into fine secondary sulfate and nitrate, leading to increases in TSP. A comparison of the concentrations of PM-10 particles relative to TSP at the south monitoring site in 1998 shows that the PM-10 fraction could account for

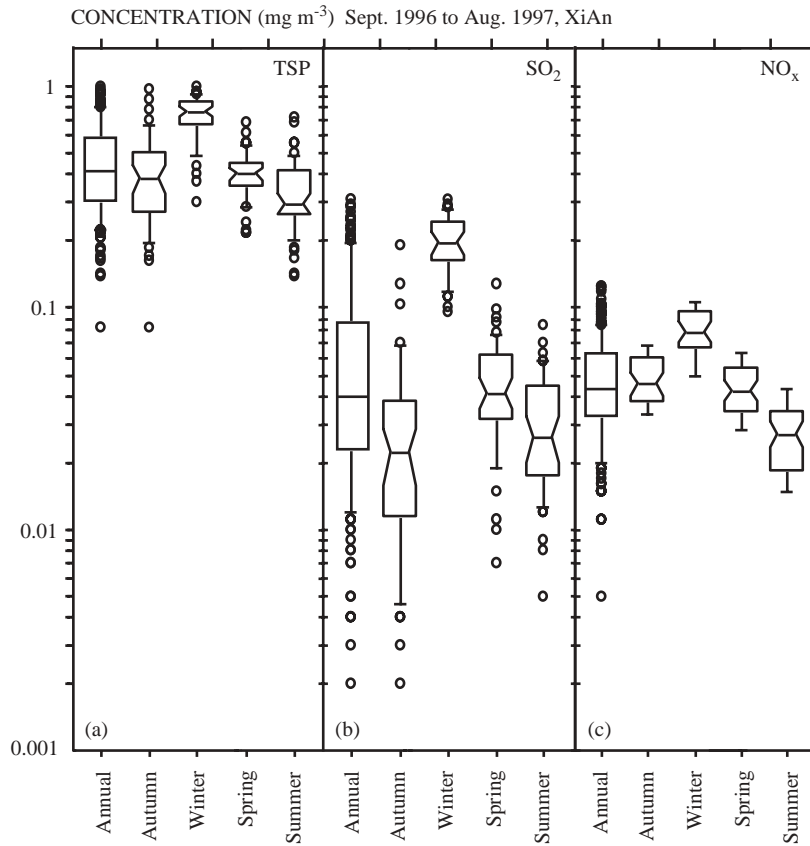


Fig. 2. Annual and seasonal average daily concentrations of TSP, SO<sub>2</sub>, NO<sub>x</sub> in XiAn (four-site average) from September 1996 to August 1997.

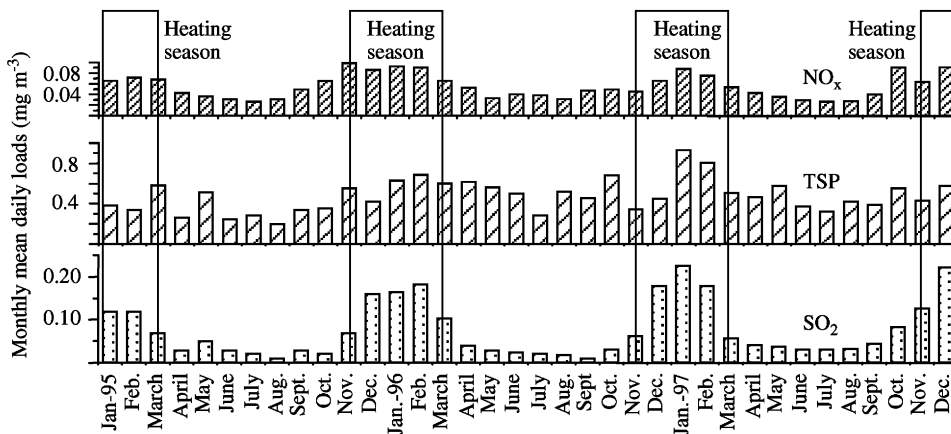


Fig. 3. Monthly average daily concentrations of TSP, SO<sub>2</sub>, NO<sub>x</sub> in XiAn (four-site average) from January 1995 to December 1997.

~60% of the TSP mass. A report by Liu (1997) similarly indicated that the PM-10 fraction in XiAn typically accounts for ~70% the TSP mass. The percentage of PM-10 relative to TSP observed in XiAn

also is consistent with data from other cities in China. For example, Ning et al. (1996) observed a similar but slightly higher percentage of PM-10 relative to TSP in samples from Dalian, China.

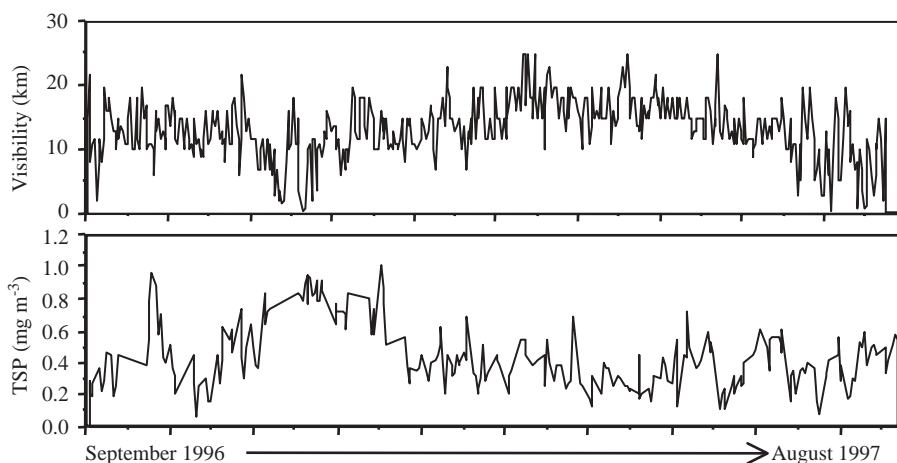


Fig. 4. Time series of TSP and visibility (14:00 observation) in XiAn from September 1996 to August 1997.

### 3.2. Elemental composition of TSP and PM-10

The concentrations of 20 elements in our TSP and PM-10 samples from the southern monitoring site are summarized in Table 1 for the Winter (December–February), Summer (June–August), Autumn (September–November) and Spring (March–May) data sets. The elemental TSP data presented in this table are the seasonal means of the concentrations for the 1997 samples averaged across the four sampling sites. One can see that the elemental proportions of six dust elements (Si, Al, Sr, Ti, K and Fe) in the TSP samples closely resemble those of material from the Earth's upper continental crust (Taylor and McLennan, 1995). This can be demonstrated by the calculation of enrichment factors relative to crustal rock using Si as a reference element ( $EF_{crust} = (X/Si)_{air}/(X/Si)_{crust}$ ).

The  $EF_{crust}$  values for Al, Sr, Ti, K and Fe were all close to unity with maximum values less than  $\sim 5$  (Table 1), indicating that the elements in the aerosol samples were dominated by mineral dust or re-suspended mineral matter. Two elements (Ca and Mn) that are generally associated with dust particles over Chinese deserts (Zhang et al., 1997), the Tibetan Plateau (Zhang et al., 2001) and the Loess Plateau (Zhang et al., 1993) had  $EF_{crust}$  values generally larger than 10 at XiAn, suggesting influences of some non-crustal sources, probably construction and industry activities. Compared with the dust-derived elements, the  $EF_{crust}$  values for As, Br, Cl, Cr, Cu, Mn, Ni, Pb, S, Se, V and Zn are much larger than 5, suggesting strong but variable the influences of non-crustal sources.

The highest concentrations of the 20 elements quantified in the TSP samples generally occurred during the winter, and they were lowest in the summer (Table 1). The autumn and spring values were relatively similar and intermediate between those of winter and

summer (Table 1). This was true for each of the four sampling sites and quite similar to the results of the TSP mass loadings mentioned above, reflecting the fact that changes in the elemental data are generally proportional to the particulate matter loadings.

The eight elements with the highest concentrations in the TSP samples were Al, Ca, Cl, Fe, K, P, S and Si. During the winter, sulfur exhibited the highest concentration at each site, reflecting the strong influence of non-dust source(s) on S concentrations (Table 1). This can be further illustrated by comparing the ratio of S/Al (0.0019) for Asian dust particles deposited onto the Loess Plateau (GSS, 1984) with the corresponding ratio for aerosols from XiAn. For comparison, the ratios of S/Al at XiAn were  $\sim 2.5$  and 1.4 for aerosol particles during winter half year (autumn and winter) and summer half year (spring and summer), respectively (Table 1). The summertime ratio of 1.4 for 1997 is also similar to the ratio of 1.6 for the PM-10 samples collected during summer of 1998 (Table 1). The S/Al ratios observed at XiAn are also much higher than the values for aerosol particles collected under northerly winds at a desert site along southern margin of the Mu Us Desert (0.10, Zhang et al., 2002).

A strong correlation ( $r^2 = 0.95$ ) between aerosol sulfate and elemental sulfur in PM-10 samples from summer (Fig. 5) indicates that the atmospheric sulfur in the fine particles existed mainly in the form of sulfate. The fact that the sulfate to sulfur ratio determined by linear regression (4.2 in Fig. 5), was slightly larger than 3, however, suggests that some amount of the sulfur was not associated with fine particles, probable with coarse particles.

In winter, the four elements with the highest concentrations followed the sequence  $S > Si > Ca > Al$ , while the loadings of the four next most abundant elements (Fe, Cl, P and K) were similar. During the

Table 1  
Observed elemental concentrations of TSP during 1997 and PM-10 at S monitoring station during 1998 (unit:  $\mu\text{g m}^{-3}$ )

	TSP												PM10		
	Winter 1997 ( $n = 75$ )			Summer 1997 ( $n = 73$ )			Autumn 1997 ( $n = 73$ )			Spring 1997 ( $n = 78$ )			July 1998 ( $n = 24$ )		
	Concentration			Concentration			Concentration			Concentration			Concentration		
	Mean	S.D.	$EF_{\text{crust}}^a$	Mean	S.D.	$EF_{\text{crust}}^a$	Mean	S.D.	$EF_{\text{crust}}^a$	Mean	S.D.	$EF_{\text{crust}}^a$	Mean	S.D.	$EF_{\text{crust}}^a$
Al	25	5.7	2.0	2.0	0.79	1.2	5.3	4.1	1.2	5.1	2.6	1.1	6.6	2.4	1.8
As	0.75	0.25	3277	0.15	0.06	4813	0.30	0.14	3624	0.26	0.14	2966	0.14	0.06	2053
Br	0.17	0.14		0.01	0.01		0.06	0.07		0.04	0.06		0.04	0.03	
Ca	36	7.0	7.9	9.2	3.7	15	19	7.9	12	19	7.3	11	6.3	2.7	4.6
Cl	11	1.8		1.7	0.48		3.5	1.5		3.2	1.2		2.3	0.83	
Cr	1.1	0.21	206	0.63	0.13	866	0.70	0.13	362	0.71	0.11	347	0.10	0.02	63
Cu	0.83	0.36	218	0.28	0.08	539	0.50	0.17	362	0.39	0.16	267	0.17	0.06	150
Fe	16	3.5	3.0	3.7	1.1	5.1	10	4.2	5.2	10	3.8	4.9	2.7	1.1	1.7
K	8.9	1.5	2.1	2.2	0.87	3.8	4.9	1.2	3.2	4.0	1.4	2.4	2.1	0.68	1.7
Mn	1.0	0.18	11	0.40	0.08	32	0.65	0.22	20	0.56	0.16	16	0.32	0.07	12
Ni	0.81	0.58	265	0.34	0.1	818	0.46	0.15	417	0.43	0.16	368	0.18	0.07	198
P	8.4	2.0	79	2.0	0.71	138	2.6	1.8	67	3.0	0.90	73	3.2	0.43	101
Pb	4.3	1.2	1409	0.06	0.09	144	0.90	0.78	815	0.62	0.76	530	0.77	0.46	847
S	59	12		2.8	0.86		13	8.1		6.4	2.8		11	5.4	
Se	0.25	0.22	33	0.04	0.03	39	0.12	0.09	43	0.09	0.09	31	0.05	0.03	22
Si	47	8.9	1.0	6.4	2.8	1.0	17	11	1.0	18	8.4	1.0	14	3.5	1.0
Sr	0.31	0.31	5.8	0.04	0.06	5.5	0.06	0.09	3.1	0.03	0.03	1.5	0.01	0.01	0.63
Ti	2.2	0.57	4.8	0.10	0.14	1.6	0.64	0.47	3.9	0.47	0.31	2.7	0.22	0.13	1.6
V	1.1	0.39	120	0.17	0.12	136	0.26	0.22	79	0.30	0.16	86	0.002	0.0004	1.0
Zn	3.0	1.2	277	0.46	0.16	312	1.6	1.0	408	1.4	1.0	337	0.49	0.15	152

<sup>a</sup>Si as the reference element.

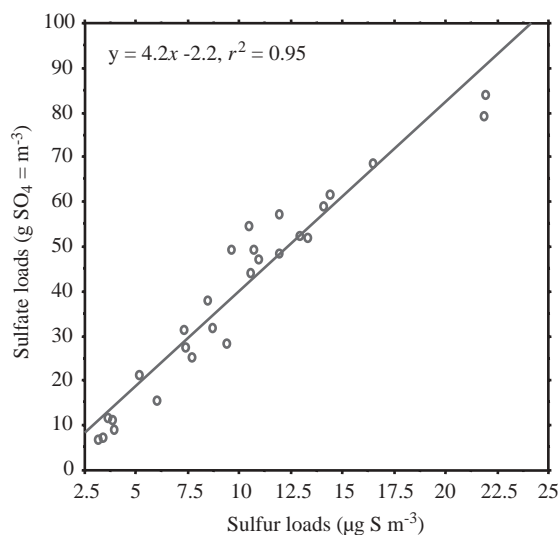


Fig. 5. Correlation between aerosol sulfate and elemental sulfur in XiAn in PM-10 samples collected in summer 1998.

non-winter seasons (Table 1), however, the sequence in loadings changed to  $\text{Ca} > \text{Si} > \text{Fe} > \text{S}$  in most samples. In addition, during the non-winter months, the Ca concentrations always exceeded those for S or Si; and

the atmospheric loading of Fe was higher than that of Al. These trends differ from those observed for Asian dust particles (Zhang et al., 1993, 1998), reflecting not only strong anthropogenic influences but also a seasonal effect in which the influence of coal-related pollutants was most evident in winter.

In samples of local coal fly ash, we find high concentrations of S and Ca, even higher than Al and Fe. In contrast, elemental data for loess sediments (Wen et al., 1996) show that the levels of Ca and Fe are lower than those of Si and Al. This comparison suggests that there are significant contributions of non-mineral dust to Ca and S, and this probably due at least in part to fly ash. Additional influences from cement dust and from other construction-related activities also would appear to be possible contributors to the observed high Ca concentrations owing to the rapid of the city. The high proportion of Fe in the samples warrants further evaluation of possible sources. For the other trace elements (Ti, Mn, V, Cr, Ni, Cu, Zn, Br, Pb, As and Se), Pb exhibited the highest concentrations in winter at the four sites, followed by Zn, Ti, Cr, Mn (Table 1).

The concentrations of twenty elements in the PM-10 samples are also summarized in Table 1. Of these elements, Al, Ca, Cl, Fe, K, P, S and Si exhibited especially high concentrations in XiAn PM-10 particles,

and this is consistent with our 1997 TSP results. The lower  $EF_{\text{crust}}$  value for Ca (4.6) in PM-10 relative to TSP indicates first that Ca in PM-10 was mainly derived from the Earth's crust; and second that the non-crustal Ca is mainly in coarse particles and thus probably locally derived. Construction and re-suspended dusts are suspected to be the major sources for the Ca in TSP.

The high  $EF_{\text{crust}}$  value for Pb in PM-10 samples suggests strong impacts of pollution sources, most likely motor vehicles on aerosol Pb concentrations. Similar to what was observed for the TSP samples, the relative proportions of Sr, Ti, Fe, Si, Al and K in PM-10 closely resembled those in upper crustal rock (Taylor and McLennan, 1995), suggesting the importance of crustal sources for them. As was true for sulfur in the TSP samples from 1997, the high concentrations of sulfur in the 1998 data set reflect the strong and pervasive influence of non-dust sources, especially coal-combustion. Other elements, including As, Cr, Cu, Mn, P, Ni, Se and Zn, were enriched in the PM-10 samples relative to crustal rock, suggesting the influences of fugitive dusts and other anthropogenic particles.

### 3.3. Characterization of sulfate, nitrate, ammonium, and carbonaceous materials

Prior studies of the major ions in aerosols from the XiAn area have been limited to only a few sampling campaigns (e.g., Gao, 1994). In particular little information is available on the temporal variability in the concentrations of aerosol ions. The data for selected ions in the 1997 sample subset is summarized in Table 2. Studies of soluble aerosol ions have suggested that after taking into account experimental errors, the imbalance between cations and anions (denoted  $\Delta C$ ) should be less than several percent of the ionic budget ( $S$ , for which the concentrations are expressed in micro-equivalents per cubic meter):

$$\Delta C = [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] - [\text{F}^-] - [\text{Cl}^-] - [\text{NO}_3^-] - [\text{SO}_4^{2-}], \quad (1)$$

$$S = [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{F}^-] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]. \quad (2)$$

Based on the following the equations for anions (3) and cations (4), the ion balance evaluations of our PM-10 and TSP for the 1998 samples are shown in Fig. 6a.

$$\begin{aligned} \text{Anion equivalence (mmole m}^{-3}\text{)} \\ = [\text{F}^-] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}], \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Cation equivalence (mmole m}^{-3}\text{)} \\ = [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}]. \end{aligned} \quad (4)$$

Comparisons show that the calculated cation equivalences were about 1% and 7% less than anion equivalences for PM-10 and TSP samples, respectively, indicating good internal data consistency (Fig. 6).

Similar to TSP,  $\text{SO}_2$ ,  $\text{NO}_x$  and the elemental data, the concentrations of all ionic species were highest during the winter and lowest during the summer, demonstrating again the strong influence of the heating season on air quality (Table 2). The average sulfate concentration in TSP was  $\sim 340 \mu\text{g m}^{-3}$  in the winter, which is about three times higher than that in autumn ( $\sim 100 \mu\text{g m}^{-3}$ ), presumably due to the influences of the heating season. The sulfate loadings were generally lower in spring and summer, with values of 59 and  $27 \mu\text{g m}^{-3}$ , respectively (Table 2). The sulfate concentrations observed in XiAn during the spring 1997 are higher than those reported for the spring of 1992 ( $\sim 20 \mu\text{g m}^{-3}$ ) by Gao (1994), probably because the earlier data were for samples collected from a rural site, Caotan, 20 km north to XiAn.

In 1998, the PM-10 sulfate concentration ( $43 \mu\text{g m}^{-3}$ ) was nearly equal to the sulfate concentration in TSP ( $45 \mu\text{g m}^{-3}$ ) (Fig. 7), indicating that sulfate was almost entirely in the PM-10 fraction. The summertime  $\text{SO}_2$  concentrations ( $20\text{--}50 \mu\text{g m}^{-3}$ ) from 1996 to 1997 were slightly lower than in 1998 when  $66 \mu\text{g m}^{-3}$  of  $\text{SO}_2$  was observed. The higher particulate sulfate concentrations in 1998 relative to earlier years were almost certainly due to the high  $\text{SO}_2$  concentration in the summer of 1998.

The summer mean nitrate concentration in 1997 was  $16 \mu\text{g m}^{-3}$ , which like the pattern observed for sulfate was lower than that in 1998 ( $22 \mu\text{g m}^{-3}$ ). Unlike  $\text{SO}_2$ , however, the levels of  $\text{NO}_x$  in the summer of 1996–1997 ( $\sim 30\text{--}60 \mu\text{g m}^{-3}$ ) were higher than or comparable to those in 1998 ( $33 \mu\text{g m}^{-3}$ ). This difference could be a consequence of the different gas-to-particle conversion rates for sulfur- and nitrogen-oxides. The nitrate concentrations in XiAn normally were about 20–30% lower than  $\text{NO}_x$ , presumably because a significant fraction of the gaseous  $\text{NO}_x$  had not been converted to nitrate. Comparable concentrations of nitrate in 1998 TSP and PM-10 indicate that the nitrate-containing aerosols, like sulfate, were mainly in PM-10 fraction in XiAn.

Ammonium ion is a major component of TSP at all sites, and it is most likely in the form of secondary ammonium sulfate/bisulfate and ammonium nitrate particles. The ammonium concentrations in TSP and PM-10 were similar, showing that this ion, like sulfate, was mainly in that particle-size fraction (Fig. 7). To evaluate the equilibrium among ammonium nitrate, ammonium sulfate and ammonia, comparisons between the calculated and observed ammonium concentrations are shown in Fig. 6a,b for PM-10 and TSP, respectively. The ammonium based on  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{HSO}_4$  is calculated from Eq. (5); whereas the ammonium based

Table 2  
Daily average TSP mass and some chemical concentrations ( $\mu\text{g m}^{-3}$ ) at four sampling sites in the period of autumn, 1996 to summer, 1997

Species	Autumn					Winter				
	W <sup>a</sup> , n = 6	C, n = 8	E, n = 7	S, n = 7	XiAn, n = 28	W, n = 4	C, n = 5	E, n = 4	S, n = 4	XiAn, n = 17
Mass	320	450	400	240	350 (190–530)	1200	1000	890	920	1000 (870–1200)
SO <sub>4</sub> <sup>2-</sup>	98	134	100	74	100 (44–190)	360	350	340	340	340 (320–400)
NO <sub>3</sub> <sup>-</sup>	18	20	23	27	22 (18–31)	56	76	68	62	65 (3.7–10)
NH <sub>4</sub> <sup>+</sup>	47	63	51	33	49 (18–79)	140	170	140	130	140 (130–180)
Carbonaceous materials and unidentified	13	29	38	13	23 (10–43)	230	39	42	24	84 (21–270)
	Spring					Summer				
	n = 4	n = 7	n = 7	n = 6	n = 24	n = 7	n = 7	n = 7	n = 7	n = 28
Mass	380	340	400	410	380 (330–420)	210	200	180	180	190 (170–230)
SO <sub>4</sub> <sup>2-</sup>	50	48	47	59	59 (44–120)	28	29	23	28	27 (21–36)
NO <sub>3</sub> <sup>-</sup>	21	34	42	35	33 (15–46)	19	16	14	17	16 (13–24)
NH <sub>4</sub> <sup>+</sup>	36	33	31	62	40 (27–83)	17	15	16	21	17 (13–22)
Carbonaceous materials and unidentified	110	56	110	96	93 (55–120)	60	63	58	36	54 (23–70)

<sup>a</sup>Sampling sites: W (West site); C (Centre); E (East); S (South).

on NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is calculated from Eq. (6):

$$\text{Ammonium (mg m}^{-3}\text{)} = 0.29(\text{NO}_3^-) + 0.192(\text{SO}_4^{2-}), \quad (5)$$

$$\text{Ammonium (mg m}^{-3}\text{)} = 0.29(\text{NO}_3^-) + 0.38(\text{SO}_4^{2-}). \quad (6)$$

The comparison between the ammonium concentrations calculated using Eq. (6) versus the observed concentrations suggests that the ammonium in the atmosphere over XiAn exists mostly in form of ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and ammonium nitrate. The level of agreement observed also supports the quality of our measurements of these aerosol ions in the 1998 samples.

The average concentration of aerosol ammonium in TSP during the summer of 1997 was 17  $\mu\text{g m}^{-3}$ , which about 30% lower than that in 1998 (22  $\mu\text{g m}^{-3}$ ) (Fig. 7). This is similar to the magnitudes of the differences in sulfate and nitrate concentrations between 1997 and 1998.

Carbonaceous materials, including organic and elemental carbon were not measured as part of this study, but carbonaceous aerosols were more than likely a non-negligible fraction of the TSP. Organic compounds

produced by incomplete combustion from motor vehicle engines in poor repair are another pollutant suspected to be important, but there are no data available to directly test this assertion. The concentrations of carbonaceous materials, which were calculated as the difference between the TSP and all identified fractions (crustal dust represented by oxide of the dust element, nitrate, sulfate, ammonium product and sum of the trace elements) exhibited a distinctly different trend in concentrations compared with most other particulate species, i.e., they were highest during the spring (Table 2). This pattern implies the dominance of non-coal sources, possibly including biomass burning, for the carbonaceous materials. The large uncertainties may exist associated with these calculations for deriving the carbonaceous fractions. Measurements of organic and elemental carbon need to be done in the future.

#### 4. Conclusions

Seasonal variations in mass concentrations and chemical compositions of TSP and PM-10 have been



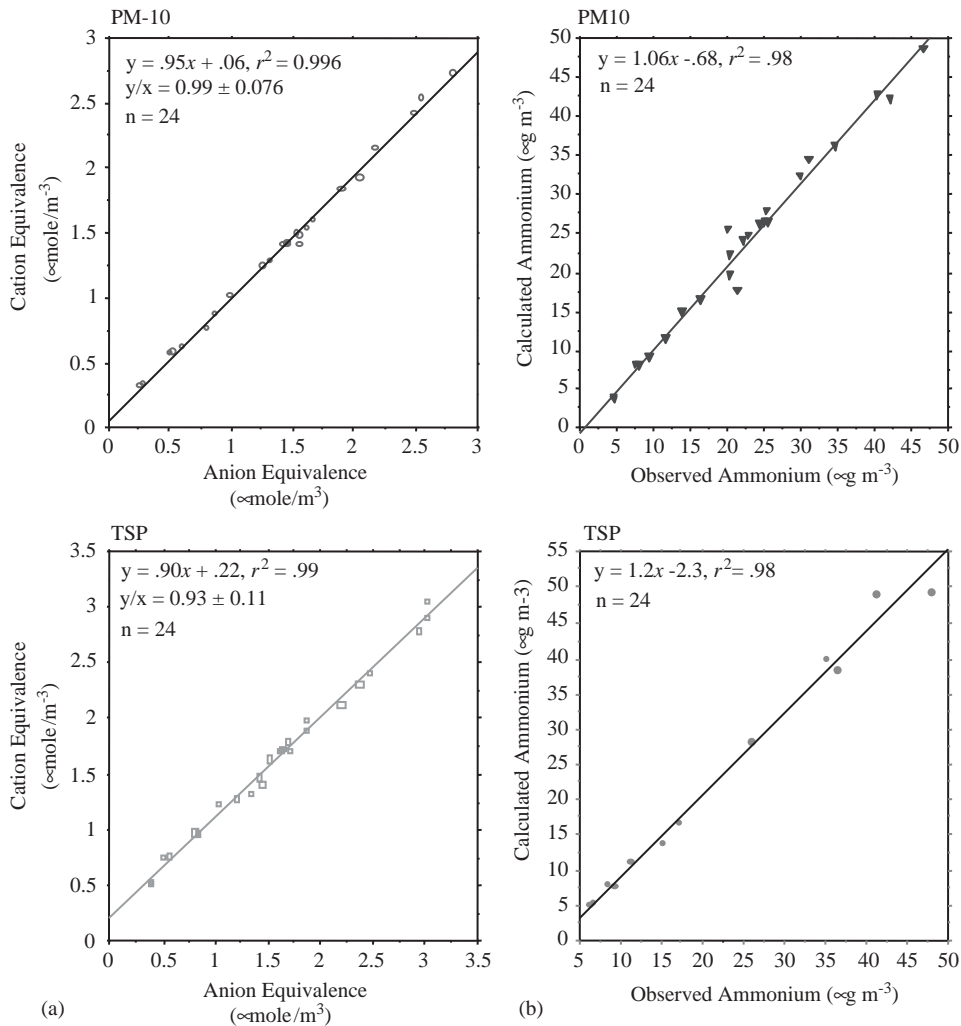


Fig. 6. Balance evaluation between cations and anions, and equilibrium calculation for ammonium nitrate, ammonium sulfate and ammonia in PM-10 and TSP samples at XiAn during summer of 1998.

examined for four sites in XiAn from 1995 to 1998. About 75% of the daily observed TSP concentrations in 1997 exceeded the Class II category of the National Ambient Air Quality Standards in China, highlighting the seriousness of particulate pollution in XiAn. Coal combustion coupled with meteorology are the likely causes of the high TSP concentrations in winter. Spring was clearly impacted by mineral dust from arid areas to the northwest. Compared with other Chinese cities, XiAn has particulate matter loadings similar to those in Baotou, Lanzhou, Beijing, Urumuqi, Chengdu and Dongying (Hashimoto et al., 1994; Briant et al., 2000). Of the TSP mass measured in the summer of 1998, about ~60–70% was attributable to the PM-10 fraction.

Changes in the elemental data are generally proportional to the particulate loadings. The most abundant elements in atmospheric particulate matter from XiAn

are Si, Ca, Al, Fe, Cl, P, K and S. These elements are not totally dominated by crustal sources; some of their loadings evidently are caused by emissions from fugitive dust/fly ash sources. For example, Ca is mainly associated with mineral dust in the PM-10 samples; but non-crustal Ca is found in the coarse particle fraction most of which is expected to be from construction activities and coal-ash.

Secondary sulfates originating from dispersed coal-combustion sources also are significant contributors to the air pollution in XiAn. The season with the second highest TSP from coal was autumn and that also includes part of the heating season. Compared with the spring and summer values, however, the loadings of coal fly ash did not increase nearly so much as sulfate. This implies some de-coupling of these two products of coal combustion, possibly through chemical processing,

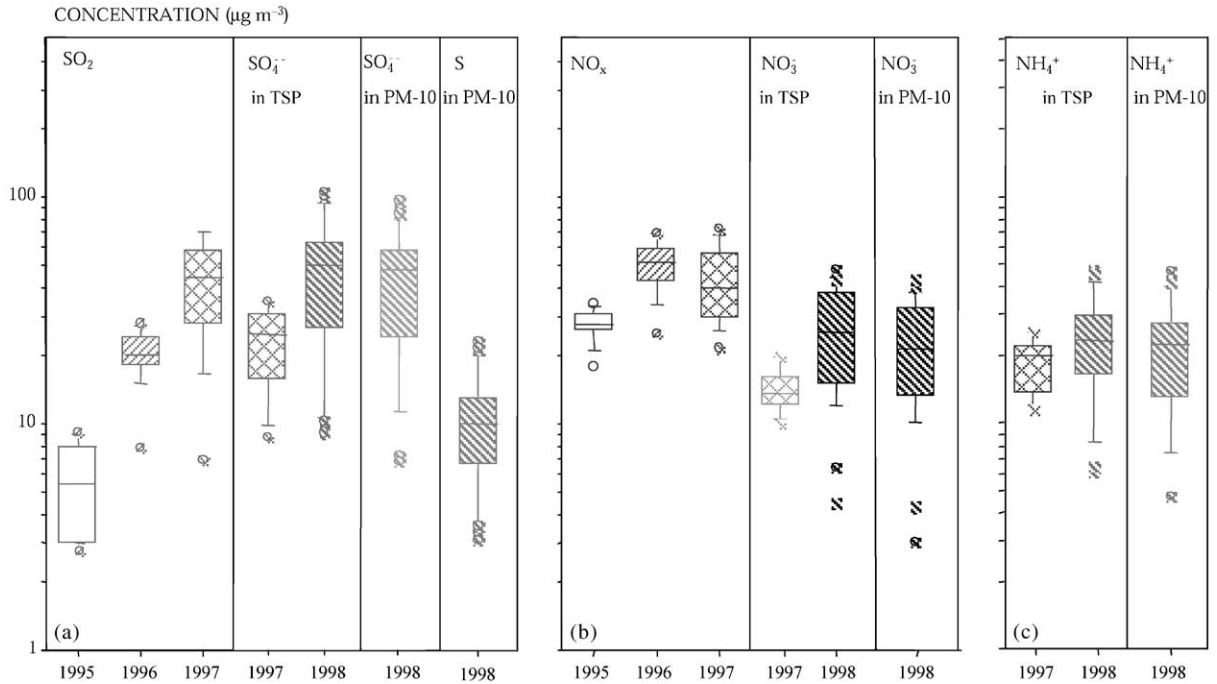


Fig. 7. Concentrations of  $\text{SO}_2$ , sulfate, sulfur,  $\text{NO}_x$ , nitrate, and ammonium products in XiAn TSP and PM-10 samples.

or this may reflect additional sources for sulfate. The high  $\text{NH}_4^+$  concentrations in aerosols from XiAn may be associated with use of fertilizers in the Guanzhong Plain as well as contributions from local sources of sanitary waste; these deserve further attention for particulate control. A comparison between calculated and observed ammonium concentrations indicates that the ammonium in the atmosphere over XiAn exists mainly in form of ammonium sulfate and ammonium nitrate.

While the characterization of XiAn aerosol has begun, additional work is still needed to address important issues; in particular to calculate mass balances and to obtain the source profiles needed to apportion source contributions. These topics will be considered in subsequent papers.

#### Acknowledgements

We thank Dr. An-Lin Liu from Shaanxi Meteorological Bureau for providing meteorological and visibility data. This research was supported by grants from the National Key Project of Basic Research (G2000048703), Chinese Academy of Sciences (KZCX2-305), a special Ph.D. fund from the CAS, NSF of China (49825105; 49894170, and a special fund for young scientist group) and the NSF of the United States (NSF ATM 0002599).

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