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Atmospheric nitrate, sulfate, ammonium and calcium concentrations in China

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ABSTRACT

We used teflon/nylon filter packs to measure concentrations of nitrate (aerosol plus vapor), sulfate, ammonium, and calcium at three locations in China during October of 1985. On the average, molar sulfate concentrations were less than twice the total nitrate concentrations. This small ratio is somewhat surprising, in view of the large amount of coal burning in China. In Beijing, calcium was the dominant cation, but at both the Xinglong Astronomical Observatory (a rural northern China site) and Changsha (the capital city of Hunan Province, in the south), there was more ammonium ion than calcium in the aerosol. During a period of northerly winds at Xinglong, the concentrations were comparable to reported background values from North America and Europe, suggesting that this may be a good site for studying Asian continental background air.

1. Introduction

Although numerous publications (Winchester and Bi, 1984; Dod et al., 1986; Zhao and Sun, 1986a and b; and Su, 1986) have discussed the chemistry of sulfur oxides in China's air, relatively few have examined its odd-nitrogen chemistry. In view of the concerns about acid deposition in some parts of China, we undertook a brief survey to examine the role that nitric acid and aerosol nitrate might play in the chemistry of China's atmosphere. The analysis of aerosol sulfate, ammonium, and calcium gave us additional insight into the relationships between China's atmospheric acids and bases.

China's heavy reliance on coal-burning results in the release of about 14.6 million tons of SO_2 per year (Wang, 1986). Of this total, 290 thousand tons were released in Beijing and 73,000 tons were emitted in Changsha in 1981 (unpublished data, Environmental Quality Report (EQR) of China, 1981). Some fraction of the emitted SO_2 is oxidized to sulfate aerosol prior to dry or wet deposition. In northern China, this acidic sulfate aerosol tends to be completely neutralized by ammonia and calcium (Zhao et al., 1985), while the lower availability of bases in southern air permits much of the sulfate to be deposited in its acidic form (Zhao and Sun, 1986a; Su, 1986).

Although China has fewer vehicles per capita than western countries, anthropogenic sources still emit significant quantities of nitrogen oxides. According to Su (1986), Chinese sources emitted 6 million tons of NO_x per year in 1983. In Beijing, 0.170 million tons of NO_x were emitted, as compared to 0.073 million tons in Changsha (EQR of China, 1981). If we assume that this is largely emitted in the form of NO, the molar ratio of emitted sulfur oxides to nitrogen oxides is 1.7 in Beijing and 7.0 in Changsha. The same ratio in the US is close to 1 (Summers and Barrie, 1986), the result of a smaller percentage of coal in the

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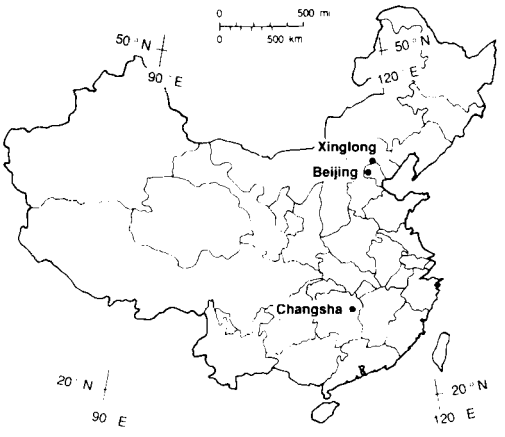

Fig. 1. Location of sampling sites.

US fuel mix (thus emitting relatively less SO_2), and of more mobile NO_x sources in the US.

Ambient concentration measurements of SO_2 and NO_x in Chinese cities cover such a wide range that it is difficult to specify a value for the ambient S/N ratio in these primary oxides. Siddiqi and Chong-xian (1984) quote "usual ranges" of concentrations in northern cities (100–390 μg SO_2/m^3 and 100–170 μg NO_x/m^3) and southern cities (130–320 μg SO_2/m^3 and 20–130 μg NO_x/m^3). Molar S/N ratios based on the mid-points of these concentration ranges would be about 2 in the north and 3 in the south (if the NO_x were assumed to be NO), but the possible range of values is large.

In precipitation, the ratio of sulfur to nitrogen is highly variable. The data reported by Zhao et al. (1985) yield a range of ratios from 5 to 11 in the north and from 5 to 36 in the south. These are clearly much higher than the emission ratio of sulfur to nitrogen, suggesting that dry deposition may remove some of the nitrogen oxides. The fact that below-cloud scavenging of SO_2 is faster than that for NO_x may also contribute to the high S/N ratio in urban precipitation. Harte (1983) found a very different situation (in just three samples) in Qinghai province, where the S/N ratio ranged from 0.03 to 0.17. This unusually low ratio is presumably due to the extremely low S/N ratio (1/10) in the coal mined in that region. In US precipitation, the annual average S/N ratio is about 1 (roughly equal to the emissions ratio), varying in the northeast between 1.5 in the summer and 0.5 in the winter (Summers and Barrie, 1986).

To learn more about the link between the gas-phase and precipitation chemistry of SO_x and NO_x in China, we made a brief survey of sulfate, ammonium, and calcium aerosol and total nitrate in northern and southern China in October of 1985. We collected filter samples for several days each in the northern Chinese locations of Beijing (on the roof of the Institute of Atmospheric Physics building) and the Xinglong Astronomical Observatory (960 m above sea level in the Yanshu Mountains about 140 km northeast of Beijing), and in southern China at Hunan Normal University in Changsha, the capital city of Hunan Province (Fig. 1). During northerly winds, the Xinglong Observatory site is effectively isolated from the Beijing area by the mountain range on which the Great Wall of China was built.

2. Experimental

We used pairs of 47 mm teflon and nylon filters (Goldan et al., 1983) for collecting nitrate and sulfate samples. A $\frac{1}{4}$ Hp vacuum pump (Gast Model 522) pulled about 0.4 kg air/min through the filters, as measured by Gilmont rotameter. Sampling times varied from 47 to 804 min. About 20% of the filters were treated as field blanks. We handled them in every way as regular samples, but exposed each for only 10 s. Filters were sealed into microclean polyethylene bags within 24 h of exposure, and returned to Colorado College for extraction and analysis. Sulfate, nitrate, and ammonium were analyzed by ion chromatography, while atomic absorption spectrometry was used for the calcium analayses.

Although teflon/nylon filter pairs are frequently used to speciate aerosol and vapor phase nitrate in very clean air, the characteristics of the air we sampled in China make it likely that sampling artifacts would obscure the phase information in our samples (Appel et al., 1980). Incoming nitric acid vapor, for instance, might tend to react with (and be retained by) the heavy deposits of calcium aerosol on the teflon prefilter, so that it would not reach the nylon filter where nitric acid vapor would otherwise be collected. Likewise, large ammonia concentrations [Zhao et al. (1985) found as much as 44 ppbv!] would

favor the formation of ammonium nitrate aerosol, which might evaporate upon warming during our long sampling times, forming artifact vapor which would then collect on the nylon filter. The total nitrate concentration (from the sum of the nylon and teflon filters) is unaffected by these artifacts, however, and will be the focus of our discussion of nitrates.

3. Results and discussion

3.1. Meteorology

We sampled in Beijing on 12 and 15 October 1985, during the daytime only. The first day was clear with light haze, after a light rain the previous night. The 2nd day was very smoky and hazy, with low clouds. Since the heating season had not yet started, we did not observe the maximum effects of residential coal burning. According to Su (1986), October typically has 17 "smoke pollution days", as compared to December's maximum of 23 and July's minimum of 8 in Beijing.

At Xinglong Astronomical Observatory, we sampled for 6 days, from 16 to 21 October. 4 samples were taken each day, representing morning, midday, late afternoon/evening, and nighttime. Ambient temperatures fell below 0°C each night and rose somewhat above freezing each day. We chose to eliminate the nighttime sample of 17 October from the data set, because of evidence that it was heavily contaminated by the Observatory's own coal-fired hot water heater emissions. A strong smell of coal smoke was noted at the sampler just as this sample was being started, and the observed concentration was more than 30 times higher than the preceeding and subsequent samples. It clearly did not represent ambient conditions in northern China.

We encountered 2 very different types of air at Xinglong. During the first 2 days of sampling the winds were consistent light breezes from the north. The air was very clear and the visibility was more than 30 km (based on visual observations of mountain ranges). The direction of the flow changed in the middle of 18 October, so that the air came from the west, which includes the Gobi Desert and the Beijing metropolitan area. After a transition period of about a day, a heavy haze arrived, starting the evening of the 19th and lasting until the end of our stay at Xinglong. We experienced no precipitation at Xinglong.

Our sampling in Changsha also spanned 6 days, from 24 to 29 October. The weather in this southern city was frequently rainy, with a fairly constant haze. Only the last day was clear of the heavy low clouds which dominated the weather during our sampling. Although we were located on the western side of Changsha, the occasional westerly winds did not bring noticeably cleaner air than the usual winds directly from the center of the city. Temperatures were generally around 10–15°C.

3.2. Concentrations and uncertainties

The measured concentrations are listed in Table 1. All are listed as pptmole (moles of analyte per 10^{12} moles of air), to facilitate comparisons of the equivalents of acids and bases. (An approximate conversion to $\mu g/m^3$ can be accomplished by dividing the tabulated nitrate values by 360, the sulfate values by 230, the ammonium values by 1240, and the calcium values by 560.) The sample number identifies the starting date and local time, as ddmmyy.hhmm.

In nearly every case, the sample analyte exceeded the blank analyte by many times more than the variability of the blanks. Thus, the major source of uncertainty in the reported concentrations is not from the blank subtraction, but is due to the measurement of the volume of air sampled. For most samples, this is around $\pm 10\%$. A few samples were terminated early by power outages or inadvertant disconnections, so their ending times had to be deduced from other information. We estimate that even in these cases the measured volume (and therefore the concentrations) are accurate to withing $\pm 20\%$. Of course, concentration ratios will be unaffected by the volume uncertainty. The ratios should generally be accurate to within $\pm 10\%$.

For statistical purposes, we have grouped the data into 4 sets. The 1st contains the six measurements made in Beijing. The 2nd consists of the 6 samples collected at Xinglong during the relatively clean northerly wind flow. The 3rd set (9 samples) is also from Xinglong, during the period of westerly winds and dense haze. The transition between these regimes (after the winds came around to the west, but therefore the heavy haze arrived) is not included in the statistical

Table 1. *Measured concentrations*

Sample No. Start time	Location	Sulfate aerosol	Nitrate total	Ammonium aerosol	Calcium aerosol	S/N Ratio	Cation/anion equivs.
12 Oct. 1985 0945	Beijing	496	379	365	4,540	1.31	6.89
12 Oct. 1985 1132	Beijing	300	350	334	3,735	0.86	8.21
12 Oct. 1985 1555	Beijing	387	370	189	2,890	1.05	5.22
15 Oct. 1985 0842	Beijing	4,720	2,715	6,933	18,800	1.74	3.66
15 Oct. 1985 0945	Beijing	2,890	3,149	6,250	12,100	0.92	3.41
15 Oct. 1985 1053	Beijing	3,517	1,713	2,845	1,990	2.05	0.78
16 Oct. 1985 1525	Xinglong, N	288	19	300	128	15.16	0.93
16 Oct. 1985 1744	Xinglong, N	170	46	340	412	3.70	3.02
17 Oct. 1985 0710	Xinglong, N	132	56	424	52	2.36	1.65
17 Oct. 1985 1140	Xinglong, N	85	50	390	65	1.70	2.36
17 Oct. 1985 1516	Xinglong, N	68	48	357	92	1.42	2.94
18 Oct. 1985 0707	Xinglong, N	170	97	413	356	1.75	2.57
18 Oct. 1985 1116	Xinglong, W	138	55	373	422	2.51	3.68
18 Oct. 1985 1528	Xinglong, W	218	62	317	214	3.52	1.50
18 Oct. 1985 1900	Xinglong, W	329	469	650	883	0.70	2.14
19 Oct. 1985 0715	Xinglong, W	250	184	520	302	1.36	1.64
19 Oct. 1985 1115	Xinglong, W	232	114	486	211	2.04	1.57
19 Oct. 1985 1522	Xinglong, W	342	489	790	1,360	0.70	2.99
19 Oct. 1985 1900	Xinglong, H	758	1,013	1,371	1,190	0.75	1.48
20 Oct. 1985 0717	Xinglong, H	1,550	1,810	2,480	925	0.86	0.88
20 Oct. 1985 1119	Xinglong, H	1,660	1,303	1,870	623	1.27	0.67
20 Oct. 1985 1520	Xinglong, H	1,300	1,736	3,100	1,010	0.75	1.18
20 Oct. 1985 1841	Xinglong, H	1,860	1,881	3,310	845	0.99	0.89
21 Oct. 1985 0714	Xinglong, H	1,460	1,446	3,240	799	1.01	1.11
21 Oct. 1985 1105	Xinglong, H	1,500	1,010	2,570	1,300	1.49	1.29
21 Oct. 1985 1513	Xinglong, H	2,280	1,598	3,880	2,640	1.43	1.49
21 Oct. 1985 1925	Xinglong, H	1,490	1,148	1,980	1,690	1.30	1.30
24 Oct. 1985 1243	Changsha	4,937	1,089	6,530	927	4.53	0.76
24 Oct. 1985 1503	Changsha	5,930	1,215	7,380	2,900	4.88	1.01
24 Oct. 1985 1836	Changsha	3,630	925	4,450	624	3.92	0.70
25 Oct. 1985 0703	Changsha	1,520	772	3,630	170	1.97	1.04
25 Oct. 1985 1408	Changsha	760	349	2,150	256	2.18	1.42
25 Oct. 1985 1649	Changsha	194	297	1,350	213	0.65	2.59
25 Oct. 1985 1855	Changsha	1,410	967	2,530	224	1.46	0.79
26 Oct. 1985 0705	Changsha	1,990	1,156	4,170	274	1.72	0.92
26 Oct. 1985 1119	Changsha	1,960	583	4,250	278	3.36	1.07
26 Oct. 1985 1630	Changsha	900	568	3,090	187	1.58	1.46
26 Oct. 1985 1857	Changsha	1,660	1,311	4,030	58	1.27	0.90
27 Oct. 1985 0722	Changsha	2,170	1,924	7,780	70	1.13	1.26
27 Oct. 1985 1429	Changsha	663	364	2,560	88	1.82	1.62
28 Oct. 1985 0625	Changsha	2,100	363	2,550	39	5.79	0.58
28 Oct. 1985 1055	Changsha	2,490	620	4,510	259	4.02	0.90
28 Oct. 1985 2235	Changsha	1,820	771	3,590	180	2.36	0.90
29 Oct. 1985 0707	Changsha	2,020	870	3,880	345	2.32	0.93
29 Oct. 1985 1217	Changsha	1,240	443	2,320	2,369	2.80	2.41
29 Oct. 1985 1501	Changsha	1,620	558	2,960	490	2.90	1.04

All concentrations are in molar parts per trillion, pptmol.

Xinglong samples are identified as N (northerly wind), W (west wind, before arrival of haze), or H (west wind, with dense haze).

Table 2. *Averages and standard deviations of concentrations*

Location	Sulfate	Nitrate	Ammonium	Calcium	*n*
Beijing	2050 ± 1700	1450 ± 1200	2800 ± 2800	7300 ± 6100	6
Xinglong (north winds)	150 ± 70	50 ± 20	370 ± 40	180 ± 140	6
Xinglong (west winds, haze)	1540 ± 390	1440 ± 320	2650 ± 760	1230 ± 580	9
Changsha	2050 ± 1380	800 ± 400	3880 ± 1690	520 ± 760	19

discussions below, because it is much less well-defined than the two regimes it links. The fourth set is the 19 samples from Changsha. Table 2 lists the concentration averages and standard deviations for these four sample populations.

3.3. *Sulfate*

The average sulfate concentrations in the two urban areas were surprisingly similar, about 2050 pptmol. A few higher values were recorded in Changsha, but the standard deviations (1700 Beijing, 1380 Changsha) are also virtually identical. The haze at Xinglong contained only slightly less sulfate (1540 ± pptmol), suggesting that it may have been transported to the observatory from urban areas near Beijing. The northerly air reaching Xinglong contained the least sulfate, 150 ± 70 pptmol. It clearly represents a different population from any of the other samples.

It is interesting to note that some of the sulfate concentrations in the clean northerly air sampled at Xinglong were in the same range as the cleanest continental samples reported in the literature. Friend (1973) uses 40 pptmol as typical of unpolluted continental regions. Georgii (1978) reported concentrations of about 300 pptmol in the free troposphere and 600–1200 pptmol in relatively unpolluted samples over Europe, while Meszaros (1978) noted somewhat lower European concentrations of about 100 pptmol. In North America, McMullen et al. (1970) cite measurements of 60–4500 pptmol sulfate, while Huebert and Lazrus (1980b) found <60 to 120 pptmol sulfate in their remote North American samples.

Yet even in a rural area such as Xinglong, air which has recently passed over urban areas can contain very high levels of sulfate. The 1500 pptmol (7 $\mu g/m^3$) at Xinglong and 2050 pptmol (9 $\mu g/m^3$) in the Chinese cities are similar to the levels of sulfate aerosol commonly observed in the more polluted North American (Appel et al., 1985) and European (Junge, 1983) cities.

3.4. *Nitrate*

The highest average total nitrate levels were observed in Beijing (1450 ± 320 pptmol). Changsha's average nitrate (800 ± 400 pptmol) was about half that in the northern polluted air. The northerly air at Xinglong contained far less nitrate than the others, averaging just 50 ± 20 pptmol. Continental total nitrate levels this low are seldom observed, except in remote areas (Huebert and Lazrus, 1980a) or after precipitation events in rural areas (Huebert et al., 1983).

3.5. *Ammonium*

In view of Zhao's (1985) observation that there is roughly an order of magnitude more gaseous ammonia in northern than southern Chinese air, we were surprised to find the highest average ammonium aerosol levels in Changsha (3880 ± 1690 pptmol). Concentrations in Beijing and the Xinglong haze were somewhat smaller (2800 ± 2800 and 2650 ± 760 pptmol, respectively). Their similarity to one another may be due to their common source in the Beijing area. The northerly Xinglong air was again the cleanest, with only 370 ± 40 pptmol of ammonium aerosol.

Zhao et al. (1985) report mean ammonia vapor concentrations of 44 ppbmol in Beijing and 22.8 ppbmol in Tianjin (both in the north), with only 5.17 ppbmol in Chongqing and 1.7 ppbmol in Guiyang (both in the south). It may be that the lower pH of aerosols in southern China (Zhao et al., 1985) causes a greater fraction of the available ammonia vapor to condense to aerosols, while the more basic aerosols in the north tend to keep ammonia in the vapor phase. The ammonium aerosol concentrations we encountered in the northerly flow at Xinglong were typical of very clean continental boundary layer air (Huebert and Lazrus, 1980b), while the others were typical of urban environments (Junge, 1963).

Table 3. *Averages and standard deviations of three ratios*

Location	S/N	Cat/an	Nyl/tot
Beijing	1.32 ± 0.44	4.70 ± 2.43	0.27 ± 0.20
Xinglong (north winds)	2.19 ± 0.82	2.25 ± 0.74	0.57 ± 0.06
Xinglong (west winds, haze)	1.09 ± 0.27	1.14 ± 0.27	0.18 ± 0.09
Changsha	2.67 ± 1.37	1.17 ± 0.53	0.24 ± 0.20

3.6. Calcium

The average Beijing calcium concentration (7300 ± 6100 pptmol) was 6 times that in the Xinglong haze (1230 ± 580 pptmol), and more than an order of magnitude above the other averages. The Changsha urban area averaged just 520 ± 760 pptmol, and the northerly air at Xinglong contained only 180 ± 140 pptmol of calcium. Dust from the Gobi desert and the north Chinese alkaline soils is partly responsible for the high calcium levels in the north, although in Beijing lime and cement dust are the major sources (Wang, 1985). Near our Beijing sampling site we observed the frequent manual resuspension of this dust by street-sweepers.

3.7. Sulfate/nitrate ratio

Although the molar ratio of emitted sulfur dioxide to nitrogen oxides is 1.7 in Beijing and 7.0 in Changsha, the ratio of ambient sulfate to nitrate was usually less than 1.7 in Beijing and much smaller than 7.0 in Changsha (Table 3). In Beijing it averaged around 1.3, and was only 1.1 in the Xinglong haze which presumably came from the Beijung area. It averaged 2.2 in the clean northerly winds at Xinglong, and 2.7 in Changsha.

Part of the reason why our measured ambient S/N ratios are smaller than the annual average emission ratios may be that the residential heating season had not yet begun, and the October SO_2 emissions were somewhat below the annual average. Presumably the nitric oxide emissions would also be below their peak values in October, however, since much of China's NO_x also derives from coal combustion. The decrease in the ratio from Beijing to the Xinglong haze may be due to the more rapid oxidation of NO_x to nitrate, relative to the rate of the oxidation of SO_2 to sulfate (Forrest, et al., 1981; Hov and Isaksen, 1981). It is likely that much of the SO_2 emitted in Beijing had still not been oxidized to sulfate by the time the haze reached Xinglong, while a greater fraction of the NO_x had been converted to nitrate during the transit. Thus, the ratio of sulfate to nitrate at Xinglong would be lower than the emission ratio in Beijing (1.7), because nitrogen dioxide is oxidized more rapidly than sulfur dioxide.

At Changsha, the air was much warmer and wetter than in the north, which should lead to a more rapid oxidation of the emission products to sulfate and nitrate (Hov and Isaksen, 1981). However, the observed ratio (2.7 ± 1.4) was still less than half of the annual-average emissions ratio (7.0). The low concentrations in the clean northerly air at Xinglong suggest that it may contain very few anthropogenic emissions, and would therefore not be expected to conform to China's anthropogenic emissions ratio.

It is still somewhat surprising that the ratio of sulfate to nitrate in most of the rainfall in China is much greater than the S/N emission ratio, while the measured ambient sulfate/nitrate ratio is equal to or smaller than the emissions ratio. This may be due in part to the fact that we made instantaneous local measurements, which we are now comparing to annual average regional emissions. However, 2 additional factors may also contribute to the difference between these ratios: first, much of the sulfur dioxide may simply not be converted to sulfate until it is oxidized either in the clouds which will ultimately rain it out or in rainwater which has scavenged it below cloud. The oxidation of SO_2 by peroxide in atmospheric liquid water has been proposed as a major oxidation pathway for SO2 (Richards et al., 1983; Hegg and Hobbs, 1986). This sulfur would bypass the form of sulfate aerosol, going directly from SO_2 to aqueous sulfate, thus keeping the aerosol sulfate/nitrate ratio small.

A second factor is the tendency of nitric acid to

dry deposit rapidly (Huebert and Robert, 1985), leaving less nitrate to be removed by precipitation. This nitric acid dry deposition (along with the slower oxidation of SO_2) would tend to increase the dry-air sulfate/nitrate ratio as emissions move farther downwind from their sources. This dry removal, which would be dependent on the relative amounts of nitric acid vapor and aerosol nitrate, would cause the S/N ratio to increase steadily after most of the NO_2 had been oxidized to nitrate.

Our overall hypothesis, then, is that NO and SO_2 emissions are added to low background levels of sulfate and nitrate. The sulfate aerosol/total nitrate ratio first decreases, as NO and NO_2 are oxidized to nitric acid and aerosol nitrate. When this conversion is largely complete (and the ratio has therefore reached its lowest value), the processes of SO_2 oxidation to sulfate and nitric acid dry deposition both cause the ratio to rise, until it becomes larger than the original background ratio by the time precipitation removes the balance of the material.

Although we did not follow the history of a single airmass with our measurements, we can compare the cases: the background sulfate/nitrate ratio in the clean northerly air at Xinglong was 2.2. In the presence of fresh emissions in Beijing it was only 1.3. The ratio was still smaller (1.1) in the older urban air which reached Xinglong in the haze. It is instructive to see that these instantaneous local ambient sulfate/nitrate raios vary in reasonable ways relative to Beijing's annual average emission ratio of 1.5. In the moist environment of Changsha, the ambient sulfate/nitrate ratio was higher (2.7) than in the north, which may be in part because of the larger emissions ratio (7.0) in Changsha.

4. Cation/anion rato

Table 3 also lists values for a ratio of equivalents, $(2 \times [Ca^{++}] + [NH_4^+])/(2 \times [SO_4^=] + [NO_3^-])$, which we refer to as the "cation/anion" ratio. Of course, this is not the total ratio of all cations and anions, many of which we did not measure. We are using this limited ratio as a way of determining what fraction of those strong mineral acids whose anions we did measure is likely to have been neutralized.

In Beijing, the cation/anion ratio averaged 4.7, indicating that virtually all of the nitrate and sulfate had been neutralized. There was never enough ammonium to have done all the neutralization, so calcium-containing aerosols must have played an important role. In the haze at Xinglong the ratio was only slightly greater than 1, the result of a much smaller concentration of aerosol calcium. Although the concentrations were all quite low in the clean northerly air at Xinglong, the cation/anion ratio averaged 2.25. In the cleanest samples, the amount of ammonium aerosol suggests that ammonia could have neutralized all the nitrate and sulfate with no help from calcium.

In Changsha, the cation/anion ratio still averaged just above 1, in spite of much lower concentrations of calcium aerosol than in the northern cities. Even though the concentrations of ammonia vapor are smaller in the south than in the north (Zhao, 1985), there was usually still enough ammonia present to neutralize the sulfate and nitrate in Changsha, based on the resulting concentrations of ammonium ion in the aerosol.

Because ammonium sulfate has a lower vapor pressure than ammonium nitrate (Stelson and Seinfeld, 1982), sulfuric acid will tend to preferentially scavenge ammonia vapor before nitric acid can. At Xinglong, in fact (Fig. 2), the ammonium/sulfate molar ratio was generally 2 or less in the haze and westerly air, suggesting that little or no ammonium nitrate could have formed. In the clean northerly air, however, the high ratios suggest that some organic acids may have been present to help keep ammonium ion from vaporizing.

4.1. Nylon/total nitrate ratio

In the clean northerly air at Xinglong, an average of 57% of the collected nitrate was found on the nylon filters. If this nylon-nitrate were a fair indication of nitric acid concentrations there, it would average 31 ± 11 pptv. With this low a vapor concentration, it seems unlikely that ammonium nitrate aerosol would form. Since the calcium concentrations were also very low in this air, it seems safe to assume that sampling artifacts were unimportant and that the nylon-nitrate does represent actual nitric acid vapor concentrations in the clean air at Xinglong. There appeared to be about twice as much nitric acid vapor as aerosol nitrate in this air.

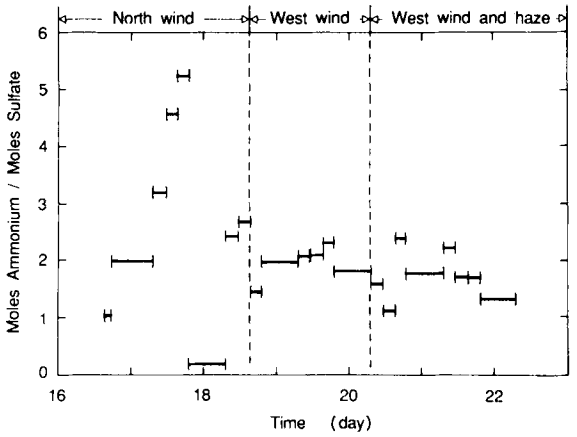

Fig. 2. Molar ammonium/sulfate ratio versus date during October at Xinglong.

We were frankly surprised to find significant fractions of the nitrate on the nylon filters in the other air masses. Large alkaline aerosol concentrations would tend to cause any incoming nitric acid vapor to condense on previously collected aerosols on the prefilter (or to condense on these same aerosols in the atmosphere itself), leaving little or no nitrate vapor to reach the nylon backup filter. But as Table 3 shows, between 18 and 27% of the nitrate was found on the nylon filter in the polluted air samples.

While we are unable to determine whether this represents a real measure of atmospheric nitric acid vapor or a sampling artifact (as from the evaporation of ammonium nitrate aerosol), it does suggest that a significant fraction of China's nitrate does exist as a vapor some of the time. One implication of this conclusion is that nitrate could then be removed by the rapid dry deposition of nitrate vapor, rather than by the slower dry deposition of nitrate aerosols. Since nitric acid vapor dry deposits more rapidly than either nitrate aerosol or sulfate (Sehmel, 1980; Huebert and Robert, 1985), this dry loss of nitrate may explain why the S/N ratio in China's precipitation is so much larger than that of its emissions.

5. Conclusions

Although some areas of China are heavily polluted by coal smoke and mineral aerosols, we sampled some very clean continental background air just a few hours drive northeast of Beijing, at the Xinglong Astronomical Observatory. Aerosol and nitric acid vapor concentrations at this site during northerly air flow were comparable with the cleanest continental sites in Europe and North America.

The sulfatre aerosol/total nitrate ratio was generally less than or equal to the annual average S/N emissions ratios of 1.5 in Beijing and 7.0 in Changsha, even though the precipitation S/N ratio is often much larger. This is probably the result of both the slow formation of sulfate aerosol from SO_2 (relative to nitrate formation from NO_x) and the rapid dry deposition of nitric acid vapor. It is likely that a substantial fraction of the SO_2 never forms aerosol sulfate, but is oxidized directly to aqueous sulfate in clouds and precipitation.

In both northern and southern China we found more equivalents of calcium plus ammonium than of nitrate plus sulfate, indicating that the strong acids had largely been neutralized. The cation/anion ratio (defined above) was greatest in Beijing, due to the high concentrations of calcium and ammonium. In southern China there was very little calcium aerosol, but generally just enough ammonium to exceed the equivalents of nitrate and sulfate.

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