Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003

Hua-Yun Xiao*, Cong-Qiang Liu

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

Abstract

Total suspended particles (TSP) were collected in 2003 to study chemical characteristics of water-soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}, Mg^{2+}) and water-soluble organic carbon (WSOC) in a karst city Guiyang, which suffers from serious acid rain problems. Concentrations of the TSP matter were 44.40–385.09 $\mu g\,m^{-3}$, closely associated with relative humidity (RH). Water-soluble matters of TSP are acidic in nature in most days of 2003 except for those in summer, in which season high pH values were observed sometimes. SO_4^{2-}, Ca^{2+} and NH_4^+ were the dominant ionic species, which accounted for 15.2%, 3.4% and 2.8% of TSP, respectively. SO_4^{2-} is the most abundant chemical component ($22.34 \pm 10.10\,\mu g\,m^{-3}$) and accounts for about 53.6% of the total mass of ions. High SO_4^{2-} levels and lower mass ratios of $[NO_3^-]/[SO_4^{2-}]$ in TSP (0.13 ± 0.06) were found because of the wide use of sulfur-containing coal. The WSOC mass concentrations varied from 1.83 to 22.44 $\mu g\,m^{-3}$, with an annual average of $5.72 \pm 3.69\,\mu g\,m^{-3}$. WSOC mass concentrations are inversely correlated with air temperature ($y = -0.14x + 5.88$, $R = 0.72$). A good linear correlation between WSOC/TSP and pH of TSP ($y = -1.79x + 14.74$, $R = 0.70$) were also found in Guiyang when pH are lower than 8. WSOC/TSP of basic TSP (pH > 8) are within the range of 1.5–3.5%. Lower mass concentrations of all water-soluble inorganic ions and WSOC were observed in rainy days relative to those in not rainy days, while their mass percentages in TSP are higher in rainy days for SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+}. It indicates that suspended matters with lower concentrations of these ions are preferentially scavenged into rainfalls.
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1. Introduction

Airborne particulate matter is a complex pollution mixture of anthropogenic and biogenic origin, consisting of both direct emissions and secondary formation within the atmosphere. In most cases, sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) and water-soluble organic carbon (WSOC) are the dominant chemical species of water-soluble matters in aerosol particles (e.g. Cheng et al., 2000; Kendall et al., 2001; Fang et al., 2002; Harrad et al., 2003). These species are formed in the atmosphere through the direct emissions of SO_2, NO_x and NH_3 gases. Equilibrium between gas and particle species was described using models (Wexler and Seinfeld, 1991) or stable isotope techniques (Xiao and Liu, 2004).

Atmospheric aerosols influence many atmospheric processes including visibility variations and cloud formation (Pueschel et al., 1986; Sloane et al., 1991), and play a major role in acidification of rainfalls and affect climate (Charlson et al., 1992). Aerosol particles

*Corresponding author. Fax: +0086 851 5891609.

E-mail address: xiaohuayun@lycos.com (H.-Y. Xiao).

have been proven to produce the major impacts on human health (Pagano et al., 1996; Wilson and Suh, 1997). Additionally, WSOC in aerosols is increasingly concerned with implication on nucleation during rain and cloud growth, although water-soluble inorganic salts such as sulfate has been taken by classical theory as major factor of cloud nucleation. Due to their high water-solubility, WSOCs have the potential to modify the hygroscopic properties of atmospheric particles (Saxena et al.,1995; Shulman et al.,1996).

Guiyang is one of the most seriously polluted cities in all China with exceptionally high levels of ambient gaseous SO_2. The average annual SO_2 concentration in the city, for instance, was about $300\,\mu g\,m^{-3}$ in 1996. The level is about six times above the WHO annual guideline of $50\,\mu g\,m^{-3}$. As one of the two-control zone for SO_2 and acid rain in China (pH of most rainfalls is lower than 5 in the city, Lei et al., 1997), several international aids have been provided to tackle the air pollution of the city. For example, United Nations Development Program (UNDP) began in 1996, Japan–China Environmental Development Model Cities Plan in 1999, and so on. In 2003, only $87\,\mu g\,m^{-3}$ of SO_2 concentration was determined in Guiyang (Table 1). Studies on chemical characteristics in wet deposition between 1984 and 2001 showed that since 1987, Ca^{2+} and SO_4^{2-} concentrations had decreased 30% and 50%, respectively, because of the banning of coal combustion (Galloway et al., 1987; Xiao and Liu, 2002). All these showed us a favorable turn for SO_2 concentrations and chemical composition in wet deposition of Guiyang after these year's efforts. Unfortunately, although some studies on total suspended particles (TSP) have also been carried out during these years, detailed data available relative to aerosols of the city are very scarce, especially those reported in scientific journals. Due to the important roles of TSP as discussed above, systematic studies on TSP of the city are needed. To our knowledge, there have been no published studies conducted to investigate the levels of aerosol particulate matters and their chemical, physical properties in Guiyang.

In this study, the first TSP were systematically collected during the year 2003 at the karst area in Guiyang with the aim of investigating the ambient suspended particles, related chemical composition and the impacts of meteorological conditions.

2. Experimental

2.1. Area description

Guiyang (26.34N, 106.43E) is capital of Guizhou Province, with more than 1.34 million urban population. The city lies in a karst basin at 1071 m (3514 ft) on the Nanming River and is surrounded by mountains.

Annual average precipitation of the city is 900–1500 mm and concentrated in summer; the average relative humidity (RH) is about 86 percent.

Guiyang City is an important industrial base in China, with pillar industries including electric power, ferric, steel, phosphorus and rubber. Twenty percent of the aluminum of the country is processed in Guiyang and one of the three largest phosphorus mines is located in the city. The major air pollution source in Guiyang is coal combustion (high sulfur coal of 1.86%; Ni, 1997), which accounts for over 90% of energy consumption of the whole city. 1n 1997, most of small-sized mills and mines as well as workshops with heavy pollution have been forced to shut down and some heavy polluting industries were relocated from downtown to suburbs. And >90% of the city residents have replaced coal by natural gas now. Owing to several seasons, large industrial pollutant emissions still exist, for instance, from Guizhou steel plant.

Although air quality (TSP, SO_2, NO_x) tended to be better than before in Guiyang from 1996 to 2003 (Fig. 1), air pollution constitutes a pressing problem, which is mainly caused by coal-fueled industries. For example, in 2002, SO_2 produced in the city was about 0.31 million tons, 67.7% of which came from industries. The total amount of emission of industrial ashes and powders was 0.10 million tons within 2002 in Guiyang (Guiyang Environmental Protection Bureau, 2002).

2.2. Sample collection and analysis

TSP from 1 m above a building (5 m) roof's surface was collected on glass fiber filters (190 mm × 240 mm, made by Laoshan Institute for Electronic Equipment, China) using a special high-flow rate ($1.05\pm3\%$ $m^3\,min^{-1}$) sampler (KC-1000, made by Laoshan Institute for Electronic Equipment, China). The sampling site, located within the Institute of Geochemistry, CAS,
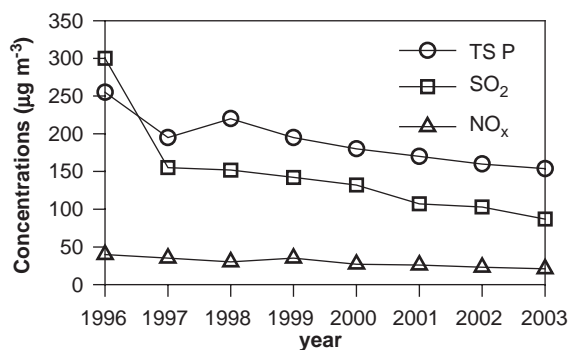

Fig. 1. Annual variations of TSP, SO_2 and NO_x in Guiyang from 1996 to 2003. Data except those of 2003 (this study and unpublished data of Xiao) were cited from Guiyang Environmental Protection Bureau (2002).

belongs to a typical urban area and lies in the southeast of the downtown of Guiyang. Prior to sampling, the glass filters were pre-baked at 500 °C for 2 h in order to eliminate nitrogen species. The sampling time was nominally 47.5 h with sampling starting at 5:30 p.m. In 2003, 182 samples in total were collected (2 days one sample). Under high-volume sampling conditions, the glass fiber filters are relatively efficient and have recoveries of more than 95% for Cl^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} and 90% for NH_4^+, NO_3^- and WSOC. The field blank was also measured by exposing the filters in the sampler without drawing air. The blank test did not show a significant change for 4 weeks.

After sampling, filters were placed in pre-cleaned 50 ml bottles, along with 20 ml of ultrapure deionized water (Milli-Q), and sonicated in a water bath for 30 min. After passing through glass filters (Whatman GF/F), the filtrates were determined for pH with a pH meter (HI9024C, made by Hanna Company in Italy). pH of the blank samples was about 6.5. Each filtrate was stored at 4 °C in a clean brown plastic bottle for anion and cation determination.

Anions in the samples were measured later by high-performance liquid chromatography within 12 h, and cations by atomic absorption spectrometry after acidification with HCl. Ammonium concentrations were determined by spectrophotometry after treatment with Nessler's reagent. The limits of detection were less than 0.02 $\mu g\,m^{-3}$ for anions and 0.005 $\mu g\,m^{-3}$ for cations. The quality assurance and control were routinely carried out by using Standard Reference Materials for Water Samples (GBW) produced by National Research Center for Certified Reference Materials. NO_3^- and SO_4^{2-} of GBW(E)080416 (NO_3^-) and GBW(E)080412 (SO_4^{2-}) were determined to within $\pm 5\%$, Ca^{2+} of GBW(E)080411 to within $\pm 2\%$ and NH_4^+ of GBW(E)080420 to within $\pm 5\%$. WSOC was measured using a thermal–optical carbon analyzer (Elementar High TOC II, made in Germany). The limit of detection of WSOC was less than 0.05 $\mu g\,m^{-3}$.

Expressed as a percent of the mean sample concentrations, measured blanks were between 5% and 10% for Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and WSOC. NH_4^+ and NO_3^- were not determined during blank test while highest blank values were observed for K^+ and Na^+ (mainly from filters), which were typically 50–80% of the respective mean sample values. Blank values were subtracted from sample determinations when they were < 10% of sample concentrations.

Surface meteorological parameters including RH, temperature and rainfall were obtained from Guizhou Meteorological Bureau.

3. Results and discussion

3.1. Mass concentrations of TSP

Mass concentrations of TSP matters are 44.40–385.09 $\mu g\,m^{-3}$, with a median of 153.55 $\pm$ 64.16 $\mu g\,m^{-3}$, within the range of the World Health Organization (WHO) regulation limits (150–230 $\mu g\,m^{-3}$). As showed in Fig. 1, annual mass concentration of TSP was lower in 2003 relative to those in 1996–2002 because several laws had been enacted to constrain the coal use since 1996. Although domestic coal use has been replaced with natural gas by > 90% of the city residents, industrial use of the biggest contributors to TSP (~70%) has not completely been forbidden yet. And when compared to the relevant values measured at other sites in China, the TSP concentrations found in this work were relatively lower. For example, in Xi'an, Northwest China, TSP varied from typical levels of ~200–400 $\mu g\,m^{-3}$ to higher wintertime values of ~800 $\mu g\,m^{-3}$ (Zhang et al., 2002).

The highest TSP concentration (385.09 $\mu g\,m^{-3}$) in Guiyang occurred on 24 December and the lowest (44.40 $\mu g\,m^{-3}$) on 3 February, which were closely associated with RH (Fig. 2). The positive peak values of TSP concentrations almost occurred on the day when
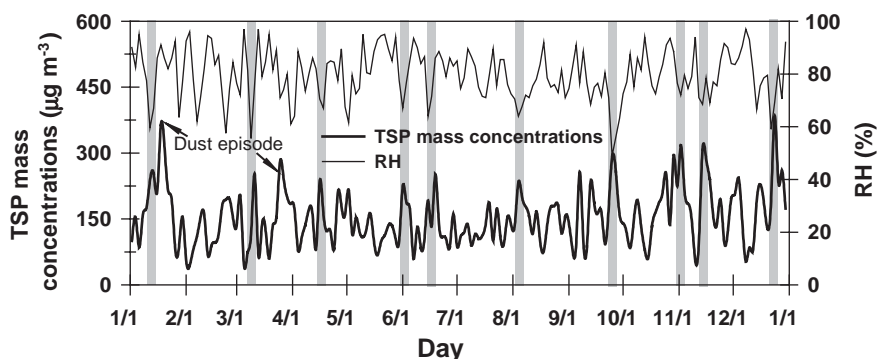

Fig. 2. Showing the inverse correlation between TSP mass concentrations and RH.

RH negative peak values were found. Since RH is usually higher than 80% throughout the year 2003 in Guiyang, particles are expected to be wet and particle–particle interactions between the collected particles occurred. Aggregation of fine particles due to particle–particle interactions would obviously enhance the deposition rate of TSP in those days with higher RH and thus caused more TSP losses. On the other hand, the hygroscopic behaviors of aerosol particles would also alter the size distribution of aerosols in the atmosphere. It is well known that aerosol particles are able to absorb water and grow with increasing RH (e.g. Svenningsson et al., 1994; Chen et al., 2003). The increases in particle sizes due to the hygroscopic growth would also lead to enhanced deposition of TSP during higher RH days.

3.2. Water-soluble inorganic ions

3.2.1. Mass concentrations and mass percentages

In this study, six major water-soluble inorganic components were detected (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}, Mg^{2+}) (Table 1), of which SO_4^{2-} is the most abundant chemical component ($22.34 \pm 10.20\,\mu g\,m^{-3}$). SO_4^{2-} accounts for about 53.3% of the total mass of ions and $15.2 \pm 4.9\%$ of TSP mass. The abundance of SO_4^{2-} could be related to high concentrations of SO_2 (Fig. 1), which are likely due to higher coal consumption in Guiyang combined with poor dispersion. Of all the other five inorganic species, Ca^{2+} had the highest concentrations of $5.29 \pm 2.68\,\mu g\,m^{-3}$, $3.81 \pm 1.64\,\mu g\,m^{-3}$ for NH_4^+, $3.03 \pm 2.48\,\mu g\,m^{-3}$ for NO_3^-, $0.89 \pm 0.86\,\mu g\,m^{-3}$ for Cl^-, and $0.60 \pm 0.33\,\mu g\,m^{-3}$ for Mg^{2+}. The typical crustal components (Ca^{2+}, Mg^{2+}) accounted for a mean of $3.8 \pm 0.8\%$ of the TSP mass, whereas the anthropogenic species, such as SO_4^{2-}, NH_4^+, NO_3^- reached $20.0 \pm 6.7\%$ of the bulk TSP. The high mass percentages of anthropogenic species evidenced a high industrial contribution with respect to the typical urban emissions.

The peaks of mass concentrations of Cl^-, SO_4^{2-}, NH_4^+ and Ca^{2+} were presented on 18 January (4.79, 65.33, 7.32 and $16.21\,\mu g\,m^{-3}$, respectively). This can be explained with the higher TSP mass ($363.6\,\mu g\,m^{-3}$) collected on that day, which was attributed to an occasional dust storm episode. Not the same as these ions, NO_3^- and Mg^{2+} showed highest concentrations on 26 December ($15.36\,\mu g\,m^{-3}$) and on 27 September ($2.17\,\mu g\,m^{-3}$), respectively, in which days higher TSP mass concentrations were also observed.

Table 2 shows the correlation coefficients among the mass concentrations of water-soluble inorganic ions. Good correlations between each other of SO_4^{2-}, Ca^{2+} and NH_4^+ were found in Guiyang, indicating that there existed forms of $(NH_4)_2SO_4$ and $CaSO_4$ in TSP. It has also been proved by that equivalent concentration ratio of $(NH_4^+ \times 2 + Ca^{2+})/SO_4^{2-}$ is 1.03. The correlation between NH_4^+ and NO_3^- revealed existence of NH_4NO_3, while that between Ca^{2+} and Mg^{2+} suggested a common source.

Lower mass concentrations are observed for all the water-soluble inorganic ions except Mg^{2+} in rainy days relative to those in not rainy days, while the mass percentages in TSP were higher in rainy days for SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+} (Table 3). The proposed reason is that suspended aerosol particles with lower concentrations of these ions are preferentially scavenged into

Table 2
Matrix of correlation coefficients (R) among the water-soluble inorganic ions ($n = 182$)

	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}
Cl^-	0.62	0.51	0.40	0.63	0.39
NO_3^-		0.69	0.62	0.56	0.26
SO_4^{2-}			0.75	0.75	0.57
NH_4^+				0.41	0.14
Ca^{2+}					0.62

Table 1
Mass concentrations and mass percentages of water-soluble components in TSP of 2003

	TSP	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	WSOC
Mass concentrations ($\mu g\,m^{-3}$)								
Mean	153.55	0.89	3.03	22.34	3.81	5.29	0.60	5.72
Min.	44.40	0.08	0.10	4.48	0.40	0.68	0.12	1.83
Max.	385.09	4.79	15.36	65.33	7.32	16.21	2.17	22.44
SD	64.16	0.86	2.48	10.20	1.64	2.68	0.33	3.69
Mass percentages in TSP (%)								
Mean		0.58	1.98	15.19	2.79	3.43	0.40	3.74
Min.		0.05	0.08	5.07	0.42	3.12	0.18	1.49
Max.		2.53	6.57	29.90	9.52	2.99	1.14	9.61
SD		0.42	1.11	4.85	1.51	0.81	0.15	1.41

rainfalls, and thus rendering the remaining particles depleted in these water-soluble components. It indicates that SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+} tends to associate more in the fine particle mode which have a longer residence time in the atmosphere than coarse particle mode.

The sulfur content of coal burned at Guiyang (stationary sources) is as high as 1.86% (Ni, 1997), while sulfur in gasoline and diesel fuel is about 0.12% and 0.2% (by weight), respectively (Kato, 1996). And NO_x of mobile sources is an important contributor to NO_3^- in aerosols. The mass ratio of $[NO_3^-]/[SO_4^{2-}]$, therefore, has been used as an indicator of the relative importance of stationary vs. mobile sources of sulfur and nitrogen in the atmosphere (Arimoto et al., 1996; Yao et al., 2002). Arimoto et al. (1996) ascribed high $[NO_3^-]/[SO_4^{2-}]$ mass ratios to the predominance of mobile source over stationary source of pollutants. In Guiyang, the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ in TSP ranged 0.01–0.38 (averaging 0.13 ± 0.06), much lower than that reported by Huebert et al. (1998) (0.3–0.5), suggesting that stationary source emissions were more important than the vehicle emissions in the area because of the industrial use of high sulfur coal existed yet.

3.2.2. Seasonal variation

The seasonal variation for water-soluble ionic components is showed in Fig. 3. There is clear seasonal

Table 3
Mass concentrations and mass percentages of water-soluble components in TSP in rainy and not rainy days of 2003

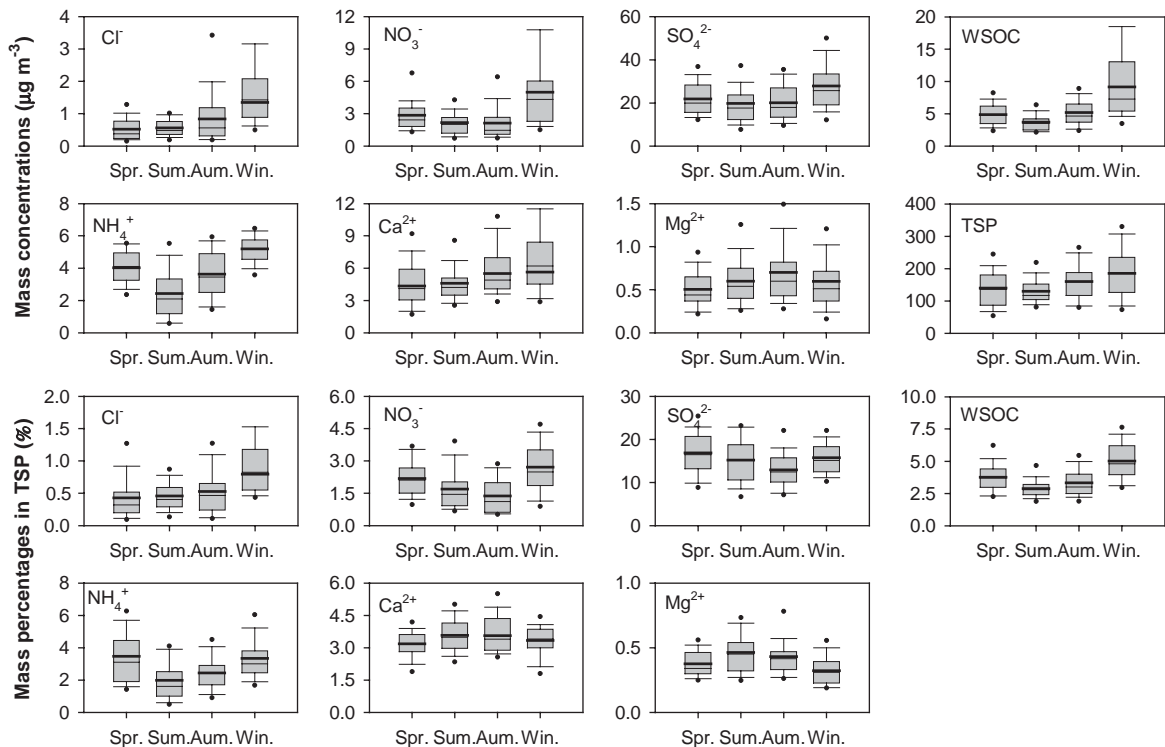|		n	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	WSOC	SUM
Concentrations ($\mu g\,m^{-3}$)	Rainy	115	0.92 ± 0.82	3.09 ± 2.42	22.02 ± 10.34	3.72 ± 1.59	5.04 ± 2.72	0.57 ± 0.30	5.26 ± 3.42	—
	Not rainy	67	2.01 ± 1.20	9.60 ± 1.60	29.18 ± 10.66	5.83 ± 0.18	6.90 ± 4.46	0.53 ± 0.36	15.19 ± 2.60	—
Percentages in TSP (%)	Rainy	115	0.7 ± 0.4	2.2 ± 1.1	16.4 ± 4.6	3.1 ± 1.6	3.6 ± 0.8	0.4 ± 0.1	3.8 ± 1.5	29.2 ± 1.2
	Not rainy	67	0.9 ± 0.2	4.0 ± 0.6	12.3 ± 0.0	2.7 ± 0.5	2.8 ± 0.6	0.2 ± 0.1	6.3 ± 0.9	30.1 ± 7.5

Fig. 3. Seasonal variations of mass concentrations (a) and mass percentages (b) of water-soluble components in TSP of 2003 in Guiyang. The boundary of the box indicates the 25th and 75th percentile. The thin and thick lines within the box mark the median and the mean, respectively. Whiskers above and below the box indicate the 90th and 10th percentiles.

patterns within 2003 for both mass concentrations and mass percentages for all the water-soluble inorganic ions in TSP. NH_4^+, NO_3^- and SO_4^{2-} showed higher mass concentrations and mass percentages in winter, and lower in summer. The same seasonal variation of NO_3^- was also observed in Qingdao (China), which was attributed to gas-to-particle conversion depending on the ambient temperature (Hu et al., 2002). Because SO_4^{2-} is more associated with ambient gaseous SO_2, the higher levels of SO_4^{2-} in winter are likely due to increased coal consumption during the heating season. The lower values of NH_4^+ in summer might be closely associated with the higher pH values of TSP (discussed below).

Ca^{2+} and Mg^{2+} did not show the same seasonal variations as those of NH_4^+, NO_3^- and SO_4^{2-}, indicating that they are of different sources. Higher mass percentages of the two elements in TSP occurred in summer and autumn relative to those in winter and spring (Fig. 3). Because Ca^{2+} and Mg^{2+} are the typical crustal elements, the largest contributor might be the airslake of the earth's surface, which is mainly dependent on air temperature and rainfalls (June–September are hot and rainy months in Guiyang). Although mass concentrations of Ca^{2+} also showed higher values in

winter and lower values in summer, this may be more associated with the corresponding TSP mass colleted in these seasons. As discussed above, mass percentages of Ca^{2+} and Mg^{2+} in TSP were higher in rainy days than in not rainy days. It also evidenced the consistence of the seasonal variations of Ca^{2+} and Mg^{2+} with that the airslake of the earth's surface was strong in summer and autumn than in winter and spring.

The mass ratios of $[NO_3^-]/[SO_4^{2-}]$ are higher in cold seasons than in hot seasons, with the maximum in December, the coldest month in Guiyang (Fig. 4a). One possible cause is that ammonium nitrate volatilized at higher air temperature and thus made the shift in the ratios. The phenomena have also been reported by other researchers (e.g. Hu et al., 2002).

3.3. pH of TSP

As shown in Fig. 4b, pH values of most samples are slightly less than the blank (6.5) and hence water-soluble matters in TSP are weakly acidic in most days of 2003 in Guiyang. This can be explained with ion balance calculation. The ion balance expressed by the equivalent concentration ratio of cation sum–anion sum
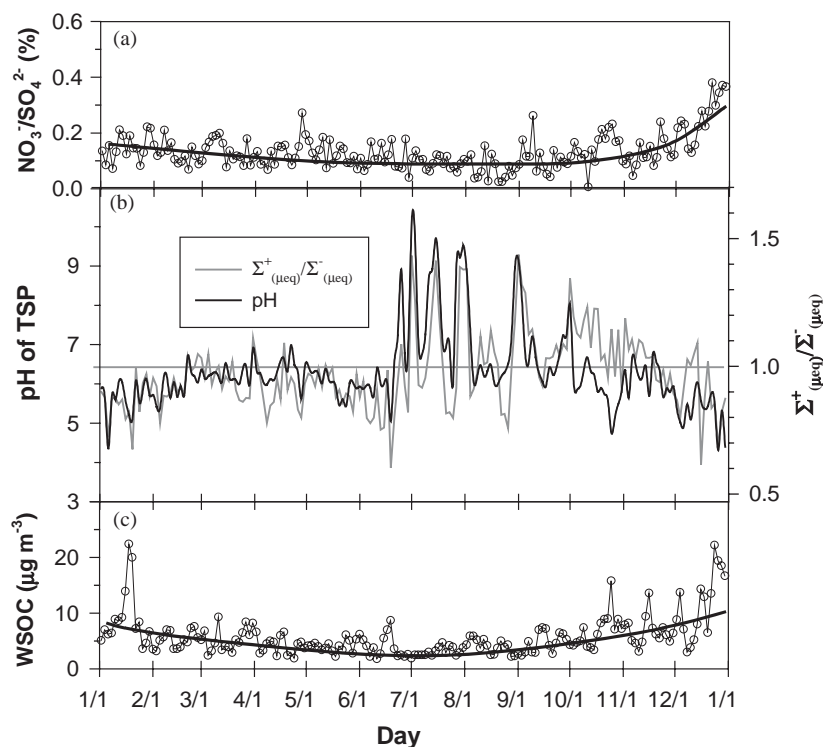

Fig. 4. Temporal variations of NO_3^-/SO_4^{2-} (a), pH of TSP and equivalent concentration ratios of cation sum to anion sum $\left[\Sigma_{(\mu eq)}^+/\Sigma_{(\mu eq)}^+\right]$ (b) and WSOC (c).

$\left[\Sigma^+_{(\mu eq)} / \Sigma^-_{(\mu eq)} \right]$ was calculated from values of these major ion species (excluding K^+ and Na^+). The equivalent concentration ratio curve agreed very well with that of pH values (Fig. 4b), indicating pH values determined were credible. The mean ratio of cation sum–anion sum ranges from 0.60 to 1.44 (mean = 0.97, SD = 0.15, $n = 182$). Since K^+ and Na^+ were not determined in this study, the mean ratio could be expected to be at a higher level (close to 1).

Higher pH values were found in summer (June–September), with the highest value more than 10. It is well known that low pH values of aerosols result from acidic matters such as sulfate, nitrate and carboxylic anions, whereas basic water-soluble elements such as NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+ and so on resulted in the increase of pH values of water-soluble matters. In Guiyang, pH values of water-soluble matters are more dependent on SO_4^{2-}, Ca^{2+} and NH_4^+, which showed much higher equivalent concentrations than Cl^-, NO_3^- and Mg^{2+}. During summer days with higher pH values of aerosols, the equivalent concentration ratios of cation sum–anion sum were much higher than 1. For instance, on 1 July, equivalent concentration of SO_4^{2-} was $0.186\,\mu eq\,m^{-3}$, while those of Ca^{2+} and NH_4^+ were 0.270 and $0.022\,\mu eq\,m^{-3}$, respectively, with a ratio of cation sum–anion sum about 1.4. Basic components are not completely neutralized by acid components and thus the sample showed a much higher pH value (10.1).

3.4. WSOC

The WSOC mass concentrations in TSP of Guiyang varied from 1.83 to $22.44\,\mu g\,m^{-3}$, with an annual average of $5.72 \pm 3.69\,\mu g\,\mu m^{-3}$, lower than those determined in London ($7.6 \pm 3.0\,\mu g\,m^{-3}$ for St Paul's and $6.3 \pm 2.5\,\mu g\,m^{-3}$ for Bounds Green; Kendall et al., 2001). WSOC is the second abundant component in TSP and accounts for about 13.6% of the total water-soluble component mass and $3.7 \pm 1.4\%$ of TSP mass (Table 1). WSOC in aerosols usually have several different sources, including primary emissions from biomass burning and fossil fuel combustion, as well as photochemical oxidation of organic precursors of both anthropogenic and biogenic origin (Chebbi and Carlier, 1996). Because Guiyang is a relatively small city relative to London, organic matters of anthropogenic origin (especially from vehicles) might be less than those in London. This should be responsible for the lower WSOC concentrations observed in Guiyang.

The peak of mass concentrations of WSOC was also presented on 18 January ($22.44\,\mu g\,m^{-3}$) as those of most inorganic ions because of the higher TSP mass ($363.6\,\mu g\,m^{-3}$) collected at the same time. The mass percentage in TSP, however, was not higher on that day, only 6.2%, lower than that on 1 January (7.4%), on which day a much lower mass concentration of WSOC ($6.2\,\mu g\,m^{-3}$) was observed.

Similar variation trends between rainy days and not rainy days as those of NO_3^- were observed for both WSOC mass concentrations and mass percentages (Table 3). It maybe suggests that particles easy to wet deposit are enriched in WSOC. Because wet precipitation concentrated in summer, the season showed lowest concentrations of WSOC in Guiyang. This has been evidenced with the seasonal variations of both mass concentrations and mass percentages of WSOC as discussed below.

Both mass concentrations and mass percentages of WSOC in TSP were lower during summertime ($3.71 \pm 1.49\,\mu g\,m^{-3}$ and $2.7 \pm 0.7\%$) than during wintertime ($9.16 \pm 5.20\,\mu g\,m^{-3}$ and $5.0 \pm 1.5\%$) (Figs. 3 and 4c). Seasonal variations of WSOC mass concentrations were also observed in London (Kendall et al., 2001). Nevertheless, contrary to that in this study, although decreases of absolute mass concentrations of WSOC were also found in London in summer and autumn, the WSOC mass percentages in TSP increased during these periods. Kendall et al. (2001) attributed the seasonal disparity to the different sources being important at different times of the year. Additionally, a study carried out at the Ireland's west coast reported (Kleefeld et al., 2002) that WSOC showed highest concentrations ($> 266\,ng\,m^{-3}$) during summertime and lowest concentrations ($148\,ng\,m^{-3}$) during wintertime due to enhanced wet depositional losses. As listed in Table 3, one-third of WSOC in TSP over Guiyang city had been wet deposited during summertime and this caused 50% decrease in WSOC mass in TSP.

Although the higher precipitation rate during summertime in Guiyang might be a significant reason for the lowest concentrations of WSOC, a good linear correlation was found between WSOC/TSP and air temperature ($y = -0.14x + 5.88$, $R = 0.72$) (Fig. 5a). It suggests that effects of air temperature on WSOC/TSP cannot be overlooked. The abundance of WSOC in winter could also come from larger emissions of organic C and root (Decesari et al., 2002), which are likely due to increased coal consumption during heating period.

A good linear correlation between mass percentages of WSOC (WSOC/TSP) and pH of TSP ($y = -1.79x + 14.74$, $R = 0.70$) was also found when pH are lower than 8 (Fig. 5b), suggesting that WSOC concentrations are strongly dependant on pH of TSP. WSOC percentages in basic TSP (pH > 8) are within the range of 1.5–3.5%. A thermographic method by Iinuma et al. (2004) for the determination of TOC showed an increase of particle phase organics by 40% for the experiments with higher acidity, indicating that particle acidity of atmospheric aerosols plays an important role in the heterogeneous reaction of secondary organic aerosols (SOAs). A similar effect of aerosol acidity on SOA
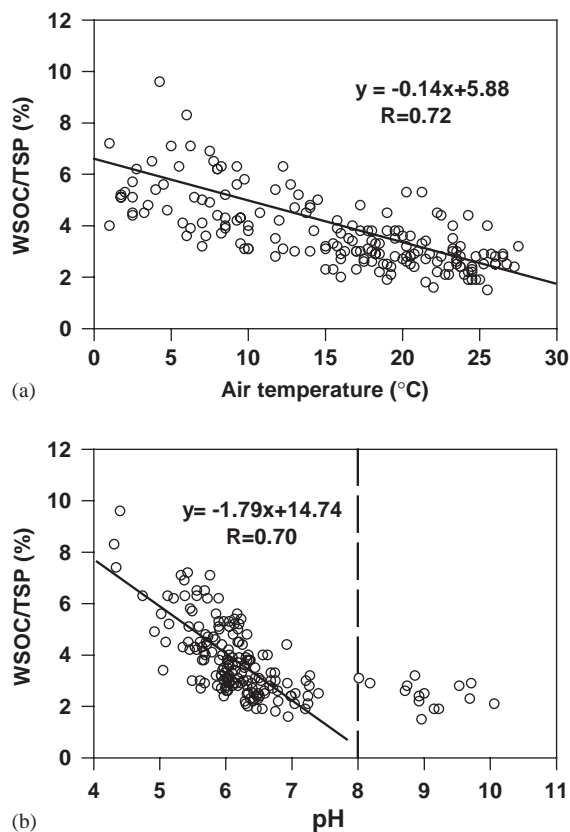
Fig. 5. Showing the correlation between WSOC/TSP and air temperature (a) or pH of TSP (b) in Guiyang. Samples with pH > 8 are not included in the regression analysis.

yields in different reaction systems was shown very recently (Jang et al., 2003a,b; Czoschke et al., 2003). Therefore, the correlation between WSOC/TSP and pH of aerosol particles should be closely associated with the dependence of aerosol acidity on WSOC yields.

4. Conclusions

This study has investigated the ambient suspended particles, related chemical composition and the impacts of meteorological conditions in Guiyang, SW China. Some principal conclusions that can be drawn from the study are presented as follows:

TSP mass concentrations decreased about 40% in 1996–2003 and only $153.55 \pm 64.16 \, \mu g \, m^{-3}$ was determined in 2003, within the range of the WHO regulation limits. RH was a controlling factor of TSP mass concentrations. Water-soluble matters of TSP showed

weak acidity except for those in summer, in which season higher pH values were observed.

SO_4^{2-}, Ca^{2+}, NH_4^+ is the most abundant inorganic ions in TSP. Good correlations among them and the equivalent concentration ratio of $(NH_4^+ \times 2 + Ca^{2+})/SO_4^{2-}$ (1.03) suggested that dominating existing forms of them in TSP are probably $(NH_4)_2SO_4$ and $CaSO_4$. High SO_4^{2-} levels and lower mass ratios of $[NO_3^-]/[SO_4^{2-}]$ in TSP (0.13 ± 0.06) were found due to the wide use of sulfur-containing coal in Guiyang.

Almost all water-soluble inorganic ions showed similar variation trends of mass concentrations between rainy days (lower values) and not rainy days (higher values). Mass percentages in TSP of rainy days, however, were found higher for SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+} relative to those in not rainy days, indicating that they tended to associate more in the fine particle mode which have a longer residence time in the atmosphere than coarse particle mode.

All water-soluble components in TSP displayed clear seasonal cycles. NH_4^+, NO_3^- and SO_4^{2-} showed higher mass concentrations and mass percentages in winter, and lower in summer, while Ca^{2+} and Mg^{2+} exhibited strong inverse seasonal cycles. This is due to their different sources: the former three ions are anthropogenic species, dependant on the coal consumption in Guiyang, while the latter two are typical crustal components, which are more associated with meteorological parameters such as air temperature and rainfalls.

Except for SO_4^{2-}, WSOC is the dominant water-soluble component in TSP, accounting for 3.7% of the total mass of water-soluble species. Both mass concentrations and mass percentages of WSOC in TSP were lower in rainy days (summer) relative to those in not rainy days (winter) due to enhanced wet depositional losses. Good linear correlations were found between WSOC/TSP and air temperature ($y = -0.14x + 5.88$, $R = 0.72$) or pH of TSP ($y = -1.79x + 14.74$, $R = 0.70$) when pH are lower than 8. It suggested that WSOC mass percentages are strongly dependant on air temperature and pH of TSP.

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