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Sulfur dioxide-hydrogen peroxide relationships and acidification of precipitation in Guiyang area—a case study*

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Abstract—The concentrations of gas phase SO_2, O_3 and chemical composition of sequential rainwater samples were measured on 6/11/88 to 6/28/88 at some sites of Guiyang area. S (IV) was present in great excess of H_2O_2 in rainwater samples collected at residential sites of the city corresponding to high level of gas phase SO_2. Considerable H_2O_2 in rainwater samples was observed in background air at suburbs. The evidence that clean rainwater samples were collected at 20km away from the city in 6/18/88 precipitation event revealed that the major process of acidification of the rain in the high polluted areas was below-cloud scavenging of trace gases. From a simulation calculation it was found that the rate of oxidation of S(IV) by O_3 and by Mn^{2+}, Fe^{3+} catalytic in high pH rainwater is significant, but for low pH the major SO_4^{2-} is produced by the reaction of S (IV) with H_2O_2.

Keywords: hydrogen peroxide; sulfur dioxide; acid rain; below-cloud scavenging.

INTRODUCTION

Sulfur dioxide, emitted into the atmosphere principally from combustion of sulfur-containing fuels, is the precursor of atmospheric sulfate aerosol and sulfuric acid that constitute a major component of "acid rain". The processes of trace gases absorption and aerosol scavenging by hydrometeors followed by aqueous phase reactions are responsible for the acidification of rain. All of these processes can occur either in-cloud or below-cloud. The contribution of in-cloud and below-cloud processes influencing the chemical composition of rain varies from event to

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event. The contribution of below-cloud scavenging of trace gases and aerosol to chemical composition of rainwater has been studied in field experiments in China (Xiong, 1987; Zhao, 1988). The key piece of field evidence of the below-cloud scavenging of trace gases is that the spatial distribution of acid rain is, in most cases, similar to that of ambient SO_2, i.e., high acidity is observed in urban areas with high SO_2 pollution, whereas SO_2 pollution is not serious and low acidity is seen in precipitation in suburban and rural areas.

SO_2 is not greatly dissolved in rainwater of Southwestern China (pH 3.5 to 5.5), but its oxidation product, H_2SO_4 is. The oxidation of gaseous SO_2 to aqueous H_2SO_4 is highly favored thermochemically in the presence of O_2 or stronger oxidants (Schwartz, 1984). One of the major issues in below-cloud scavenging studies concerns the identification of aqueous phase reaction pathways for the oxidation of SO_2. Kinetic evaluations indicate that although O_2 and O_3 can induce appreciable oxidation of SO_2 under some below-cloud scavenging conditions, H_2O_2 is thought to be the principal oxidant of SO_2 at representative pH values (Durham, 1981; Shen, 1989A). Atmospheric H_2O_2 is produced mainly by the recombination of HO_2 radicals, which are formed through NO to NO_2 conversion, O_3 formation and radical chain reactions involving the OH and organic peroxy radicals (RO_2) formed from the hydrocarbons and their oxidation products (Calvert, 1985). The average ratio of SO_4^{2-}/NO_3^- in precipitation of Southwestern China was 5:1 (Zhao, 1988), whereas it was 1:1 in Northwestern United States (Lee, 1986B). The NO_x level in Southwestern China is lower than that in Northwestern United States, it might be caused by different energy structure. The gaseous and aqueous chemistry for oxidation of SO_2 in Southwestern China might be different from that in other areas. There have been only a few measurements of oxidants species in this area. So, the contribution of the aqueous H_2O_2-S (IV), O_3-S(IV) reactions to oxidation of SO_2 for acidification of rain remains highly uncertain.

This paper addresses the $SO_2-H_2O_2$ relationship and acidification of precipitation in Guiyang area. Chemical composition of precipitation at the ground and gaseous SO_2, O_3 were measured simultaneously. These measurements provide information for H_2O_2, O_3 regarding their temporal and spatial variabilities, their abundance with respect to SO_2, and their possible sources. A numerical simulation was performed to address the hypothesis that below-cloud scavenging of trace gases for acidification of rain would play an important role in the high polluted area and its plume.

EXPERIMENTAL

Measurements reported here were conducted in Guiyang area in July 1988. Three sites were elected to collect rainwater samples. One site was at residential area of the city, another was located at Guiyang airport which is about 20 km away from the city in the southwestern direction, the third one was located at about 20 km away from the city but in opposite direction to the airport.

The sequential rainwater samples were collected in polyethylene containers. The collector was thoroughly cleaned by rinsing with deionized water before it was set up. The collector was placed at the top of a high building at center of the city or a spot in an open field well removed from buildings, trees and plants, so as to avoid causal contamination at the airport and the third site. To minimize the contribution of dry deposition, the collector was not set up until rain had actually started to fall. Polyethylene bottles were used to store samples for subsequent chemical analysis.

The duration of sample collection varied, depending on the rainfall intensity, because of volume requirements for chemical analysis. Typically, the duration of the sample collection was half hour, except in period of low rainfall intensity for which the maximum sampling time was up to 3 hours.

The concentration of total peroxide (hydrogen peroxide plus organic peroxides) of the rainwater samples was determined by enzyme-fluorescence method (Lazus, 1985; Kok, 1986; Kelly, 1985; Shen, 1989B). Briefly, 1 ml p-hydroxyphenylacetic acid (PHOPAA) reagent was added to 10 ml of rainwater (Kelly, 1985; Shen, 1989B). Fluorescent dimer species which were stable for more than 10 days were formed by the oxidation of PHOPAA by H_2O_2 (and/or organic peroxides), catalyzed by the enzyme horseradish peroxidase. The sample was stored at 0°C in Dewar ice bottle until analysis in central laboratory. The fluorescence intensity was directly proportional to the total peroxide concentration of the sample. The response of the measuring system was linear over the concentration range tested, most of time, 0.02 to 20 μmol/L, 0.02 μmol/L being the limit of detection (LOD). When the concentration of H_2O_2 was higher than 20 μmol/L, the sample was diluted with a mixture of PHOPAA reagent and deionized water, so that the relative variance remained the same because of propagation of the error.

The concentration of S(IV) in rainwater samples was determined by West-Gaeke method. 1 ml 0.4 mol/L tetrachloromercurate was added to 10 ml rainwater sample. The sample was kept at 0°C in a Dewar ice bottle until analysis in a central laboratory.

The ionic species were measured in a central laboratory of Guiyang. H^+ was calculated from pH (10^{-pH}) which was measured by pH meter, model PHS-2 made in China. SO_4^{2-}, NO_3^-, Cl^-, K^+, Na^+ and NH_4^+ were measured by ion chromatography, Dionex Model 16. Mn^{2+}, Fe^{3+} was measured by inductively coupled plasma atomic emission spectroscopy.

Real-time measurements of SO_2 and O_3 were performed using commercial instruments. SO_2 was measured by UV fluorometer (Kimoto Inc. Osaka, Japan) or Coulometer (Model KZL-SO_2, made in China) continuously. The LOD of SO_2 for UV fluorescence was 1 ppbv, while that for Coulomb was 0.02 mg/m^3 (about 7 ppbv) nominally, but carefully handing in clean air measurements, it can be as low as 0.01 mg/m^3.

Ozone was measured by using commercial UV absorption instrument (8810 model, Monitor Lab.) with zero and standard gas (say 100 ppbv) built-in. Every midnight the instrument checked the zero and standard gas for each 10 minutes automatically. LOD for measurement of O_3 was 1 ppbv.

The signals of O_3 and SO_2 were recorded on strip card with speed 60 mm/h or 120mm/h. An average datum was read for 10 minutes from the strip card, 6 data were averaged for an hour value.

RESULTS AND INTERPRETATION

We present here in some detail a set of simultaneous measurements which illustrates the relationship between SO_2 and O_3 or between SO_2 and H_2O_2. The measurements were conducted in Guiyang area on June 11 to 28 in 1988. During the measurement period there were five precipitation events studied.

The 500 mb isobaric charts from 6/16/88 08:00 to 6/17/88 08:00 showed that a trough of low pressure lied over Eastern Asia. Guiyang site was in the band of confluence of warm and cold masses, a cold wind shear existed at low level of 850 mb, its 700 mb level was controlled by warm and moist air flow. Correspondingly, on the surface weather maps a front line passed through Guiyang site nearby and precipitation events appeared in the period. From 6/17/88 20:00 to 6/18/88 a trough still maintained over Eastern Asia. The warm and moist advection prevailed at the low and middle level of Guiyang site. A sharp warm wind shear controlled 850 mb isobaric level, and stronger precipitation was on surface correspondingly.

Fig. 1 presents time records of the concentrations of gas phase SO_2 and O_3 in the city. For the time records and here inafter zero on abscissa represents for 6/10/88 00:00 and 1 for 6/11/88 00:00. The typical diurnal variations of SO_2 and O_3 of Chinese cities were observed, namely the concentrations of SO_2 had two peaks in the morning and evening, the highest level of O_3 was in the afternoon. The high fluctuation of concentration of SO_2 took place when the sampling site was in the plume of nearby chimneys, because coal was burned generally in medium and small boilers and household stoves, the emissions were released through short chimneys. The hour average concentration of SO_2 was 43.7 ± 40.1 ppbv. Contract to SO_2, little fluctuation of O_3 was observed. The hour average of concentration of O_3 was 23.8 ± 6.9 ppbv.

Fig. 2 shows a portion of time records from Fig. 1 on an expanded time scale in order to allow examination the relationship of the gaseous signals and the chemical composition of the sequential rainwater samples. The sequential samples collected in the city were all acidic with volume weighted pH 4.05 in this case study. Significant level of H_2O_2 was not detected in the samples. However, the concentration of S(IV) fluctuated very much. The H_2O_2 and S(IV) in the sample was fixed after collection, so that H_2O_2 and S(IV) had enough time to react. The high level of S(IV) in rainwater samples was corresponding to the peaks of gas phase SO_2

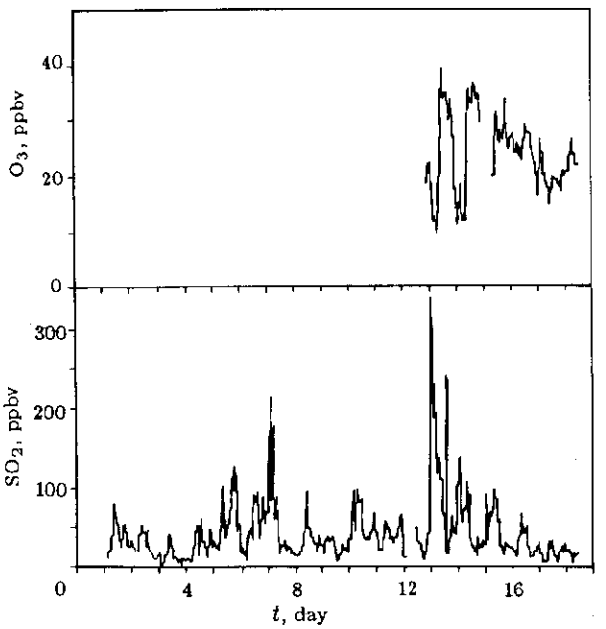

Fig. 1 Time records from measurements of SO_2 and O_3 from 6/11/88 to 6/28/88 in a residential site of Guiyang City (Gaps represent missing data)

at time 6/16/88 11:20 to 11:50 (6.472 to 6.493), 6/17/88 03:30 to 04:00 (7.146 to 7.188) and 6/18/88 10:00 to 12:15 (8.490 to 8.531). In order to refer to figures after the time values of normal format in the text the time values of decimal format on abscissa of the figures defined in the paper were listed in paratheses. The low value of S(IV) was fallen in valley of concentration of SO_2 at time 6/18/88 05:00 to 09:00 (8.208 to 8.375). But no relation was observed between S(IV) and pH (or H^+ concentration) in the samples. For example, on 6/17/88 01:40 to 04:30 (7.069 to 7.188) the pH in the sequence samples increased (H^+ concentration decreased) and the S(IV) concentration also increased. However, on 6/18/88 11:45 to 13:50 (8.490 to 8.576) the concentration of SO_2 and aqueous S(IV) fluctuated very much, the corresponding pH was remained nearly constant.

Fig. 3 is the time records of concentration SO_2 and O_3 at the airport. The records shows evidence of urban plumes superimposed on a background concentration of about 10 ppbv of O_3 and 1—4 ppbv of SO_2. Around the airport there are no strange SO_2 sources. It can be found from Fig. 1 that the fluctuation of SO_2 did not company any fluctuation of O_3 in the city, however, the concentration of SO_2 and O_3 fluctuated together. The typical diurnal variations of concentration of SO_2 and O_3 in the city disappeared at the airport. O_3 is relatively insoluble and non-reactive in liquid water (discuss below) and with high level in

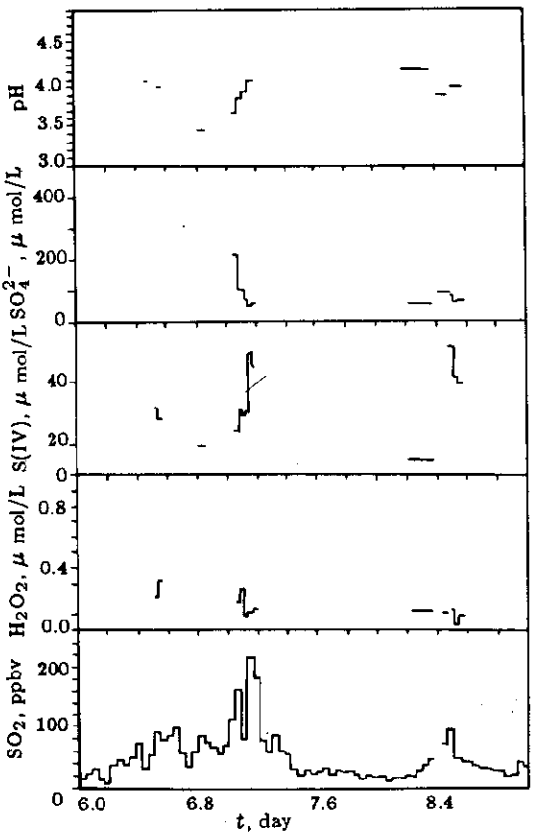

Fig. 2 Time records from a portion of measurements of SO_2 and O_3 in the city and chemical composition of the sequential rainwater samples collected in this period (Gaps represent missing data or no rain at all)

urban plumes, the major SO_2 are emitted from the city, thus, SO_2 and O_3 may serve as tracers of the urban plume. In this regard, we distinguish urban plumes and background air from the data records of simultaneously measurement of SO_2 and O_3 by which the chemical composition of precipitation in urban plume or in background air may be compared. Therefore, the airport sometimes exposed in urban plumes, sometimes can be treated as background. For this reason the average data at the airport may not be used as the data for clean area of Guiyang City.

The other feature is that the concentration of SO_2 was much higher than that of O_3 in the city, but they had the same level or sometimes the concentration of O_3 was higher than that of SO_2 at the airport. The width of the urban plume peaks of O_3 was much broader than that of SO_2. This might be resulted from higher dry deposition rate and more reactivity in hydrometeors of SO_2. In this regard, the behavior of O_3 as tracer of the urban plume might

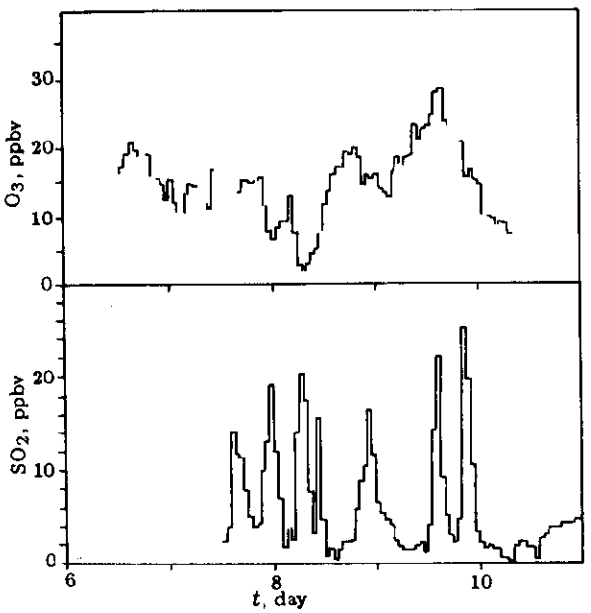

Fig. 3 Time records from measurements of SO_2 and O_3 from 6/16/88 to 6/22/88 in the airport of Guiyang (Gaps represent missing data)

be more reliable.

Fig. 4 shows a portion of time records from Fig. 3 on an expanded time scale in order to allow examination the relationship of the gaseous signals and the composition of the sequential rainwater samples. At the airport significant content of H_2O_2 or S(IV) were detected in rainwater samples, but not both. On 6/18/88 02:35 to 04:00 (8.108 to 8.167) the concentration of H_2O_2 increased in sequential samples from 0.08 to 15.2 μmol/L, the pH also increased from 4.21 to 6.78. At that time, the concentration of SO_2 and O_3 was fallen in valley, which was the level of the gases in the background air. On 6/18/88 08:00 to 08:30 (8.333 to 8.354) the concentration of SO_2 was at another peak, the concentration of S(IV) again increased to 18 μmol/L. The rainwater sample was acidic with pH 4.0. At that time the concentration of H_2O_2 was below the limit of detection. Therefore, a significant amount of constituents of the precipitation were resulted from below-cloud scavenging of the urban plume.

Fig. 5 shows the variation of the chemical composition of sequential rainwater samples collected at the third site. Almost all samples had significant amount of H_2O_2 with the highest of 58 μmol/L, whereas the S(IV) concentrations were very low. The high concentrations of H_2O_2 on 6/17/88 01:45 to 03:15 (7.073 to 7.135) and 6/18/88 04:05 to 08:30 (8.170 to 8.354) were corresponding to the high pH (>6.0). The low H_2O_2 values at 6/17/88 16:25 to 17:00 (7.684

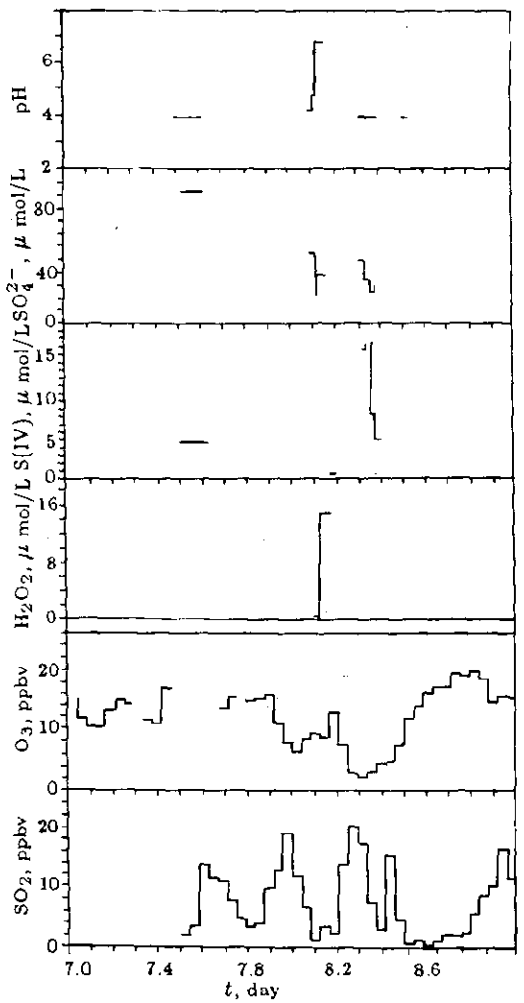

Fig. 4 Time records from a portion of measurements of SO_2 and O_3 at the airport and chemical composition of the sequential rainwater samples collected in this period (Gaps represent missing data or no rain at all)

to 7.08) and 6/18/88 11:40 to 12:40 (8.486 to 8.528) were corresponding to the low pH (about 4.0). On 6/18/88 the pH values changed very much from one sample to next, the corresponding concentration of H_2O_2 and SO_4^{2-} were also changed very much. From the evidence of fluctuation together of the concentrations of H_2O_2 and SO_4^{2-} and pH of the rainwater samples, it might be assumed that they were subject to interference from urban plumes or the precipitating cloud was polluted.

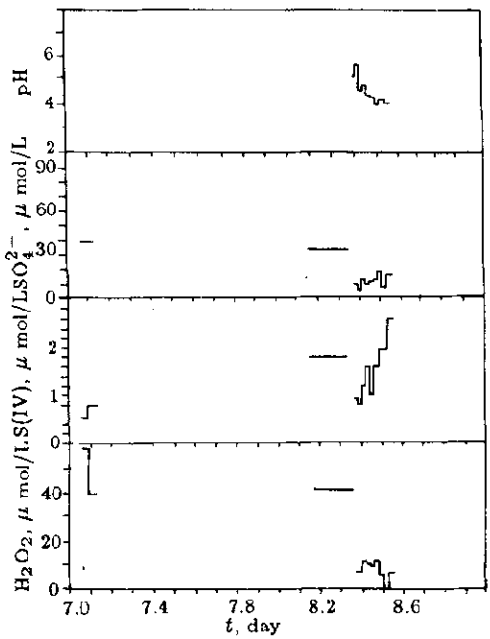

Fig. 5 The variation of the chemical composition of the sequential rainwater samples collected at the third site with time (Gaps represent missing data or no rain at all)

On 6/18/88 08:00 to 12:00 (8.333 to 8.500) many rainwater samples from a heavy precipitation event were collected at the three sampling sites. For comparison the chemical composition of some rainwater samples collected in the city and its suburbs on that day was listed in Table 1. Three different types of chemical composition of rainwater can be distinguished. First, clean not acidic rainwater were collected at the suburbs in background air, with high level of H_2O_2. This rainwater can be chosen as surrogate of clean cloud water. Second, light polluted rainwater samples were collected at suburbs in urban plumes, which were acidic sometimes with significant H_2O_2, sometimes with S(IV), but not both. Then, heavy polluted rainwater samples were always collected in the city, which were acidic with high level of S(IV) and the concentrations of H_2O_2 were close to the limit of detection. We can not assumed that the composition of the precipitating cloud over this area of this event would be the same, however, clean rainwater samples were collected at 20 km around the city at opposite direction, it had to be assumed that in this event the precipitating cloud at the high altitude would be clean and that the major process of acidification of the rain in the city and its urban plume would be below-cloud scavenging trace gases and oxidizing SO_2 in lower air through which it passes.

Table 1 The chemical composition of some rainwater samples collected in Guiyang area on 6/18/88

Site	Start time	End time	pH	H_2O_2, μmol/L	S(IV), μmol/L	NH_4^+, μmol/L	SO_4^{2-}, μmol/L	NO_3^-, μmol/L
City	05:00	09:00	4.2	0.1	5.2	5.6	56.8	8.1
City	10:00	11:30	3.9	0.1	50.0	26.7	96.4	12.3
City	11:45	12:15	4.0	0.1	41.4	16.1	85.6	8.1
City	12:15	12:50	4.0	0.0	31.8	NA	62.1	4.0
City	12:50	13:50	4.0	0.1	29.9	NA	68.5	20.4
Airport	02:35	02:50	4.2	0.1	1.2	41.7	54.9	11.5
Airport	02:50	03:00	4.8	0.8	NA	NA	20.6	NA
Airport	03:00	04:00	6.8	15.2	NA	39.3	38.9	4.6
Airport	07:30	08:00	4.0	0.0	16.8	13.9	48.0	9.2
Airport	08:00	08:30	4.0	0.1	17.6	NA	34.3	4.6
Airport	08:30	09:00	4.0	0.1	8.2	NA	24.1	4.6
Airport	09:00	09:30	4.0	0.0	5.1	9.4	29.7	9.2
Airport	12:15	12.45	4.0	0.0	3.1	20.0	46.9	13.7
Third site	04:05	08:30	6.0	41.0	1.8	40.6	32.8	20.4
Third site	09:00	09:20	5.1	7.1	0.9	NA	8.8	4.0
Third site	09:20	09:40	5.7	6.5	0.8	NA	4.4	NA
Third site	09:40	10:10	4.6	11.9	1.2	4.4	13.1	4.0
Third site	10:10	10:40	4.8	10.8	1.6	NA	8.8	4.0
Third site	10:40	11:10	4.4	9.5	1.0	NA	10.9	4.0
Third site	11:10	11:40	4.3	12.2	1.6	NA	13.1	4.0
Third site	11:40	12:10	4.0	5.8	2.0	NA	17.5	4.0
Third site	12:10	12:40	4.2	1.0	2.0	NA	6.6	NA
Third site	12:40	13.20	4.1	7.0	2.5	NA	16.5	12.3

NA means no available value for below LOD

DISCUSSION

Three different ambient air conditions and corresponding three types of chemical composition of rainwater were observed during the field experiment over this area. First, the severe SO_2 pollution was observed, a large amount of S(IV) was measured in all rainwater samples and the concentration of H_2O_2 was below 0.5 μmol/L in Guiyang City (Fig. 2). Second, urban plumes of about 20 ppbv SO_2 sometimes occurred in suburbs, the rainwater was acidic sometimes with significant H_2O_2, sometimes with S(IV), but not both (Fig. 4). Third, at the same suburb sites there was very clean air (background air) prevailed between plumes (Fig. 4), at that time, the concentration of H_2O_2 in rainwater samples was much higher than that of S(IV) (Fig. 4 and Fig. 5). The mutual exclusivity of H_2O_2 and S(IV) is consistent with the rapid aqueous phase reaction (1) of these two species (Lee, 1986A).

$$S(IV) + H_2O_2 \longrightarrow 2H^+ + S(VI). \quad (1)$$

The reaction occurred either in hydrometeors prior to deposition or in the precipitation collected subsequent to collection and prior to fixing the titer of H_2O_2 and S(IV) (Schwartz, 1988). One compound presents in great excess over the other, it is suggested that in the rapid reaction one or the other species is the limiting reagent. H_2O_2 was the limiting reagent available at the city, however, SO_2 was in suburbs except when covered by urban plumes.

The characteristics of H_2O_2 and S(IV) occurrence in precipitation over the research area is not unexpected in view of the below-cloud scavenging of trace gases. In atmosphere the lowest H_2O_2 concentration is below the boundary layer, above the boundary layer the H_2O_2 concentrations increase. This pattern of H_2O_2 increasing with altitude was frequently observed (Kok, 1986; Heikes, 1987; Schwartz, 1988). The ambient SO_2 is mainly from low emission sources in Guiyang City (Xiong, 1987), therefore, the severe SO_2 pollution was observed below boundary layer over the city and its urban plume. It is assumed that the H_2O_2 from higher altitudes by scavenging with rainwater oxidize SO_2 in lower air through which it passes.

In order to address this hypothesis we performed a model calculation. The model for below-cloud scavenging of trace gases are described (Overton, 1979; Duhaum, 1981; Shen, 1989A), and repeated here for completeness with update collected kinetic data (Martin, 1984; Hoffmann, 1986).

The atmosphere has been divided into two regions. Raindrops are formed in the upper region in the presence of CO_2 and other compounds. The drops enter and fall through lower polluted region at their terminal velocities. In the polluted region there are trace gases CO_2, O_3, SO_2, HNO_3, NH_3 and H_2O_2. As the drops fall the gases are absorbed, react and produce SO_4^{2-}, NH_4^+ and NO_3^- and acidity of the drops changes. The concentrations are assumed to be uniformly distributed at all times throughout the drop. The temperature of the raindrops is assumed to be in equilibrium with an isothermal atmosphere at 25°C.

The rate, per unit falling distance, at which for species i concentration C_{il} (mol/L) increases by mass transfer and reactions in a drop of radius R (mm) is given by:

$$\frac{dC_{il}}{dZ} = \frac{3k_g}{UR}(C_{ig} - H_i C_{il}) + \frac{\Gamma_i}{U}, \tag{2}$$

where C_{ig} (mol/L) is concentration of species i in gas-phase, Γ_i is the reaction rates of species i and H_i is Henry's law constant.

The terminal falling velocity U (m/s) is obtained from a formula by Markowitz.

$$U = 9.58\{1 - \exp[-(R/0.885)^{1.147}]\}. \tag{3}$$

The mass transfer coefficient k_g is obtained from Frössling correlation.

$$k_g = \frac{D_i}{R}[1 - 0.3(\frac{RU}{r})^{1/2}(\frac{r}{D_i})^{1/3}], \tag{4}$$

where D_i is the diffusion coefficient of gas species i (cm^2/s), r is the kinetic viscosity of the air, 0.133 cm^2/s. The average ground level concentration of a species C_{il} (mol/L) after a fall distance Z (m) is computed as weighted average by drop size distribution of Best (Best, 1950).

$$C = \frac{\int U(R)C(R,Z)f(R)dR}{\int U(R)f(R)dR}, \tag{5}$$

Equation (5) is the raindrop size distribution function by Best.

$$f(R) = \frac{2n}{a}\left(\frac{2R}{a}\right)^{n-1}\exp\left[-\left(\frac{2R}{a}\right)^{n}\right], \tag{6}$$

a=$1.3P^{0.232}$, P is the intensity of rainfall (mm/h), n=2.25.

Table 2 are the chemical reactions selected for calculating the acidification of falling raindrops. Equations 1—7 are the reversible equilibrium reactions for the CO_2—SO_2—HNO_3—NH_3— H_2O system. Equations 8—11 are the irreversible oxidation steps for formation SO_4^{2-}

Because we did not measure the vertical profiles of gas phase H_2O_2, SO_2 and other trace gases in these experiments, for simplification the below-cloud scavenging of traces gases in 1000 m polluted zone with uniform vertical profile was used for simulation. In the city this assumption may not be correct, but in the suburb it might be a good approximation. Three different polluted or unpolluted zones namely in the city or in the suburb with or without urban plume in background air were calculated. Three different concentrations of SO_2 and O_3 were selected for them, that is, 50 ppbv SO_2, 25 ppbv O_3 for the city; 20 ppbv SO_2, 20 ppbv O_3 for urban plume and 1 ppbv SO_2, 10 ppbv O_3 for background air. The gas phase concentrations of NH_3, HNO_3 and H_2O_2 were assumed the same for all cases, namely, 2, 1, 0.5 ppbv respectively from previous measurements (Shen, 1987; Pang, 1985). The rainwater which fell through the polluted zones initially contained 60 μmol/L H_2O_2, 0.5 μmol/L Mn^{2+} and 2 μmol/L Fe^{3+}, which were the highest value in this field measurement, the rain intensity being 1 or 10 mm/h. The rainwater with or without 50 mol/L H_2SO_4 was used for simulation of initial acidic or neutral rainwater.

The simulation results are listed in Table 3 with 100% conversion. It is instructive to compare the measured data in Table 1 and the simulated data in Table 3. Although the data are not exactly the same, because the scavenging of particulate did not included and concentrations of trace gases and their profiles and the concentrations of initial aqueous species were variable in real event, the whole picture are much like. The most of findings in results and interpretation section of this paper can also be found in Table 3. For example, the higher the SO_2 level in gas phase the higher the S(IV) concentration in rainwater the lower the H_2O_2 concentration and the more acidity.

Table 2 Thermodynamics and kinetics of aqueous phase reactions

$H_2O \xrightarrow[1.0E-14^*]{K_1} H^+ + OH^-$	(1)
$SO_2+H_2O \xrightarrow[1.7E-2]{K_2} H^+ + HSO_3^-$	(2)
$HSO_3^- \xrightarrow[6.24E-8]{K_3} H^+ + SO_3^{2-}$	(3)
$NH_4^+ \xrightarrow[5.7E-10]{K_4} NH_3 + H^+$	(4)
$HNO_3 \xrightarrow[2.75E+3]{K_5} H^- + NO_3^-$	(5)
$CO_2+H_2O \xrightarrow[6.4E-6]{K_6} HCO_3^- + H^+$	(6)
$HCO_3^- \xrightarrow[4E-10]{K_7} CO_3^{2-} + H^+$	(7)
$O_3 + SO_2 \xrightarrow[5.9E+2]{K_8} 2H^+ + SO_4^{2-}$	(8)
$O_3 + HSO_3^- \xrightarrow[3.1E+5]{K_9} H^+ + SO_4^{2-}$	(9)
$O_3 + SO_3^{2-} \xrightarrow[2.2E+9]{K_{10}} SO_4^{2-} + O_2$	(10)
$S(IV) + H_2O_2 + H^+ \xrightarrow[9.6E+7]{K_{11}} 2H^+ + SO_4^{2-} + H_2O$	(11)
$S(IV) + 0.5\ O_2 \xrightarrow{Mn^{2+},Fe^{3+}} S(VI)$	(12)

If pH <4 and $[S(IV)] > 10^{-5}$mol/L

$$(K_{12}\frac{[Mn^{2+}]^2}{[H^+]} + K_{13}\frac{[Fe^{3+}][S(IV)]}{[H^+]}) \times \{\frac{[1 + 1.7 \times 10^3[Mn^{2+}]^{1.5}}{6.3 \times 10^{-6} + [Fe^{3+}]}\}$$

If pH <4 and $[S(IV)] < 10^{-5}$mol/L

If both $[Fe^{3+}]$ and $[Mn^{2+}]$ are non-zero $N=3$, otherwise $N=1$

$$N(K_{14}\,[Mn^{2+}]\,[HSO_3^-] + K_{13}\frac{[Fe^{3+}][S(IV)]}{[H^+]})$$

If pH > 4 and $[S(IV)] > 10^{-5}$ mol/L

$$K_{12}\frac{[Mn^{2+}]^2}{[H^+]} + K_{15}\,[Fe^{3+}]\,[S(IV)]^2$$

If pH > 4 and $S(IV) < 10^{-5}$ mol/L

$K_{14}\,[Mn^{2+}]\,[HSO_3^-]$

$K_{12} = 4.7$

$K_{13} = 0.817$

$K_{14} = 5 \times 10^3$

$K_{15} = 1 \times 10^7$

* $1.0E\text{-}14 = 1.0 \times 10^{14}$

Some more important information can not be obtained directly from field observation but for simulation it can be done (Table 3). Below-cloud scavenging of gaseous HNO_3 by precipitation and of gaseous NH_3 by acidic precipitation are irreversible (Shen, 1988). For a given intensity of rainfall the concentration of NO_3^- and NH_4^+ in rainwater are nearly invariable no matter what other conditions are. The rate of oxidation of S(IV) by H_2O_2, O_3 and Mn^{2+}, Fe^{3+} catalytic are variable depending on the conditions. The initial H_2O_2 and scavenged

gaseous H_2O_2 are all reacted with S(IV) to produce H_2SO_4 in the city.

Table 3 The simulation results of below-cloud scavenging of trace gases

Site	INT., mm/h	H_2SO_4, μmol/L	$SO_4^{2-}1$, μmol/L	$SO_4^{2-}2$, μmol/L	$SO_4^{2-}3$, μmol/L	$SO_4^{2-}4$, μmol/L	pH	H_2O_2, μmol/L	S(IV) μmol/L	NO_3^-, μmol/L	μ
City	1	0	67.0	0.9	13.8	81.7	3.8	0.0	7.4	12.9	3
City	10	0	62.3	0.7	4.5	67.5	3.9	0.0	2.7	5.0	1
Plume	1	0	62.9	0.7	3.7	67.3	3.9	2.6	0.0	13.0	3
Plume	10	0	26.4	0.7	0.8	27.9	4.3	34.3	0.0	5.0	1
Background	1	0	5.3	3.5	1.7	10.6	5.3	52.3	0.0	13.0	3
Background	10	0	2.5	1.3	0.6	4.4	5.4	56.3	0.0	5.0	1
City	1	50	67.1	0.3	0.5	117.9	3.7	0.0	5.0	12.9	3
City	10	50	62.4	0.1	0.1	112.6	3.7	0.0	0.8	5.0	1
Plume	1	50	62.1	0.1	0.4	112.7	3.7	3.6	0.0	13.0	3
Plume	10	50	42.9	0.0	0.1	93.0	3.8	18.7	0.0	5.0	1
Background	1	50	7.5	0.1	0.0	57.6	4.0	50.8	0.0	12.9	3
Background	10	50	3.5	0.0	0.0	53.5	4.0	55.6	0.0	5.0	1

INT is the intensity of the rainfall.
$SO_4^{2-}1$ is the concentration of SO_4^{2-} produced by oxidation of H_2O_2.
$SO_4^{2-}2$ is the concentration of SO_4^{2-} produced by oxidation of O_3.
$SO_4^{2-}3$ is the concentration of SO_4^{2-} produced by oxidation of Mn^{2+}, Fe^{3+} catalytic.
$SO_4^{2-}4$ is the concentration of total SO_4^{2-}

If the rainfall intensity is small, say 1 mm/h, most of initial H_2O_2 in rainwater and scavenged gaseous H_2O_2 are reacted with S(IV) in the typical urban plume, but if the intensity is large, say 10 mm/h, the time is not enough to scavenge SO_2 for reacting, a certain amount of H_2O_2 can be remained without reaction with S(IV) until the drops reach the ground. Considerable amount of H_2O_2 are in rainwater with 100% conversion at ground in background air. The rate of oxidation S(IV) by O_3 and Mn^{2+}, Fe^{3+} catalytic in high pH rainwater are significant, for example, the ratio of amount of SO_4^{2-} produced by reaction with H_2O_2, O_3 and Mn^{2+}, Fe^{3+} catalytic are about 4:2:1 for scavenging background air without H_2SO_4 in initial rainwater. But for low pH rainwater the major SO_4^{2-} are produced by the reaction of S(IV) with H_2O_2. We previously reported that the rate of oxidation of S(IV) by Mn^{2+}, Fe^{3+} catalytic are less than that by O_3 very much (Shen, 1989A), but in this calculation the situation is different for some conditions. This may be caused by the different kinetic data of Mn^{2+}, Fe^{3+} catalytic oxidation used (Martin, 1984).

Comparison of different intensity of rainfall, for example 1 and 10 mm/h in Table 3, the concentrations of NO_3^-, NH_4^+ and SO_4^{2-} which are resulted from scavenging trace gases and oxidation of S(IV) are higher for light rain than those for heavy rain. Smaller drops which are more populated in light rain have larger ratio of surface to volume with slower terminal velocities, therefore, there is much time for absorption of trace gases and for reactions to take place and more efficient for scavenging SO_2.

The concentration of H_2O_2 in rainwater collected at Guiyang City most of time was close to the limit of detection. To illustrate this a below-cloud scavenging of 1000 m polluted zone with rainwater which initially contained 100 μmol/L H_2O_2 for intensity of 10 mm/h was simulated, the other conditions were the same as for Table 3 except for the variable concentration of SO_2. Fig. 6 shows the variation of concentrations of SO_4^{2-}, S(IV) and H_2O_2 in precipitation collected at ground (no conversion in collector) as a function of SO_2 concentration in polluted zone. When SO_2 concentration increases the H_2O_2 concentration decreases dramatically. The concentrations of H_2O_2 and S(IV) in precipitation at ground when they are equal are defined as equivalent point of the titers, which corresponds to ambient SO_2 concentration of 74 ppbv or 37 ppbv for intensity 10 and 1 mm/h respectively.

The level of 100 μmol/L H_2O_2 in precipitation was occasionally observed in our experiments or reported in North Eastern American (Lee, 1986B). Moreover, the ambient SO_2 in residential area of Guiyang City was sometimes much higher than 50 ppbv (Zhao, 1988). Therefore, H_2O_2 could not be detected and high level S(IV) was observed in precipitation collected in Guiyang City except very heavy rain event. When H_2O_2 is consumed in reaction with S(IV) the equivalent amount of sulfuric acid is produced though acidity of rain is also dependent on alkali species such as Ca^{2+}, Mg^{2+}, and NH_4^+ in the rainwater. S(IV) is in excess of precipitation

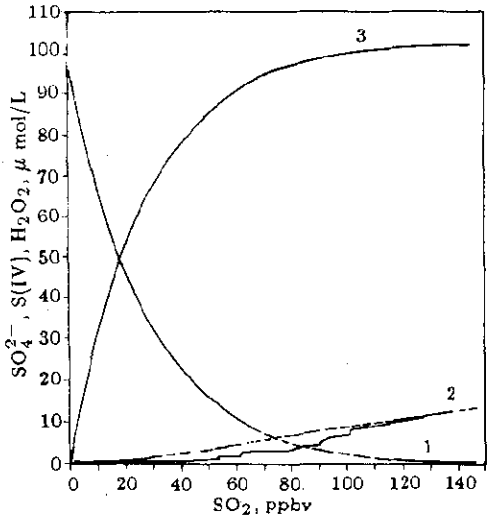

Fig. 6 Simulation results of concentrations of aqueous SO_4^{2-}, S(IV) and H_2O_2 as a function of ambient SO_2; 3 SO_4^{2-} by H_2O_2 means that curve 3 presents the concentration of SO_4^{2-} produced by oxidation of H_2O_2, the same for others; 1 H_2O_2, 2 S(IV), 3 SO_4^{2-} by H_2O_2, 4 SO_4^{2-} by O_3, 5 SO_4^{2-} by Mn^{2+}, Fe^{3+} catalytic

in Guiyang City means that all H_2O_2 initially in rainwater and absorbed from below-cloud scavenging of gas phase H_2O_2 is converted to sulfuric acid.

For evaluation of kinetics, 25 ppbv O_3 and the maximum level of Mn^{2+}, Fe^{3+} were involved in simulation calculation. As shown in Fig. 6 oxidation of S(IV) by O_3 and Mn^{2+}, Fe^{3+} catalytic is not very important in these conditions, except for oxidation by Mn^{2+}, Fe^{3+} catalytic while high level of SO_2 in gas phase.

SUMMARY AND CONCLUSION

Real-time gas phase SO_2 and O_3 measurements on 6/11/88 to 6/28/88 were performed and chemical composition, especially H_2O_2 and S(IV), in sequential precipitation samples collected in Guiyang area was measured. Three different types of situation of atmosphere and corresponding chemical composition during this field experiment were observed, that is episode of SO_2 in the city, urban plume and background air in suburb.

The mutual exclusivity of H_2O_2 and S(IV) exists in these rainwater samples. H_2O_2 was detected in suburbs, whereas, a large amount of S(IV) was measured in samples collected at a residential site of Guiyang City, which might be formed by below-cloud scavenging of ambient SO_2 emitted mainly from local low sources. The high level of S(IV) in rainwater corresponded

to the peaks of the concentration of SO_2 in gas phase of the city and its urban plumes. When the concentration of H_2O_2 rose to a peak the concentration of SO_2 was fallen in a valley of background air. The evidence that clean rainwater samples were collected at 20 km away from the city in 6/18/88 precipitation event while the rainwater samples collected in the city were still acidic revealed that the major process for acidification of the rain in the city and its urban plumes was below-cloud scavenging of trace gases and oxidizing SO_2 in lower air through which it passes.

It is found by comparison of observation and below-cloud scavenging simulation that H_2O_2 might be the most important aqueous oxidant for SO_2 oxidation and all H_2O_2 available would be converted to sulfuric acid in Guiyang urban area and its plume. The SO_2 is in excess of the oxidant in Guiyang City and only the portion of SO_2 that equals to the oxidant content can be converted to sulfuric acid and deposited at this receptor site. Thus, a reduction in SO_2 emission may not lead to a directly observable reduction in sulfuric acid deposition. This notation would be bear in mind for formulating control strategies.

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