

The Chemical Characteristics of Springtime Precipitation in Lushan Mountains, East China

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(Manuscript received 5 November 1996, in final form 29 September 1997)

ABSTRACT

A comprehensive field measurement was set up in the springtime of 1993 to study the chemical characteristics of precipitation in the Lushan Mountains. The results showed that the concentrations of gaseous SO_2 , NO_x , NH_3 , and HNO_3 were low and precipitation was seriously acidified. The pH of all samples was less than 5.6 with an average of 4.6 and a minimum of 3.71. Sulfuric acid was the primary acidic substance to cause the acidification and nitric acid was the secondary. Both acidity and concentrations of compositions in cloud water were much higher than those in rainwater. Comparisons of different phases of precipitation showed that concentrations of ionic components in the solid phase were two to five times higher than those in rainwater, and its pH was 0.6 higher than that of rainwater. According to the measurement results, it was postulated that the acidification of precipitation was caused by joint effects of washout of local atmospheric pollutants and long-distance transportation of acidic substances.

1. Introduction

Precipitation chemistry at high-elevation sites was studied intensively both inside and outside China in the last decade (M. Wang 1992; Mohnen and Kadlec 1989; Falconer et al. 1980; Castillo et al. 1983). In China, the studied areas were mostly located in the southwest and the south. According to historical records of acid rain observations, the highest acidified frequency of precipitation always appeared in the springtime in Guangdong, Guangxi, Hunan, and Jiangxi Provinces, East China. To investigate these occurrences, a series of experiments were conducted to study precipitation chemistry and the mechanism of acid rain formation in the Lushan Mountains, Jiangxi Province (1100 m); Hengshan Mountains, Hunan Province (1290 m); Lion Mountains, Guangdong Province (1050 m); and Baiyunshan Mountains, Guangdong Province (380 m) (M. Wang 1992; W. Wang 1992; Ding et al. 1992; Bi et al. 1992). All of these mountains are located in eastern China. They all lie in the passageway of a spring northern cold front to the south, and are suitable sites for studying the acidification mechanism of precipitation in East China. In addition, with the characteristic of less local pollution, these mountains can represent the pollution state of cleaner areas in East China.

A comprehensive field measurement on atmosphere,

cloud water, rainwater, frozen rainwater, and snow was set up in the Lushan cloud-fog station from 10 to 28 March 1993 by the Department of Geophysics and Center of Environmental Sciences, Peking University (Qin et al. 1995). This paper presents the air pollution state and chemical characteristics of precipitation in the Lushan Mountains in springtime and compares the chemical compositions among different phases of precipitation. Combining historical chemical data in Lushan and taking pollution in the Hengshan, Lion, and Baiyunshan Mountains in the springtime into account, air quality and acid precipitation in these mountains are discussed briefly.

2. Measurements

The Lushan Mountains are located in the northern part of Jiangxi Province, as shown in Fig. 1. It borders the Yangtze River, and faces Boyang Lake with most peaks at about 1000 m. Large cities and industrial areas such as Jiujiang, Wuhan, Nanchang, Jindezheng, and Huangshi are within a 100-km diameter centered at Lushan. At the mountaintop there is a small town, Guolin, with a population of 11 000 inhabitants. Most residents engage in tourism and related businesses. Spring is an off-season for tourism, therefore, local emission of pollutants is very low. The sampling sites are located at the Lushan cloud-fog station (1100 m), northwest of the town and Baitianchi (1150 m).

From 10 to 28 March 1993, six precipitation systems were observed: four rainfall processes and two snow or frozen rain processes. All the precipitation systems were

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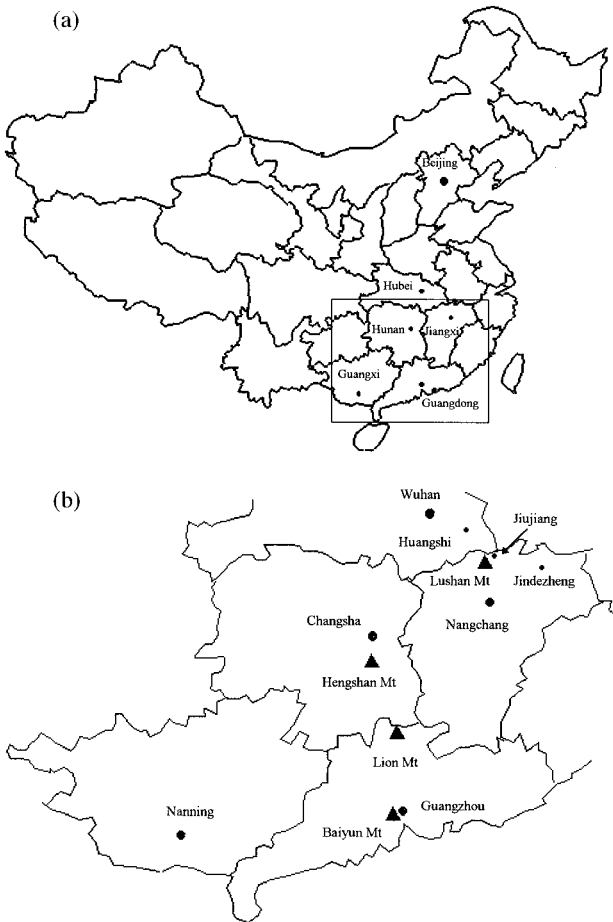


FIG. 1. (a) A map of China in which studied area is shown. (b) The location of sampling sites in high mountains in southern China.

controlled by a northern cold front during the field measurements. The observation items included SO_2 , NO_x , NH_3 , HNO_3 , O_3 , total suspended particles (TSPs) and water soluble components, and pH, SO_4^{2-} , NO_3^- , Cl^- , F^- , Ca^{2+} , Mg^{2+} , NH_4^+ , NO_2^- , SO_3^{2-} , and H_2O_2 in different phases of precipitation. The SO_2 , NO_x , NH_3 , HNO_3 , and TSP samples were collected by filter packs with impregnated filters and then water-soluble components were analyzed in the laboratory by ion chromatography (Liang et al. 1995; Wang et al. 1988; Ferek et al. 1991). Two methods were used to collect TSPs, SO_2 , NO_x , NH_3 , and HNO_3 samples. An inlet with four-

layer filters in sequence was used to collect TSPs, SO_2 , and NO_2 . Glass fiber membranes were used as filters. Aerosols were collected in the first layer. The second layer of glass fiber impregnated with sodium chloride was used to remove HNO_3 . The third and the fourth filters impregnated with triethanolamine solvent were used to absorb SO_2 and NO_2 . An inlet with three-layer filters was used to collect TSPs, HNO_3 , and NH_3 . The first-layer filter was glass fiber to collect TSPs. The second-layer filter was a nylon membrane made by the Gelman Science Corporation and was used to absorb gaseous HNO_3 . The third-layer filter was glass fiber impregnated with 4% oxalic acid solvent and was used to absorb NH_3 . Gaseous O_3 was measured in situ by a spectrophotometric method of indigo disulphonate (IDS) (Chen et al 1992; NNI 1982). The pH and aqueous H_2O_2 of rainwater and cloud water were measured soon after the samples were collected. Aqueous H_2O_2 was measured by a spectrophotometric method of leuco crystal violet, respectively (Sun et al. 1993; Lazrus et al. 1986). After filtration by a $0.2\text{-}\mu\text{m}$ microfilter, the rainwater and cloud water were kept at a low temperature and sent to the laboratory. The SO_4^{2-} , NO_3^- , Cl^- , F^- , NH_4^+ , NO_2^- , and SO_3^{2-} were measured by ion chromatography and Ca^{2+} and Mg^{2+} by an atomic absorption spectrophotometer.

3. Results and discussions

a. Atmospheric pollution in Lushan

During the measurement period, the average concentrations of SO_2 , NO_x , and O_3 were $2.56 \mu\text{g m}^{-3}$, $1.26 \mu\text{g m}^{-3}$, and 37.5 ppb, respectively. The first time for measurement of NH_3 and HNO_3 in Lushan was March 1993. Due to constant girdling of cloud-fog and high humidity, HNO_3 was not detected. Although NH_3 was always detected in Lushan, its concentration was only $1.13 \mu\text{g m}^{-3}$ on average, which is much lower than that in an urban area. In aerosol samples, the SO_4^{2-} concentration was the highest among water-soluble ion compositions of aerosol with a value of $8.81 \mu\text{g m}^{-3}$; the NH_4^+ concentration with a value of $1.76 \mu\text{g m}^{-3}$ was second.

Table 1 shows the SO_2 and NO_x concentration variations in Lushan together with those in Hengshan and Lion Mountains. The SO_2 concentration was very low

TABLE 1. SO_2 and NO_x concentrations in Lushan, Hengshan, and Lion Mountains.

	Lushan			Hengshan			Lion	
	May 1987	May 1989	March 1993	March 1988	March 1989	March 1993	March 1988	March 1989
SO_2 ($\mu\text{g m}^{-3}$)	0.50	0.21	2.56	17	16	<3	<6	20
	0.04–1.49	0.00–0.72	0.80–7.06					
NO_x ($\mu\text{g m}^{-3}$)	3.40	2.57	1.26	4	7	7	13	20
	0.07–7.48	0.00–4.26	1.01–1.94					
SO_2/NO_x ($\mu\text{g } \mu\text{g}^{-1}$)	0.15	0.08	2.03	4.25	2.28	0.43	0.48	0.67

TABLE 2. Water-soluble ion composition of aerosol in Lushan, Hengshan, and Lion Mountains.

Mountains	Date	SO ₄ ²⁻ (μg m ⁻³)	NO ₃ ⁻ (μg m ⁻³)	Cl ⁻ (μg m ⁻³)	F ⁻ (μg m ⁻³)	NH ₄ ⁺ (μg m ⁻³)	SO ₄ ²⁻ /NO ₃ ⁻ (μg μg ⁻¹)
Lushan	May 1987	9.18	0.32	1.16	0.21	0.36	28.7
Lushan	May 1989	3.03	0.03	0.10	0.05	0.98	101
Lushan	March 1993	8.81	1.24	1.32	0.20	1.76	7.1
Hengshan	March 1988	163.4	69.9	21.3	—	141.7	2.3
Hengshan	March 1993	320.0	25.0	6.0	—	199.0	12.8
Lion	March 1988	162.4	19.1	9.9	—	122.7	8.5

and varied a little during 1987–89, but it increased dramatically—by a factor of 12—from 1989 to 1993. This steep increase of SO₂ was mostly attributed to the increase of local human activities, especially coal burning. However, NO_x had a tendency to decrease continuously and slowly. In corresponding to the changes of SO₂ and NO_x, the SO₂/NO_x ratio increased from 0.08–0.15 to 2.03 μg μg⁻¹. Table 2 shows the concentration variations of water-soluble ionic compositions of aerosol. The SO₄²⁻ did not change very much from 1987 to 1993 in Lushan, though its concentration was very low in 1989. The NO₃⁻ increased greatly, its concentration in 1993 was much higher than in 1987. In contrast to SO₂/NO_x, the ratio of SO₄²⁻/NO₃⁻ showed a continuous decreasing tendency—7.1 μg μg⁻¹ in 1993. From Tables 1 and 2, it can be seen that SO₂, NO_x, and aerosol concentrations in Lushan were much lower than those in the Lion and Hengshan Mountains, indicating that the air in Lushan was relatively clean and local air pollution was not serious because local emission was low and large cities and industry areas were far from the Lushan Mountains.

b. Atmospheric oxidizability in the Lushan Mountains

Atmospheric oxidizability was an important factor influencing acidification of precipitation. The average ozone concentration in the Lushan atmosphere was 37.5 ppb, which was in the range of the ozone background. Its daily variation was rather smooth with small differences between maximum and minimum. Ozone concentration was only a little higher in the afternoon than in the morning, similar to that in the Whiteface Moun-

tains in the United States. Although the ozone concentration in Lushan was low, atmospheric oxidizability was very strong. The observations in 1987 and 1989 showed that gaseous H₂O₂ concentration was high in Lushan; its average value was 1.7 ppb (Ding et al. 1992), which was the same as that in the upper air in southern China. In 1993, gaseous H₂O₂ was not measured, but the great amount of H₂O₂ in precipitation was an indicator of a very high gaseous H₂O₂ concentration in the Lushan atmosphere (Table 3).

In Lushan cloud water, the detection rate of H₂O₂ was 81.3%. Seven out of a total of 16 samples had a red deposit appear in the measurement process, which revealed that H₂O₂ concentration was very high in cloud water over the upper limit of the measurement method (the spectrophotometric method with leuco crystal violet). According to the experimental condition, the detection upper limit of the method was 19.0 μmol L⁻¹. The measurement results showed that 44% of H₂O₂ concentrations was less than 5 μmol L⁻¹ and 55% was more than 5 μmol L⁻¹. There was no obvious correlation between H₂O₂ concentration and electric conductivity in cloud water. The pH in cloud water showed a tendency to decrease when the H₂O₂ concentration went up. In rainwater, the aqueous H₂O₂ detection rate is 92%. Red deposit appeared in 6 out of all 12 samples. Fifty percent of the H₂O₂ concentration was less than 10.5 μmol L⁻¹, and the other 50% was higher than 10.5 μmol L⁻¹. Table 3 gives the comparisons of H₂O₂ concentration between rainwater and cloud water at nearly the same time. The H₂O₂ concentration in rainwater was obviously higher than that in cloud water. As the sampling sites were close to the mountaintop and girdled by clouds, precipitation was a process inside clouds. Since H₂O₂ concentration in rainwater was higher than that in cloud water, it was predicted that H₂O₂ concentration in upper cloud water would be much higher, that is, H₂O₂ concentration in cloud water increased with height as well as in rainwater.

The H₂O₂ concentration level in a different precipitation system was quite different. The average H₂O₂ concentration in the second precipitation system (16–17 March) was 4.87 μmol L⁻¹ and those in the third precipitation system (22–24 March) were all higher than 19 μmol L⁻¹. Such a high detection rate of aqueous H₂O₂ in cloud water and rainwater indicated that the

TABLE 3. The comparison of H₂O₂ concentration in rainwater and cloud water.

Sampling time (March)	H ₂ O ₂ in cloud water (μmol L ⁻¹)	H ₂ O ₂ in rainwater (μmol L ⁻¹)
14/2000–15/0800	0.000	0.507
15/2215–16/0700	1.091	9.315
22/0700–22/0945	2.844	>19.0
22/0955–22/1025	0.000	>19.0
22/1039–22/1115	2.844	>19.0
22/1518–22/1712	>19.0	>19.0
22/1712–22/2155	10.33	>19.0

TABLE 4. Chemical compositions of rainwater and cloud water in Lushan.

	pH	Ion	Ca ²⁺ μeq L ⁻¹	Mg ²⁺ μeq L ⁻¹	NH ₄ ⁺ μeq L ⁻¹	H ⁺ μeq L ⁻¹	SO ₄ ²⁻ μeq L ⁻¹	NO ₃ ⁻ μeq L ⁻¹	Cl ⁻ μeq L ⁻¹	F ⁻ μeq L ⁻¹
Cloud water	4.19	Concentration	156.3	27.2	179	64.6	411	128	40.6	17.0
	3.62–5.93	Percent of total anion or cation	36.6	6.4	41.9	15.1	68.6	21.4	6.8	2.9
Rainwater	4.26	Concentration	26.1	3.4	38.7	54.8	66.3	21	6.7	2.2
	3.71–5.48	Percent of total anion or cation	21.2	2.7	31.5	44.6	69.1	22	7.0	2.3
Ratio of cloud to rain (μeq μeq ⁻¹)			6.0	8.1	4.6	1.2	6.2	6.2	6.1	7.7

precipitation in this area was in a strong oxidative atmosphere. Therefore, the measured S(V) and NO₂ concentrations were very low in the cloud water and rainwater, usually less than 0.5 μmol L⁻¹. Since there was residual H₂O₂ in precipitation in most cases, the acidification of precipitation in Lushan was very sensitive to S(V). With increased gaseous SO₂ concentration, the acidification would become more serious.

c. Chemical compositions of cloud water and rainwater

Table 4 showed the concentration of ion compositions in cloud water and rainwater in the Lushan Mountains together with their percentages in total cation and anion concentrations. Since the cloud water was collected at ground level in Lushan, these samples could not represent average condition in clouds; they only represented the status in the lower part of clouds that were influenced by the terrain. The pH of cloud water varied from 3.62 to 5.39 with an average of 4.19. The frequency of pH less than 5.6 was 97%, indicating that cloud water was very acidified. Among anions, SO₄²⁻ was the highest with 68.6% of total anion concentration, NO₃⁻ was second with 21.4%, and Cl⁻ was the third with 6.8%. These three ions contributed to 97% of total anion concentrations. In the cation, the concentration of NH₄⁺ was the highest with 41.9% of total cation concentrations, Ca²⁺ was second with 36.6%, and H⁺ was third with 15.1%. These three ions contributed to 94% of total cation concentrations.

The pH values of rainwater samples were all less than 5.6. The average pH calculated by a rainfall-weighted arithmetic mean H⁺ concentration was 4.26 with minimum and maximum of 3.71 and 5.48, respectively. In cation, the concentration of H⁺ was the highest with 44.6% of total cation concentrations, which was caused by serious acidification of rainwater, NH₄⁺ was second with 31.5%, and Ca²⁺ was third with 21.2%. These three ions accounted for 97.3% of total cation concentrations. In anion, SO₄²⁻ concentration was the highest with 69.1% of total anion concentrations, NO₃⁻ was second with 21.6%, and Cl⁻ was third with 7%. These three ions contributed to 97% in the total anion concentra-

tions. As shown in Table 4, SO₄²⁻ in precipitation accounted for about 70% of total anion, which was in good agreement with the fact that air pollution was caused mainly by coal consumption in China.

It is a common phenomenon that concentrations of ionic compositions in cloud water were higher than those in rainwater at the same period (Gervat et al. 1984; Castillo et al. 1983). Ionic concentrations in cloud water were generally five to eight times higher than those in rainwater, slightly lower than that in measurements of Gervat et al. (1984). The exception was the H⁺ ion, which had a close concentration both in rainwater and cloud water. In cloud water, Ca²⁺ and NH₄⁺ concentrations contributed to 78.5% of the total cation concentration, and H⁺ concentration was only about 15.1%. In rainwater, the Ca²⁺ and NH₄⁺ concentrations were 52.7% of total cation concentration, and the H⁺ concentration was the highest among cations with up to 44.6% of total cation concentration. The percentage distribution of anion in rainwater was the same as that in cloud water.

Figure 2 showed concentration variations of the main ions in all 34 rainwater samples. The compositions in cloud water had the same variations. From the figure, note that concentrations of ions were quite different for different sampling times, different weather conditions, and different precipitation processes. However, Ca²⁺, Mg²⁺, SO₄²⁻, NH₄⁺, NO₃⁻, and Cl⁻ had nearly the same variation pattern, almost decreasing or increasing at the same time. It implied that the variations were influenced by the same or similar factors, such as air current origin, cloud–fog drop size distribution, and raindrop size distribution. The correlation of ions in rainwater was shown in Table 5. A good correlation among Ca²⁺, Mg²⁺, and Cl⁻ was observed. The SO₄²⁻ and NO₃⁻ were highly correlated with NH₄⁺ in rainwater with the correlation coefficient up to 0.954 and 0.936, respectively. The same good relationship between SO₄²⁻ and NH₄⁺ was found in cloud water. In Lushan, SO₄²⁻ and NH₄⁺ in precipitation mostly came from the scavenging of ammonium sulfate and ammonium bisulfate aerosol. Aerosols did not provide much H⁺, therefore H⁺ was only weakly positively correlated with SO₄²⁻ and NH₄⁺ in Lushan precipitation. The results of multiple regression analysis revealed H⁺ had no obvious relationship with any other single ion.

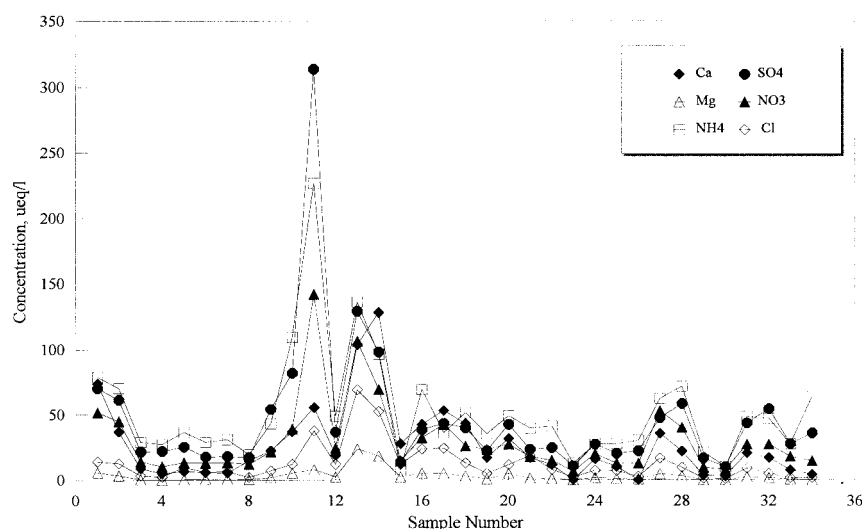


FIG. 2. Concentration variations of main ions in rainwater samples.

This meant that H^+ was determined by only the total balance of all anion and cation.

d. Ion ratio in rainwater and cloud water

Table 6 gives the SO_4^{2-}/NO_3^- ratio of rainwater and cloud water in Lushan as well as that in the other mountains. In rainwater, the ratio SO_4^{2-}/NO_3^- in Lushan was close to that in the Hengshan, Lion, and Baiyunshan Mountains, higher than that in Miaoershan, and much less than that in Emeishan in southwest China. In cloud water, the ratio in Lushan was less than that in the Hengshan, Lion, and Baiyunshan Mountains, and higher only than that in Miaoershan. From Table 6, note that the SO_4^{2-}/NO_3^- ratio in cloud water was higher than that in rainwater in these mountains except for Lushan, where the ratio was about $3.2 \mu\text{eq } \mu\text{eq}^{-1}$ both in cloud water and in rainwater. In Lushan, the ratio of SO_4^{2-}/NO_3^- in precipitation was $3.2 \mu\text{eq } \mu\text{eq}^{-1}$, which was close to the gaseous SO_2/NO_2 ratio $3.4 \mu\text{eq } \mu\text{eq}^{-1}$ (assume NO_2

= $0.85 NO_x$), but much less than the SO_4^{2-}/NO_3^- ratio $9.4 \mu\text{eq } \mu\text{eq}^{-1}$ in aerosol. Since the local SO_2 concentration was low, gaseous SO_2 had a very small contribution to SO_4^{2-} in precipitation, which was about 9% in 1989 (Ding et al. 1992). Most of the SO_4^{2-} in precipitation came from the scavenging of aerosol in or below clouds.

The ratio of NH_4^+/Ca^{2+} in Lushan precipitation was close to or less than that in other mountains, as seen in Table 7, which indicated that NH_4^+ neutralization in Lushan was lower than that in other mountains because of the low NH_3 concentration in the Lushan atmosphere. The model calculations revealed that 46.5% of NH_4^+ in rainwater was from below-cloud scavenging (Zhang et al. 1995). In the contribution from below-cloud scavenging, 84.8% of NH_4^+ was mainly from the washout of gaseous NH_3 by rainwater. During the measurement period, the average concentration of gaseous NH_3 in Lushan was $1.13 \mu\text{g } m^{-3}$, which was less than $2.9 \mu\text{g } m^{-3}$ in Baiyunshan and $8.4 \mu\text{g } m^{-3}$ at the top of the

TABLE 5. Correlation coefficient of main ions in rainwater (total sample number 34).*

	H^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
Ca^{2+}	-0.184						
Mg^{2+}	-0.139	0.925 (0.01)					
NH_4^+	0.445 (0.01)	0.633 (0.01)	0.654 (0.01)				
SO_4^{2-}	0.539 (0.01)	0.557 (0.01)	0.563 (0.01)	0.954 (0.01)			
NO_3^-	0.338 (0.05)	0.752 (0.01)	0.771 (0.01)	0.936 (0.01)	0.933 (0.01)		
Cl^-	-0.101	0.892 (0.01)	0.959 (0.01)	0.699 (0.01)	0.634 (0.01)	0.819 (0.01)	
F^-	0.020	0.654 (0.01)	0.643 (0.01)	0.555 (0.01)	0.543 (0.01)	0.642 (0.01)	0.709 (0.01)

* The number in parentheses is the significant level.

TABLE 6. Comparison of $\text{SO}_4^{2-}/\text{NO}_3^-$ in rainwater and cloud water in four mountains.

	Lushan March 1993	Hengshan March 1989	Hengshan March 1993	Lion March 1988	Lion March 1989	Miaoershan March 1988	Baiyunshan March 1988
Rainwater ($\mu\text{eq } \mu\text{eq}^{-1}$)	3.2	3.28	3.84	1.23	3.59	0.94	3.63
Cloud water ($\mu\text{eq } \mu\text{eq}^{-1}$)	3.2	4.5	4.2	6.2	4.25	1.93	5.3

Guangzhou television tower and close to $1.3 \mu\text{g m}^{-3}$ in Hengshan and $1.12 \mu\text{g m}^{-3}$ in the Lion Mountains. Thus, the contribution of gaseous NH_3 to NH_4^+ in precipitation was very limited.

In Lushan, the cloud water composition and aerosol concentration in Lushan changed with the weather system (Ding et al. 1992), and the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio in precipitation was quite different from that in aerosol. Therefore, composition of precipitation in Lushan was not solely from the washout of local aerosol and gaseous pollutants. As the low concentrations of SO_2 , NO_x , NH_3 , and aerosol were put into consideration, influence of local air pollution on acidification was very limited in Lushan. Long-distance transportation of pollutant was suggested to be one of the sources for the acidification. In 1989, Ding et al. (1992) found that the concentrations of components in aerosol and precipitation showed significant increases when the air current came from the northwest, where strong emission areas existed about 100 km away from Lushan.

e. Comparisons of the chemical characteristics of various states of precipitation

On 15 and 20 March 1993, there were two frozen rain or snow processes in Lushan. Seven solid precipitation samples were collected. The compositions between solid and liquid phase precipitation were compared in Table 8 to reveal the differences of pH and ion concentrations in various phase precipitation in the same season.

Average pH of solid precipitation was 0.6 higher than that of liquid precipitation, that is, liquid precipitation was more acidic than solid precipitation. As for ion concentration, Ca^{2+} and Mg^{2+} concentrations as well as their percentages in total cation concentrations in solid precipitation were much higher than those in liquid precipitation by a factor of 4–6. The NH_4^+ had nearly the same percentages in total anion concentration in both liquid and solid precipitation. The percentage of SO_4^{2-}

in liquid precipitation was higher than that in solid precipitation. Relatively high SO_4^{2-} and relatively low Ca^{2+} and Mg^{2+} concentrations in liquid precipitation was the main reason why liquid precipitation was more acidic.

Concentrations of all ions except for H^+ in solid precipitation was normally 2–5 times higher than those in liquid precipitation, but H_2O_2 concentration in solid precipitation was obviously less than that in liquid precipitation. In solid precipitation, H_2O_2 concentrations of all samples were less than $19.0 \mu\text{mol L}^{-1}$ with the average of $4.46 \mu\text{mol L}^{-1}$. In liquid precipitation, 75% of the samples of the H_2O_2 concentration was higher than $19.0 \mu\text{mol L}^{-1}$. When the supercooled cloud droplets rimed on the snow surface, H_2O_2 dissolved in cloud droplets could be vaporized due to releasing the frozen heat, which increased temperature and decreased the solubility of H_2O_2 . Thus, the concentration of H_2O_2 in snow could be lower than that of rainwater. The Ca^{2+} and Mg^{2+} ions in precipitation were from scavenged particles in coarse mode. From Table 6, it was found that the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in snow and rainwater was very close, indicating that those two ions in both kinds of hydrometeors were from the same source. Their higher concentrations in solid precipitation showed that its scavenging was more efficient than that of rain in the same water content and scavenging distance. The samples of the solid precipitation were snowflakes falling from cloud and the major shape was planer. The snowflake, with the same water content as the raindrop, had a larger effective scavenging diameter, even if the collection coefficient was not greater than that of the raindrop. The ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ in both kinds of precipitation was the same—about $0.55 \mu\text{eq } \mu\text{eq}^{-1}$. These ions in precipitation were from scavenged fine particles and dissolved NH_3 and SO_2 . The higher concentrations of NH_4^+ and SO_4^{2-} in solid samples can be explained by the reason that the planar form snow had higher collection efficiency in the Greenfield gap (P. K. Wang 1992). The average ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ was $2.6 \mu\text{eq } \mu\text{eq}^{-1}$ in solid precipitation and $3.3 \mu\text{eq } \mu\text{eq}^{-1}$ in liquid precipitation, indicating that NO_3^- was more easily scavenged by snow.

TABLE 7. The comparison of $\text{NH}_4^+/\text{Ca}^{2+}$ ratio in rainwater in four mountains.

	Lushan March 1993	Heng- shan March 1989	Heng- shan March 1993	Lion March 1988	Lion March 1989	Baiyun- shan 1984– 85
Rainwater ($\mu\text{eq } \mu\text{eq}^{-1}$)	1.48	1.61	2.5	2.17	1.04	7.15

f. Comparisons of precipitation characteristics at the top and foot of the Lushan Mountains

Lushan is surrounded by a broad flat area and its altitude is about 1000 m higher than the Meilin and Gaofang areas near the city of Nanchang. Nanchang lies

TABLE 8. The comparison of pH and ionic concentration in solid and aqueous precipitation.

	pH	Ion	Ca ²⁺ ($\mu\text{eq L}^{-1}$)	Mg ²⁺ ($\mu\text{eq L}^{-1}$)	NH ₄ ⁺ ($\mu\text{eq L}^{-1}$)	H ⁺ ($\mu\text{eq L}^{-1}$)	SO ₄ ²⁻ ($\mu\text{eq L}^{-1}$)	NO ₃ ⁻ ($\mu\text{eq L}^{-1}$)	Cl ⁻ ($\mu\text{eq L}^{-1}$)	F ⁻ ($\mu\text{eq L}^{-1}$)	SO ₄ ²⁻ /NO ₃ ⁻ ($\mu\text{eq } \mu\text{eq}^{-1}$)
Solid	4.87	Concentration	108 ± 75	16.3 ± 16	57.4 ± 36.3	13.6 ± 11.5	105.0 ± 75.5	40.7 ± 29.8	27.2 ± 20.8	7.5 ± 5.6	2.6
	4.41–5.48	Percent of anion or cation	55.4	8.3	29.4	6.9	58.2	22.5	15.0	4.1	
Liquid	4.24	Concentration	20.4 ± 6.2	2.5 ± 0.7	37.4 ± 6.1	57.7 ± 6.1	63.6 ± 15.9	19.3 ± 3.9	5.3 ± 1.2	1.9 ± 0.8	3.3
	3.71–4.83	Percent of anion or cation	17.3	2.1	31.7	48.9	70.4	21.4	5.8	2.1	

south of Lushan and is the main industrial area in Jiangxi Province with high emission rates of SO₂ and NO_x. In the springtime, a northern cold front usually moves southerly. As Fig. 1 shows, Meilin is 20 km (upwind direction) north of Nanchang, and Gaofang (downwind direction) is south of Nanchang. The local emission of air pollutants was low in the two areas: SO₂ concentration was 3.7 and 8.5 ppbv, and SO₄²⁻ in aerosol was 4.9 and 6.7 $\mu\text{g m}^{-3}$, respectively, in Meilin and Gaofang (Tang et al. 1995). The precipitation characteristics between the Lushan, Meilin, and Gaofang areas are compared in Table 9.

From Table 9, note that the total concentrations of ionic components in rainwater at the three sites increased from Lushan to Meilin to Gaofang. Precipitation was influenced by local air pollution in Meilin. Due to below-cloud scavenging of raindrops, the total ionic concentration in Meilin was higher than that in Lushan. Gaofang had high concentrations of air pollutants, probably influenced by Nanchang emission, because Gaofang was located in the downwind direction of Nanchang. As the consequence of below-cloud scavenging, the total ionic concentration in Gaofang precipitation was higher than that in Meilin. Although total ionic concentration showed an increase tendency from Lushan to Meilin to Gaofang, individual ions did not show the same changing tendency as the total ionic concentration. The NH₄⁺ concentration in Lushan was much higher than that in Meilin and Gaofang because less NH₃ was emitted from the acidic red soil in Meilin and Gaofang. For ion ratios in rainwater, the SO₄²⁻/NO₃⁻ ratio was 3.14, 14.7, and 8.5 $\mu\text{eq } \mu\text{eq}^{-1}$, respectively, in Lushan, Meilin, and Gaofang, which showed that H₂SO₄ played a dominant role in the acidification in urban rainwater. The Ca²⁺/NH₄⁺ ratio was 0.67, 31.3, and 18.5 $\mu\text{eq } \mu\text{eq}^{-1}$ in the precipitation of the three sites, respectively. The ratio in Lushan was obviously less than that in Meilin and Gaofang, which showed that the neutralization of gaseous NH₃ to acidification of precipitation was less important in the Nanchang area, which is characterized by acidic red soil.

g. Acidification tendency of precipitation in mountains

Tables 10 and 11 give the comparisons of characteristics of cloud water and rainwater in four mountains. The pH of cloud water and rainwater was less than 5.6 in the four mountains. The acidification of cloud water and rainwater was steadily getting more and more serious from 1987 to 1993 in the Lushan Mountains, from 1987 to 1989 in the Lion Mountains, and from 1986 to 1988 in the Baiyunshan Mountains. The average pH decreased year by year, and the acidified frequency increased in the mountains except Hengshan, where the average pH of cloud water increased year by year. For rainwater, in Lushan, the average pH was 5.41 in 1982–83, 5.18 in 1987–89, and 4.26 in 1993. The H⁺ con-

TABLE 9. The chemical characteristics of precipitation at the top and foot of the Lushan Mountains.

Sites	H ⁺ ($\mu\text{eq L}^{-1}$)	NH ₄ ⁺ ($\mu\text{eq L}^{-1}$)	Ca ²⁺ ($\mu\text{eq L}^{-1}$)	Mg ²⁺ ($\mu\text{eq L}^{-1}$)	SO ₄ ²⁻ ($\mu\text{eq L}^{-1}$)	NO ₃ ⁻ ($\mu\text{eq L}^{-1}$)	Cl ⁻ ($\mu\text{eq L}^{-1}$)	F ⁻ ($\mu\text{eq L}^{-1}$)	Total ions ($\mu\text{eq L}^{-1}$)	SO ₄ ²⁻ /NO ₃ ⁻ ($\mu\text{eq } \mu\text{eq}^{-1}$)	Ca ²⁺ /NH ₄ ⁺ ($\mu\text{eq } \mu\text{eq}^{-1}$)
Lushan	44.6	31.5	21.2	2.7	69.1	22	7.0	2.3	200.4	3.14	0.67
Meilin	30.2	1.7	53.2	21.0	177.6	12.1	12.0	0.0	307.8	14.7	31.3
Gaofang	81.3	3.4	62.8	30.0	185.4	21.7	12.8	0.6	398	8.5	18.5

centration increased 13 times during the 10 years and acidified frequency increased from 77% in 1982–83, 61.8% in 1987–89, and 100% in 1993. In Hengshan, the average pH was 4.47, 4.26, and 4.22 in 1988, 1989, 1993, respectively, with a little increase in acidity and 100% acidified frequencies. In the Lion Mountains, the average pH was 4.52, 4.47, and 3.89 in 1987, 1988, and 1989, respectively. The acidity of precipitation showed an increasing tendency, but the acidified frequency decreased steadily year by year. In Baiyunshan, acidification of precipitation was very serious in 1987–88 and the acidified frequency increased yearly.

In view of variations of ionic concentrations in cloud water, ionic concentrations had a little change during 1988 and 1989 in Hengshan, and even had a decreasing tendency during 1987–89 in Lushan; however, they increased greatly during 1989–93 in Lushan and Hengshan. The concentrations of main ions increased 2–7 times in Lushan except for NH₄⁺ and 1.5–9 times in Hengshan except for Ca²⁺ and H⁺. The ionic concentrations in cloud water increased quickly during 1987–89 in the Lion and Baiyunshan Mountains. The temporal variation of ionic concentrations in rainwater was similar to that in cloud water.

The temporal variation of ion concentration in precipitation was highly correlated with regional economic development and air pollution. Lion and Baiyunshan Mountains were located in between Guandong and Guangxi Provinces, where fast economic development was started much earlier than other areas of China. The environmental problems caused by the fast economic development were dominant and resulted in a great in-

crease in ionic concentrations in precipitation during 1987–89 in the Lion and Baiyunshan Mountains. Lushan and Hengshan, located in the middle of China where fast economic development was started much later than that in southern China, have just recently begun having environmental problems such as acidification of precipitation. The ionic concentrations in precipitation had a little variation and even had some decrease during 1987–89, but there were great increases in Lushan and Hengshan during 1989–93 because atmospheric pollution got worse after 1990.

In view of spatial variation, concentrations of main ions in cloud water increased from Lushan to Hengshan to Lion Mountains in 1989, that is, from the north to the south. In spring, these areas were under the control of a northern cold front. Moving southward, the northern cold front carried and accumulated pollutants continuously, which caused a high concentration of ions in cloud water from north to south.

The SO₄²⁻/NO₃⁻ ratios in cloud water in the four mountains were all greater than 3 $\mu\text{eq } \mu\text{eq}^{-1}$ and those in rainwater were about 1.2–4.5 $\mu\text{eq } \mu\text{eq}^{-1}$, much less than the ratio in other areas in China. The ratio in rainwater was equal to or less than that in cloud water, which revealed that SO₂ or SO₄²⁻ aerosol was washed out effectively in the process of cloud formation. Comparing the ratio temporal variation in cloud water, the ratio in Lushan, Lion, and Baiyunshan Mountains had an obviously decreasing tendency, but the ratio in Hengshan had almost no variation in recent years. The low SO₄²⁻/NO₃⁻ ratio and its decreasing tendency in precipitation of the four mountains implied that nitric acid was

TABLE 10. The comparison of chemical characteristics in cloud water in four mountains.

	Lushan			Hengshan			Lion			Baiyunshan	
	1987	1989	1993	1988	1989	1993	1987	1988	1989	1987	1988
pH	5.36	4.47	4.20	4.08	4.33	4.78	4.53	4.37	3.56	5.36	4.64
Percent, pH < 5.6	32	89	96	89	100	71	—	79	93	—	—
F ⁻ , $\mu\text{eq L}^{-1}$	9.1	8.46	17.0	12.7	8.5	77.9	—	23.6	16.4	—	168
Cl ⁻ , $\mu\text{eq L}^{-1}$	25.6	22.5	40.6	34.0	39.4	78.2	6.5	16.0	36.4	331	1307
SO ₄ ²⁻ , $\mu\text{eq L}^{-1}$	440	178	411	363	332	712.5	93.0	229	914	3094	3776
NO ₃ ⁻ , $\mu\text{eq L}^{-1}$	73.5	33.4	128	89.2	74.4	168.0	15.0	49.4	214.9	160.8	707
NH ₄ ⁺ , $\mu\text{eq L}^{-1}$	323	153	179	333	308.9	468.3	80.8	199.7	538.2	2496	2642
Ca ²⁺ , $\mu\text{eq L}^{-1}$	213	21.5	156	101	129.7	99.4	45.0	61.5	171.6	—	1302
Mg ²⁺ , $\mu\text{eq L}^{-1}$	25.2	9.3	27.2	32.3	31.7	69.6	27.6	10.2	43.9	—	307
H ⁺ , $\mu\text{eq L}^{-1}$	4.4	33.9	64.6	83.4	47.0	16.6	29.8	42.4	273.5	4.28	22.9
SO ₄ ²⁻ /NO ₃ ⁻ , $\mu\text{eq } \mu\text{eq}^{-1}$	6.0	5.3	3.2	4.1	4.5	4.2	6.2	4.6	4.3	19.2	5.3

TABLE 11. The comparison of chemical characteristics in rainwater in four mountains.

	Lushan		Hengshan			Lion			Baiyunshan		
	87-89	1993	1988	1989	1993	1987	1988	1989	1986	1987	1988
pH	5.18	4.26	4.47	4.26	4.22	4.52	4.47	3.89	3.87	4.23	3.66
Percent, pH < 5.6	67.3	100	100	100	100	100	89	80	—	80	95
F ⁻ , $\mu\text{eq L}^{-1}$	—	2.2	1.6	1.1	1.4	—	—	0.7	4.6	<0.01	5.9
Cl ⁻ , $\mu\text{eq L}^{-1}$	44.0	6.7	10.4	21.7	9.1	16.8	18.7	15.9	24.6	39.7	58.3
SO ₄ ²⁻ , $\mu\text{eq L}^{-1}$	25.9	66.3	83.6	118	175	23.7	31.6	176	94.3	64.1	173
NO ₃ ⁻ , $\mu\text{eq L}^{-1}$	6.56	21	37.9	36.0	45.6	12.6	25.5	48.9	33.6	26.3	47.6
NH ₄ ⁺ , $\mu\text{eq L}^{-1}$	27.2	38.7	79.9	63.1	90.9	22.1	40.5	74.1	74.8	55.7	103
Ca ²⁺ , $\mu\text{eq L}^{-1}$	83.9	21.2	33.4	37.4	36.3	28.1	27.7	71.4	38.9	—	47.5
Mg ²⁺ , $\mu\text{eq L}^{-1}$	2.14	2.7	14.6	14.7	6.1	7.2	4.8	27.6	8.6	—	8.4
H ⁺ , $\mu\text{eq L}^{-1}$	6.60	54.8	33.8	55.3	60.2	30.1	34.1	129.7	134	58.9	218.8
SO ₄ ²⁻ /NO ₃ ⁻ , μeq^{-1}	4.50	3.21	2.21	3.28	3.84	1.88	1.24	3.60	2.81	2.44	3.63

becoming a more significant factor in causing acid precipitation, although local HNO₃ concentration was low. The ratio temporal variations of SO₄²⁻/NO₃⁻ in cloud water of Lushan, Hengshan, and Lion Mountains had a different tendency from SO₂/NO_x in local air, which showed that the pollution of cloud water did not have a good correlation with local NO_x and SO₂ in the air. Long-distance transportation was implied to be the significant acidified mechanism.

4. Conclusions

The rainwater and cloud water in Lushan was greatly acidified in springtime. The average pH of cloud water and rainwater was 4.19 and 4.26, respectively. The causes and mechanism of acidification are very complicated. The concentration of local air pollutants was low and chemical compositions in precipitation were high, which indicated that the acidification was caused by a washout of local air pollutant as well as by long-distance transportation of acidic substances.

In various states of precipitation measured in Lushan, ion concentrations in cloud water and solid precipitation were 5–8 and 2–5 times higher than those in rainwater, respectively. But H₂O₂ concentration in rainwater was higher than that in cloud water and solid precipitation.

The main acidic substance to cause the acidification of precipitation was H₂SO₄. This result was consistent with air pollution characterized by coal consumption in China. The SO₄²⁻/NO₃⁻ ratio in rainwater and cloud water in Lushan was less than that in other mountains. More attention should be paid to the role of HNO₃ in the acidification. The NH₄⁺/Ca²⁺ ratio in Lushan was also less than that in other mountains, which showed that the neutralization of NH₄⁺ in precipitation in Lushan was lower than that in the other areas.

From the results measured in recent years, cloud water and rainwater in Lushan, Hengshan, Lion, and Baiyunshan Mountains in eastern China were acidified. The acidification in most of the mountains tended to be serious with pH decreasing and acidified frequency increasing gradually.

In view of temporal variation, the ion concentrations in cloud water and rainwater in Lushan and Hengshan remained relatively stable during 1987–89 but increased greatly during 1989–93. The ion concentrations in cloud water and rainwater in Lion and Baiyunshan Mountains during 1987–93 increased greatly too. It implied that these increases had a relationship with economic development.

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