CHARACTERISTICS OF ACID RAIN IN JINYUN MOUNTAIN, CHONGQING, CHINA

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Abstract. The pH and chemical composition of 126 precipitation samples, which were collected from April 1998 to November 1999 in Jinyun Mountain, Chongqing, China, were analyzed. The results showed: the average pH was 5.23 and the average electrical conductivity was 33.90 µs/cm, which showed that the pollution situation in Jinyun Mountain was more favourable than that in the other acid rain regions of southern China and Chongqing urban areas. The concentration of SO_4^{2-} accounted for 84.61% of total anions, and the concentration of NH_4^+ and Ca^{2+} accounted for 77.36% of total cations of rainfall in Jinyun Mountain. The high concentration of NH_4^+ and Ca^{2+} neutralized greatly the acidity of acid ions, which resulted in relatively high pH and lower frequency of acid rain, but the acidifying rain may exert potential injury to forest ecosystem. The seasonal variations in the rainfall pH and chemical composition were evident, which may be related to the seasonal variations in precipitation amount in Jinyun Mountain. The effects of acid rain on forest ecosystem have time lag, so it is necessary to study the dynamic characteristics of acid deposition more carefully and comprehensively.
Keywords. *pH , major ions, air pollution, acidifying rain*

Introduction

The air pollutants from burning the coal with high sulfur and high ash content without any treatment are the source of serious air pollution. Especially, Chongqing Municipality, which is located at Southwestern China, is well known as a typical area polluted by coal combustion and has suffered from serious air pollution and acid rain [6, 17, 19]. This situation in Chongqing downtown has been improved in recent years since some SO_2 emission control technologies have been developed, such as SO_2 emission by high chimneys, bio-briquette technique, the installation of the desulfurizing equipment, and so on [3, 4, 20]. But, in general, Chongqing still suffers from serious air pollution and acid rain, and the acid deposition has tended to extend from urban site to the suburb sites in recent years [3, 16, 22]. With the proceeding of Three Gorges Reservoir of Yangtze River, the government has paid more attention to the ecological and environmental problems including serious air and water pollution in Chongqing region. Thus, it is necessary to study the new dynamic characteristics of precipitation chemistry in Chongqing (especially, in the suburb regions of Chongqing) in order to protect the forest vegetation and ecological environment better.

The National Nature Reserve of Jinyun Mountain is located in Beibei district, 60 km north from Chongqing downtown. Having good vegetation and lacking heavy industry, Jinyun Mountain was thought to be free from serious air pollution and acid rain

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compared with the situations in Chongqing downtown and other urban areas (e.g. [1]). But, in recent years, the plant damage caused by acid rain has emerged in this region. The objective of our research in this experiment was to analyze the dynamic characteristics of precipitation chemistry and pH value in Jinyun Mountain in order to monitor those air pollutions and control the damage to forest ecosystem.

Materials and methods

Experiment site

Jinyun Mountain (29°49'N, 106°20'E) covers 1400 ha and the altitude is 350–952 m. The typical vegetation is sub-tropical broadleaved evergreen forest, which is the one of best-protected broadleaved evergreen forests in the Yangtze River basin. The plant species are abundant (over 1400 species), and the coverage of vegetation is over 90%. Some sensitive plant species in this region had been hazarded by acid rain in recent years.

Jinyun Mountain region belongs to sub-tropical humid monsoon climate zone. Annual mean temperature is 18.2°C, the frost-free period is 334 days and the annual hours of sunshine were 1288.1. The bulk of rain falls from April through October; the average annual precipitation is 1143 mm and the annual relative humidity is 80%. The main soil type is locally called yellow mountain soil, which corresponds to Haplic Acrisol in the FAO classification system.

Sampling and chemical analysis

126 rainfall samples were collected on a daily basis using a wet-only sampler in Jinyun mountain (alt. 500 m) from April 1998 to November 1999. The stored samples were sent in ice-cooled boxes to the laboratory at the foot of Jinyun Mountain. The analytical parameters were pH value, electrical conductivity and the concentrations of major ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^- and Cl^-). The pH value of each sample was measured by the pH meter with a glass electrode and conductivity was measured by a digital conductivity meter. In the samples, SO_4^{2-}, NO_3^- and Cl^- concentrations were measured by ion chromatography. K^+, Na^+, Ca^{2+} and Mg^{2+} concentrations were measured by atomic absorption spectrometry, and NH_4^+ concentration was measured by spectrophotometric indophenol method. Each data point was generated as an average of three measurements.

Data from monitoring acid rain in Jinyun Mountain were analyzed to characterize the pH value and chemical compositions of precipitation. The seasonal differences of pH and electrical conductivity were analyzed by the analysis of variance (ANOVA) and the relationships between different major ions were examined by the principal component analysis (PCA) and correlation analysis.

Results

The pH value and electrical conductivity

The general characteristics

The average pH value of 126 rainfall samples in Jinyun Mountain was 5.23. In comparison to the other regions, this value was lower than pH in Northern China, but was much higher than the mean pH in Southern China, the downtown and Nanshan Mountain in Chongqing urban (*Table 1*).

Although the average pH was higher than other typical acid rain areas in Chongqing, pH of individual rainfall in Jinyun Mountain showed a very large fluctuation, ranging

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***Table 1.** The average pH value of precipitation in various regions of China*

China (north)[a]	China (south)[a]	Chongqing (downtown)[b]	Chongqing (Nanshan Mt.)[c]	Chongqing (Jinyun Mt.)
5.80	4.70	4.11	4.60	5.23

[a] [12], [b] [6], [c] [15].

from 3.80 to 7.30 (see *Fig. 1*). The number of samples below pH 5.6, the pH of unpolluted water equilibrated with atmospheric CO_2, was 77, accounted for 61.1% of total samples. About 0.8% of the rainfall showed a pH of lower than 4.0 and 44.4% had pH between 4.0 and 5.0. The frequency distribution of precipitation pH was similar to a bimodal distribution and the kurtosis is -1.079.

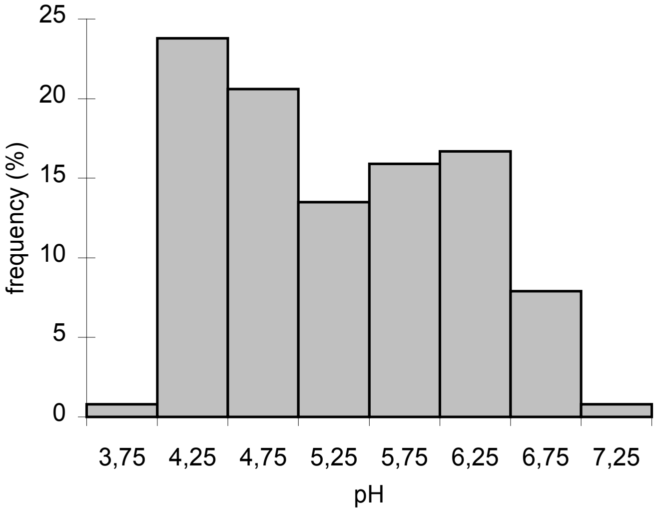

***Figure 1.** The pH frequency distribution of precipitation in Jinyun Mountain*

The pH values of precipitation were not correlated directly with the concentrations of major ions, but were related to the neutralized effects of acid anions and alkaline cations [16, 20]. Thus, the single precipitation pH could not reflect the degree of precipitation pollution. The average conductivity of rainfall in Jinyun Mountain was 33.90 µs/cm (the maximum value was 131.0 µs/cm and the minimum value was 5.5 µs/cm), which significantly was lower than that in Chongqing downtown (73.5 µs/cm) [18]. That is to say, the situation of air and precipitation pollution in Jinyun Mountain were really much favourable than that in Chongqing urban areas.

Seasonal variation

Table 2 lists the results of seasonal differences of pH and electrical conductivity analyzed by ANOVA. The precipitation pH and conductivity showed pronounced seasonal variations. The average pH (4.24) in the winter was lower significantly than that in other three seasons and the frequency of acid rain in the winter was also significantly higher ($P<0.01$), which may be related with the seasonal variation of precipitation amount. The conductivity had maximum value in the winter and minimum value in the summer, which showed the situation of air and precipitation pollution in Jinyun Mountain were much severe in winter than in summer.

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Table 2. *The seasonal variation of precipitation pH and conductivity in Jinyun Mountain*

season	pH			conductivity (μs/cm)	frequency of acid rain (%)
	mean	min	max		
spring	5.37±0.83[a]	4.00	6.55	39.52[a]	53.1
summer	5.17±0.77[a]	4.10	7.30	21.69[b]	65.1
autumn	5.36±0.82[a]	4.00	6.90	38.88[a]	50.0
winter	4.24±0.22[b]	3.80	4.50	56.81[a]	100.0

The different letter in the same column means the values have significant difference (p<0.01)

Major Ions

Anions

The acid rain in Jinyun Mountain was also classified to sulfuric acid type as in Chongqing urban areas and Southern China. Among all measured anions, SO_4^{2-} was the most abundant with an average of 212.85 μeq/l (see *Table 3*), which accounted for 84.61% of the total anions (*Fig. 2a*). The second most abundant anion was Cl^- with an average concentration of 24.70 μeq/l. The average NO_3^- concentration, 14.02 μeq/l, was lower than one tenth of SO_4^{2-} and accounted for 5.57% of the total anions.

The sum of all anions amounted to 288.45 μeq/l, which was much lower than those of the Chongqing urban areas (see *Table 3*), but considerably higher than those of the typical acid rain areas in Northeast American and Central Europe [6, 9, 10, 15]. If all these ions existed as free acid forms, the precipitation pH would have been lower than 5.23. This large discrepancy indicated that the acids present in the precipitation of Jinyun Mountain had gone through a significant neutralization process.

The concentration of NO_3^- was much lower than that of SO_4^{2-}. Thus, the ratio of the concentration of NO_3^- to SO_4^{2-} (N : S ratio), 0.07, was much lower than the value obtained from some developed countries [8, 9, 10, 11], which showed intensive influence of SO_2 from the coal burning and weak influence of NO_x from traffic on precipitation. But, with the development of vehicle-industry and living standard of people in China, emissions of NO_x are expected to increase rapidly and will become another important source of air pollution.

Cations

As seen in much of the monitoring data for precipitation in China, the difference among the developed countries in Northeast American and Central Europe resulted from high levels of cations, such as NH_4^+ and Ca^{2+} [6, 7]. The measured mean concent

Table 3. *The average ion composition of precipitation in various regions of Chongqing*

ion	downtown	Nanshan Mountain	Jinyun Mountain
K^+	17.0	82.6	18.15
Na^+	17.0	23.9	28.34
Ca^{2+}	125.0	418.0	80.78
Mg^{2+}	31.0	40.3	18.82
NH_4^+	123.0	106.0	142.37
SO_4^{2-}	299.0	469.0	212.85
NO_3^-	23.0	45.0	14.02
Cl^-	30.0	27.6	24.70
∑anions	352.0	541.6	251.57
∑cations	313.0	670.8	288.45
∑anions : ∑cations	1.12	0.81	0.87

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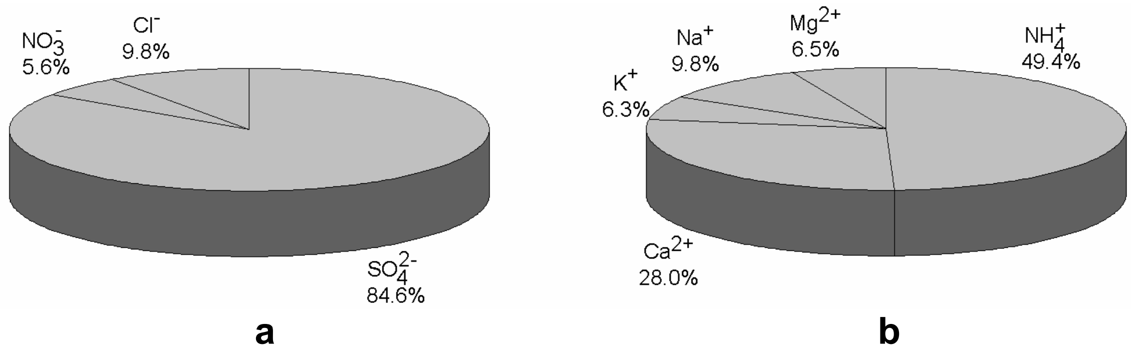

Figure 2. *The major ion composition of precipitation in Jinyun Mountain.* a: *anions;* b: *cations*

rations of NH_4^+ and Ca^{2+} in Jinyun Mountain were 142.37 μeq/l and 80.78 μeq/l respectively (see *Table 3*), which accounted for 49.36% and 28.00% of all cations respectively (see *Fig. 2b*). The NH_4^+ concentration was higher than that in Chongqing urban areas while the concentration of Ca^{2+} was much lower. The high level of NH_4^+ in precipitation coincides with level of ammonia emissions in the neighboring region of Jinyun Mountain. The Nature Reserve is surrounded by farm fields, thus the intensive fertilization and relatively poor treatment of waste from barns and houses might be the reasons for the higher levels of gaseous ammonia. The low level of Ca^{2+} in the precipitation may be related the high coverage of vegetation in Jinyun Mountain and it's neighboring areas which decreased the natural alkaline dust from roads and fields.

Statistical analysis

Relationships between measured major ions were examined through factor analysis and correlation analysis. The results analyzed by principal component analysis (PCA) by varimax rotation to a set of orthogonal axes for 1008 precipitation data were presented in *Table 4*.

Component 1 accounted for 57.6% of the total variance and had high loadings for K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+ and SO_4^{2-}. In component 2, NO_3^- was strongly loaded and accounted for 15.6% of the total variance. In component 3, Cl^- was loaded highest and accounted for 9.1% of total variance. The first three components accounted for 82.3% of total variance.

The correlations among major ions were presented in *Table 5*. The highest correlations appeared between every alkaline cation and SO_4^{2-}. Especially, the correlation coefficients between Ca^{2+} and SO_4^{2-}, NH_4^+ and SO_4^{2-} were 0.752 and 0.735 ($P<0.01$), respectively, revealing their co-occurrence in precipitation mostly as $CaSO_4$, $(NH_4)_2SO_4$, $(NH_4)HSO_4$ and so on. In other words, SO_4^{2-} ions in the precipitation were present mostly as neutralized forms and significantly decreased the precipitation acidity, which reduced the direct damage of acid rain to forest ecosystem in Jinyun Mountain.

Seasonal variation

Fig. 3 presents the seasonal variation of major ions in Jinyun Mountain. Among the major ions, the most abundant anion, sulfate ion (SO_4^{2-}), showed pronounced seasonal variation. A distinctive SO_4^{2-} contribution maximum occurred during the winter and dropped to a minimum in the summer because SO_2 emissions were more prevalent in the winter. The two most abundant cations, ammonium (NH_4^+) and calcium (Ca^{2+}), also

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Table 4. *The PCA results for the precipitation of Jinyun Mountain*

ions	components		
	1	2	3
K^+	0.879	-0.207	-0.044
Na^+	0.726	-0.345	0.145
Ca^{2+}	0.852	0.251	0.190
Mg^{2+}	0.762	0.420	-0.067
NH_4^+	0.846	0.298	-0.080
SO_4^{2-}	0.856	0.007	0.377
NO_3^-	0.459	0.738	0.429
Cl^-	0.588	-0.462	0.578
Eigenvalue	4.610	1.249	0.729
percent of trace%	57.6	15.7	9.1

Table 5. *The correlations between ions of precipitation in Jinyun Mountain*

	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
K^+	0.632**	0.775**	0.509**	0.690**	0.738**	0.262*	0.558**
Na^+		0.610**	0.450**	0.466**	0.509**	0.145	0.521**
Ca^{2+}			0.540**	0.617**	0.752**	0.170	0.506**
Mg^{2+}				0.668**	0.649**	0.552**	0.241*
NH_4^+					0.735**	0.541**	0.332*
SO_4^{2-}						0.251*	0.343*
NO_3^-							0.141

**P<0.01, *P<0.05

showed seasonal variations. NH_3 concentration in the air was much higher in spring and winter and substantially lower in the rest of the seasons because of the agricultural activities in Chongqing. Thus, NH_4^+ had high concentration in spring and winter and low concentration in summer and autumn. On the other hand, Ca^{2+}, an ion mainly introduced from dust, showed the highest concentration in the dry season of winter due to the minimum dilution effect and relatively lower coverage of vegetation.

Discussion and conclusions

Data from the acid rainfall monitoring in Jinyun Mountain from April 1998 to November 1999 were analyzed to characterize the chemical composition of precipitation. Major conclusions were summarized as follows.

The air pollution and acid rain in Jinyun Mountain were relatively less serious compared with those in Chongqing urban areas. The average precipitation pH in Jinyun Mountain was 5.23 due to the neutralization and the average conductivity was 33.90 μs/cm, which showed the air environment in Jinyun Mountain was better than that in Chongqing urban region. But the frequency of acid rain was over 60% and the pollution in winter was severe (the minimum pH was only 3.80 and the average pH was 4.24) in Jinyun Mountain. If no measures are taken to reduce the sulphur emissions, the effects seen today are likely to increase to large areas with impacts on the health of forest ecosystem in the Nature Reserve of Jinyun Mountain. Jinyun Mountain is located in Chongqing suburb, where the precipitation was mainly influenced by the local air pollutants due to the special topography and air environment [12]. But in recent years, the air and precipitation pollution tended to become much severe in Jinyun Mountain. This may be related to two reasons. First, the local air pollutants increased with the

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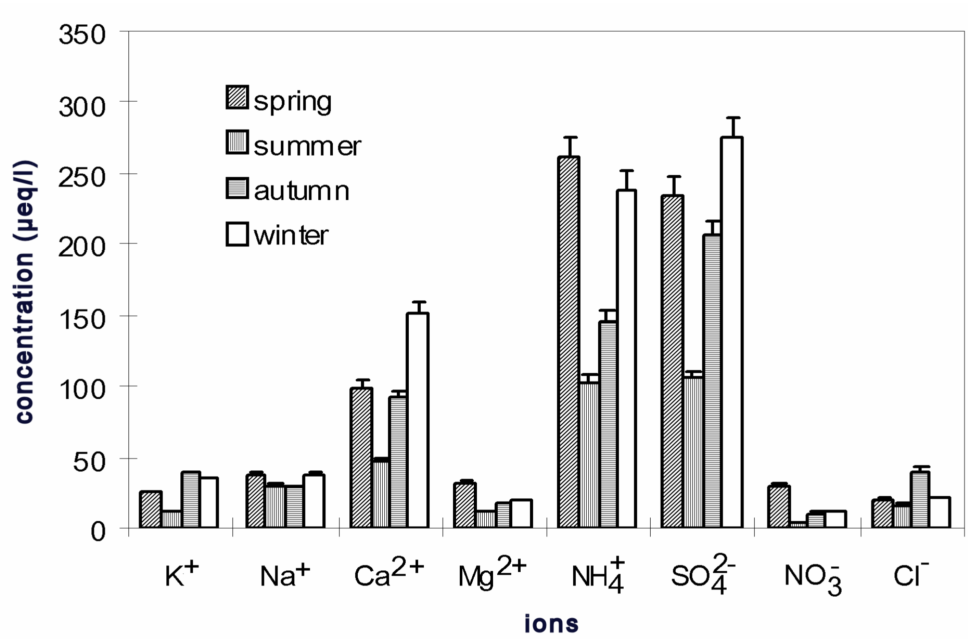

Figure 2. *The seasonal change of precipitation ions in Jinyun Mountain*

development of the regional economy. Second, a part of SO_2 emissions were transferred to Jinyun Mountain from downtown due to high-chimney emission in urban regions. Therefore, in order to decrease the precipitation acidity in Jinyun Mountain and protect the forest ecosystem in the Nature Reserve, it is useful to control the total SO_2 emissions including in the suburb and urban areas of Chongqing. It is also suitable in other cities of China.

The acid rain in Jinyun Mountain was also classified to sulphuric acid type and the concentration of SO_4^{2-} accounted for more than 80% of the total anions. The concentration of anions, especially, SO_4^{2-} was significantly lower than that in Chongqing urban areas, but was still much higher than that in other developed countries in Northeast America, Europe and East Asia and did harm to the health of ecosystem. NH_4^+ and Ca^{2+} were the most abundant cations in Jinyun Mountain precipitation, which accounted for 77.36% of the total cations. Compared with the precipitation in Northern China and Chongqing urban areas, the concentration of Ca^{2+} was much lower while the concentration of NH_4^+ was significantly higher, which were related to the characteristics of local environment in Jinyun Mountain. The chemical composition of precipitation in Jinyun Mountain showed obvious seasonal variation. The air pollution was much severe in winter and more favourable in summer, which may be related to the seasonal variation in precipitation amount.

The analysis of PCA and correlation on major ions of precipitation showed that the abundant NH_4^+ and Ca^{2+} neutralized greatly the acidity of acid ions. Consequently, precipitation with relatively high pH was observed and reduced the direct damage to forest vegetation. But some scientists have found that this neutralized precipitation with weak acid substance [such as $(NH_4)_2SO_4$] is harmful to the ecological environment after it gets into the soil [20]. The NH_4^+ can acidify the soil through the plant absorption and the nitrosation of nitrous bacteria; the movement of sulphate ion can also lead to the soil acidification by improving the loss of base cation. Such precipitation called acidifying precipitation is not acid precipitation, but still can hurt the health of plant communities

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finally by influencing the soil quality. There are no direct negative influences when SO_4^{2-} coexists with K^+, Na^+, Ca^{2+} and Mg^{2+}, but it is still a potential threat to ecosystem [20]. Therefore, it is necessary to control the acid and alkaline sources simultaneously in order to protect the acid and alkaline balance in the ecological environment and reduce the damage caused by air pollutants.

In the terrestrial ecosystem, forest communities have large biomass and usually became the direct victims of the acid deposition due to the interception by the tree canopy. At the same time, the soil quality decreased because of the long-term influence of acid rain and acidifying rain, which also do harm to the plant health. There have been many research works conducted on the influence of acid rain on coniferous forest ecosystem due to its sensitivity [13, 21, 22]. The main vegetation type in Jinyun Mountain is sub-tropical broadleaved evergreen forest that has better ability to absorb acid ions and resist the damage of acid rain compared with coniferous forest [1, 13, 22]. But the number of detailed research works on broadleaved evergreen forests is limited. The broadleaved evergreen forest is the climax vegetation in subtropical regions, the ecological restoration is more difficult than other forest if destroyed. There may be time delays between the onset of acid deposition and any resulting ecosystem impacts; so careful and integrated consideration is required to assess acid and acidifying deposition in broadleaved forest ecosystem.

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