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GRADIENT DISTRIBUTION OF ACID RAIN IN THE SCENIC RESORT OF THE BAIYUN MOUNTAIN IN GUANGZHOU

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ABSTRACT: This paper analyzes the samples of rainwater from January to October 1999 at three monitoring sites of Baiyun Mountain and of aerosol composition in near-surface layer in January and June 1999 at two sites. The results suggest that (1) The pH value of rainwater is between 3.13 and 7.18, and the frequency of acid rain is more than 58 %. With the ascent of the monitoring sites, the pH value of rainwater decreases, and the frequency of acid rain increases. (2) In January, the chemical aerosol compositions at different altitudes are similar, but in June the acidity of aerosol rises at the higher site because of the increase of SO_4^{2-}. (3) In rainwater, the proportion is such that SO_4^{2-} is the most significant anion and Ca^{2+} is the most important cation, but both of them decrease as the altitude ascends. The proportion of NO_3^- and NH_4^+ rise at the higher site and have more contribution to the acidity of rainwater. (4) As the impact of automobile emissions around Baiyun Mountain, the proportion of NO_3^-/SO_4^{2-} molecular concentration reaches 0.40, and NO_3^- is relatively more important to the rain acidity at the higher site.

Key words: Baiyun Mountain; rainwater; aerosol; chemical composition

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1 INTRODUCTION

Sitting in the central part of the Pearl River Delta, Guangzhou is one of the cities in China that are most polluted by acid rain. Broad attention has been brought to the problem. Since the early 1980's, a series of observation and studies have been launched to analyze the temporal and spatial distribution of precipitation acidity, frequency of acid rain and main ionic components in rainwater, and resulted in further understanding of the causation, characteristics of acid rain pollution in the city, their association with sources of pollution and meteorological conditions[1, 2][2], and microphysical processes of acid rain[3, 4]. Nicknamed the "town's lungs", the Baiyun Mountain is the only part of the city that is covered with large area of forest. It used to be a point of cleanness background in acid rain watch. With the development of social and economic infrastructures over the recent years, air pollution is getting worse in the immediate surroundings of the mountain and changes are observed in its characteristics of acid rain pollution. It is then important for the protection of ecological environment of the Baiyun Mountain and the exploitation of resources of its natural environment if we know more about the status and characteristics of acid rain there.

2 DATA AND METHODS

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Biography: HUANG Jian (1964 –), male, native from Guangdong Province, senior engineer, Ph.D. candidate, mainly undertaking the study of atmospheric physics.

[1] WU Yan-biao, GU De-jun, YE Yan-xiang, YANG Ji-hong, MAO Wei-kang, DENG Xue-jiao and HUANG Hao-hui took part in field observation.

[2] Guangdong Bureau of Environmental Protection. Summary report on "The Current Status of Acid Rain Pollution in Guangdong and its Evolution Tendency". 1998.

In January 1999, the Guangzhou Institute of Tropical and Marine Meteorology began a 10-month-long watch of acid rain conditions of the Baiyun Mountain at three sites of the scenic resort. They are, respectively, the Administration bureau of the Baiyun Mountain Scenic Resort (the Guangyuan Road) with an A.S.L. about 50 m, Zhi-qin Building (inhabitable) with an A.S.L. about 210 m, and the cableway (the Mountain Top Park) with an A.S.L. about 270 m. See Fig.1 for detailed location. The three sites of observation are arrayed in terrace with horizontal distance less than 4 km.

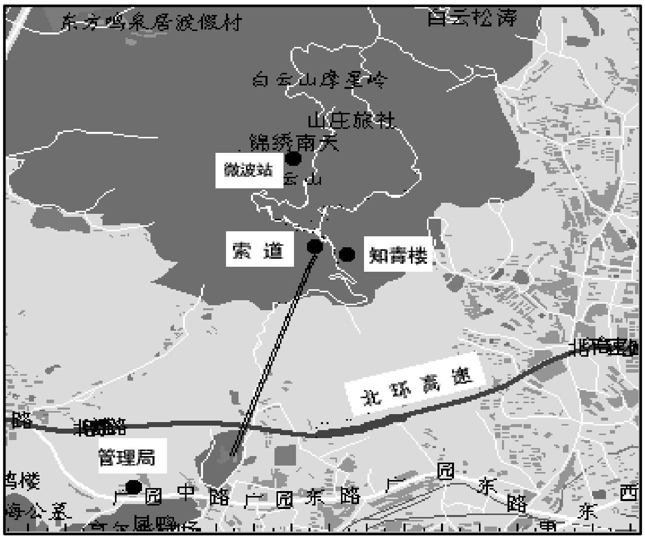

Fig.1 Sites of acid rain monitoring in the Baiyun Mountain.

Automatic samplers and recording hyetographs were installed at the three sites of observation to gather rainwater simultaneously. The samples were all collected at 0800 L.T. for the amount of precipitation over the past 24 hours. For the three sites, precipitation over the period from January to October was gathered. A total of 260 sets of precipitation samples were obtained, 73 sets for the administration bureau, 84 sets for Zhi-qin Building and 76 sets for the cableway. In addition, the Andersen graded aerosol samplers were used in January and June in two simultaneous observations of atmospheric aerosol near the ground surface at the bureau building and Zhi-qin building, each lasting 3 days.

Items to be assayed include the pH value and the electric conductivity of precipitation and total concentration of atmospheric aerosol. Chemical compositions, F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}, were assayed of 115 sets of precipitation samples and two sets of aerosol samples.

The sampling, analyzing and detecting methods used in the work follow relevant specifications in the "Unified Detection and Analysis Methods for Chemical Components of Precipitation" issued by the National Environmental Protection Agency in 1984. The pH values and electric conductivity of precipitation as well as rainfall were measured using the pH meters, electric conductivity meters and recording hyetographs and ions in precipitation and water-soluble ions in aerosols employing the ionic chromatography and atom-absorbing spectrophotometry.

3 DISTRIBUTION OF POLLUTION SOURCES IN SURROUNDING REGIONS AND SURFACE WIND FIELD

Locating south of the Tropic of Cancer, Guangzhou is of subtropical maritime monsoon climate that is both warm and humid with abundant rainfall. Prevailing wind directions are distinctly clear, with the winter dominated with the northerly and the summer with the southerly and southeasterly. Being in the north of the city, the scenic resort of the Baiyun Mountain borders with the town districts of Yuexiu, Dongshan and Tianhe. It covers a total area of about 40 km^2 and stands 372 m A.S.L. at the highest point. Vegetation is thriving in the mountain and hardly hosts any sources of pollution. It is generally a clean area.

In addition to the effect of large-scale polluted environment in Guangzhou and the area of Pearl River Delta, the Baiyun Mountain is also directly subjected to the immediate effect of local sources of pollution. Two kilometers off the line of protection control for the scenic resort, there are major sources of pollution like a rubber factory, a steel mill and a cement workshop to the west, an international airport and affiliated services facilities to the northwest, a shoes workshop, food processing factory, pharmacies and chemical coating factory to the east and southeast, and a main local pharmacy factory to the northeast. In general, pollutants, especially fly ash, have larger impact if they come from the west rather than from the other directions. The mountain is also affected by a number of main traffic routes —to the south the Guangyuan Road and North Ring Express go from the east to the west; to the east and west, two highways (respectively called the New and Old Guangzhou-Conghua Highways) extend southwest-northeast. According to our field surveys, there are as many as 15000 vehicles per day on the North Ring Express making passage over the section of the mountain, attributing to a mean NO_x emission of 20.3 — 32.1 kg/k m・h; the Guangyuan Road and the two southwest-northeast highways flanking both sides of the mountain measure mean daily traffic volume of 6500, 12000 and 7500 vehicles on the Guangyuan Road, New and Old Guangzhou-Conghua Highways, respectively.

As a barrier that alters the distribution of airflow within the planetary boundary layer through mechanical forcing, the Baiyun Mountain is of such terrain that it also induces thermodynamic circulation and convection activity due to the variation of thermal nature of the underlying surface. Because of terrain effect, the transportation of airflow is changed to complicate the dispersion of airborne pollutants. It inevitably leads to complicated changes in the nature and composition of precipitation in the Baiyun Mountain. To comprehensively study the patterns with which acid rain distributes and varies in the mountain, observation that aimed at revealing the characteristics of surface wind fields was carried out in parallel to acid rain monitoring at the sites of the administration bureau, Zhi-qin building and cableway. It is known, in association with the wind field data from the Tianhe weather station, Guangzhou, that the pattern of northerly wind appears the most (52.9%) in winter and that of southerly wind occurs most frequently (69.1%) in summer, in terms of the surface wind field of the city. The correlation for the wind direction at the weather station to be related to that at the bureau, building and cableway is 0.1, 0.4 and 0.6, respectively; the correlation coefficients are –0.3, –0.2 and 0.4, respectively, for the wind speed. In summer, they are 0.3, 0.2 and 0.8, respectively, for the wind direction; they are 0.2, –0.1 and 0.6, respectively, for the wind speed. It is obvious that the topographic effect of the Baiyun Mountain has caused complicated changes in the wind field of the mountain so that it differs greatly from the governing wind field over the city. It is also known from the above analysis that the wind direction / speed at the cableway is better correlated with the weather station than the other two sites, suggesting that the atmospheric pollution up in the mountain tends to vary similarly with the background field of large-scale atmospheric pollution in Guangzhou while the wind field obtained at the sites of the administration bureau and Zhi-qin Building is characteristic of by-passing and up-sloping airflow and distorted wind speed, localizing the conditions of atmospheric pollution.

Fig.2 gives the measured values of total concentration of SO_2, NO_x and aerosol for January and June of 1999 in the city proper, the Baiyun Mountain Administration Bureau and Zhi-qin building. It shows that the increasing amount of automobiles in Guangzhou has made it possible

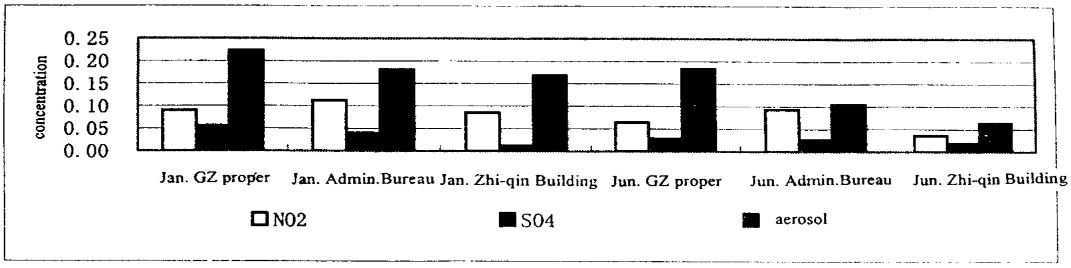

Fig.2 Graphic statistics of the monitoring of atmospheric pollutants concentration (unit: mg/m³).

that NO_x has a much higher level near the surface than SO_2 among artificial airborne pollutants. Compared with the city proper, the Baiyun Mountain has a more serious pollution of NO_x. The levels of SO_2 and aerosol are lower to some extent in the mountain, with the fall of SO_2 level more significant in January and the decrease of aerosol level more apparent in June. The conditions of atmospheric pollution in the mountain are not only affected by the background field of large-scale atmospheric pollution, but also by local emission of pollution from the neighborhood area. The detected SO_2, which is not released by the mountain itself, apparently comes from sources outside it. The high concentration of NO_x and aerosol can be explained by the fact that it is being surrounded by traffic mainlines like the Guangyuan Road, North Ring Expressway, New Guangzhou-Conghua and Old Guangzhou-Conghua Highways, which are letting out large amount of NO_x and flying dust that have the immediate effect on it.

4 CHARACTERISTICS OF ATMOSPHERIC AEROSOL

The atmospheric aerosol is an important intermediate ring during the transportation and removal of airborne pollutants and it greatly affects the acidity and composition of precipitation as a major substance to form acid rain. Tab.1 gives some of the results achieved in monitoring and analyzing the aerosol in the Baiyun Mountain.

Tab.1 Rainfall (mm), total concentration of aerosol ($\mu g/m^3$) and proportion of water-soluble ions in the aerosol (%) for the Baiyun Mountain

Time	Sampling sites	rainfall	Total concentration	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Jan.	Admin. bureau	29.9	180.4	0.7	0.8	0.3	55.6	3.9	1.2	1.3	28.4	7.9
	Zhi-qin building	28.3	167.2	0.6	0.7	0.3	52.6	4.0	1.4	1.4	29.5	9.4
Jun.	Admin. bureau	130.1	104.7	1.7	8.5	0.4	39.8	8.3	1.7	1.1	28.0	10.5
	Zhi-qin building	123.9	63.5	0.9	3.3	0.2	49.0	7.2	1.9	0.5	26.9	10.1

4.1 *Total concentration of aerosol and water-soluble components*

Comparing the values at different altitudes as listed in Tab.1, we note that the total aerosol concentration in January and June at the Administration Bureau is 180.4 $\mu g/m^3$ and 104.7 $\mu g/m^3$, respectively, higher than those measured at the Zhi-qin Building (167.2 $\mu g/m^3$ and 63.5 $\mu g/m^3$ respectively). The aerosol has a higher level at the foot of the mountain than it does up in the mountain, being consistent with the general pattern of vertical distribution of aerosol. In comparison with June, it is much higher in January, which agrees with the result that the area of Guangzhou has the highest level of aerosol and dust fall in winter. It is mainly explained by the fact that the amount of precipitation is usually the smallest in winter but relatively large in summer. Precipitation usually inhibits surface-level particles from entering the atmosphere and has the effect of cleansing and removing the aerosol in the atmosphere, reducing the total concentration of aerosol being left behind.

In addition, related studies have shown that in the near-surface layer of Guangzhou there is a layer of aerosol that is alkaline, which acts as a buffer zone for the acidity of the rain[5]. With the season varying, the layer of alkaline aerosol changes with height and exerts large influence on the acidity of precipitation up in the mountain. From Tab.1, we know that the four main ions, SO_4^{2-}, NO_3^-, Ca^{2+} and NH_4^+, are taking similar share in January in the composition of water-soluble ions at both the Administration Bureau and Zhi-qin Building and differences are also mild in other ions of the aerosol. It indicates that wintertime aerosol is made up of components varying little in proportion with the altitude of the mountain. For June, the proportion of SO_4^{2-} at the altitude of 210 m (the Zhi-qin Building) has increased by nearly 10% while the proportions of the other components are decreasing with varying extent. It shows that summertime aerosol is made up of components varying somewhat in proportion with the altitude of the mountain. From the observation that in June the SO_4^{2-} level at the Zhi-qin Building is much higher at the Administration Bureau than at the foot of the mountain while cations like Ca^{2+} are decreasing to some degree, we note that some changes have taken place in the composition and proportion of aerosol at the altitude of 210 m in summer so that the alkaline level should be higher than at the foot, reducing the buffer effect on precipitation acidity.

4.2 *NO_3^- in the aerosol*

Tab.1 also shows that the level of NO_3^- is low in the aerosol of both sites, which is less than 1% in the water-soluble components of aerosol. It is consistent with the observation by Wu et al. made at other parts of the city[3, 4]. It is attributed to the fact that Guangzhou is a city that lies in the subtropics that marks with high temperature and strong insolation to make it easy for liquid nitric acid and nitrous acid to evaporate and for nitrate to break up.

5 STATUS OF ACID RAIN

5.1 *pH values of precipitation and acid rain frequency*

Mean pH values listed in Tab.2 are weighted with rainfall over the period from January to October for the sites of Administration Bureau, Zhi-qin Building and cableway. The pH measurement ranges from 3.13 to 7.18, averaging at 4.83, 4.88 and 5.29, respectively. The frequency of acid rain and severe acid rain (pH $\leq$ 4.5) also increases with the rising of A.S.L., with the lowest at the administration bureau (58%) and highest at the cableway (91%) in the case of acid rain and 19% and 39%, respectively, in the case of severe acid rain. For the precipitation in the Baiyun Mountain, rainwater shows high levels of acidity up in the mountain, with a much higher frequency of acid rain and severe acid rain than the gradient distribution at the foot. The less polluted and cleaner up in the mountain, the lower the value of pH, which is a feature shared by observation in many localities[6, 7]. It can be explained by the fact that airborne aerosol is usually alkaline near the surface and neutralizes acid substances in rainwater. With pollution being heavier in the lower part of the mountain, atmospheric aerosol is relatively high in concentration and the neutralization of acid substances is greater, and rainwater is then made less acid and the pH value higher. With pollution being lighter in the upper part of the mountain, atmospheric aerosol is lower in concentration than the lower part and aerosol that enters rainwater is relatively little. Then the neutralization of acid substances is smaller and rainwater is then made more acid and the pH value lower.

Tab.2 Statistic results of precipitation monitoring for the Baiyun Mountain over January – October, 1999

Sampling sites	Sample size	pH mean	pH range	Frequency with pH < 5.6 / %	Frequency with pH ≤ 4.5 / %
Administration bureau	73	5.29	3.64～7.18	58	19
Zhi-qin Building	84	4.88	3.13～7.16	85	32
cableway	76	4.83	3.26～6.78	91	39

Rainfall-weighted averaging is done of the monthly precipitation pH values and electric conductivity for the three sites of the mountain to obtain changes in the monthly mean (Fig.3). As the monthly mean precipitation doesn't differ much between the three sites (less than 5%), the monthly mean represents the tendency of precipitation changes of the Baiyun Mountain in our study of the relationship between it and pH value and electric conductivity of rainwater.

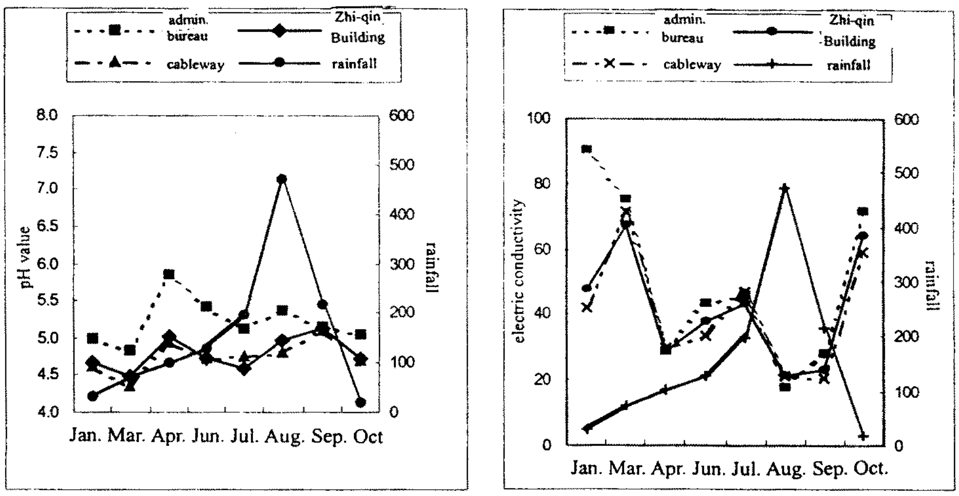

Fig.3 a. Mean pH values of monthly precipitation in the Baiyun Mountain; b. electric conductivity (μs/cm) and precipitation (mm)

For the 8-month observations used in the statistic work, the pH values of the monthly mean for the three sites range between 4.84 and 5.86, 4.49 and 5.12, and 4.35 and 5.10, respectively. They tend to vary in a consistent direction, with the curves showing obvious decrease from the administration bureau at the foot and Zhi-qin Building up in the mountain and down to the cableway. Fig.3a shows that the amount of precipitation and the variation of pH values don't have significant patterns of activity, indicating no direct relationship between the two. Fig.3b shows the change of electric conductivity with altitude, which is increasing with the increase of altitude of the mountain. Seasonal changes in precipitation also play a part in the electric conductivity of precipitation in the Baiyun Mountain, though being not the decisive factor. As shown in Fig.3b, the electric conductivity is much larger in autumn and winter when precipitation is relatively small; it doesn't fall with the increase of rainfall in April, June and July when precipitation is relatively mild. In fact, electric conductivity of rainwater is a comprehensive indicator of the ions contained wherein and relates to large extent with factors of the concentration of atmospheric pollutants, rain intensity and density of raindrop number.

6 GRADIENT VARIATION OF CHEMICAL COMPOSITION OF RAINWATER

Due to restriction in terms of chemical analysis, conventional chemical compositions, rather than organic compositions, were assayed of the rainwater samples gathered for January, June and July. Fig.4 gives the mean variation of total ionic concentration with the weight of rainfall for equivalent concentration of all ions at the three sites of observation.

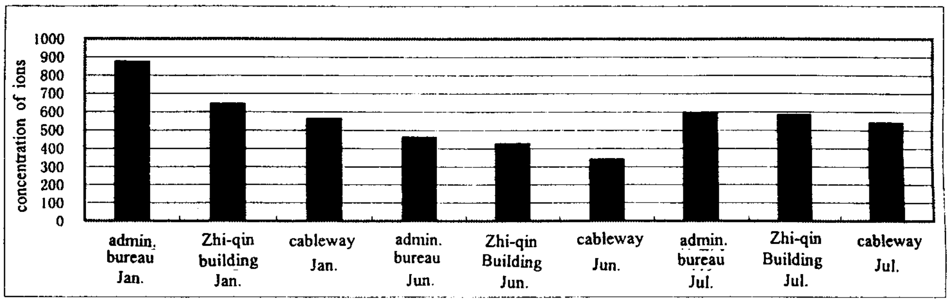

Fig.4 Variation of total ionic concentration of monthly mean precipitation in the Baiyun Mountain ain (unit: μ eq/l).

6.1 *Total concentration of ions in rainwater*

Whether it be winter or summer, total concentration of ions increases with the rising altitude of the Baiyun Mountain and the main effect of seasonal changes on the total concentration of ions is the magnitude of concentration gradient. Fig.4 shows that the gradient is large in January but small in June and July in the total concentration of ions. For January when precipitation is relatively small (about 29 mm), the ionic concentration varies significantly in the vertical direction, being more than 850 μ eq/l at the foot (the administration bureau) but decreasing by 27% from the bureau to the cableway and by about 10% from the Zhi-qin building to the cableway. With the change of seasons, however, precipitation increases in June and July, which is 125 mm and 202 mm, respectively, when the total ionic concentration decreases as compared to January, though with milder extent. It is well known that apart from being capable of preventing artificial or natural particles like ground-surface soil and dust from entering the atmosphere, precipitation removes and reduces the pollutants in the atmosphere and dilutes those in rainwater. With large precipitation, the rainwater pollutants will be diluted to decrease the difference in absolute concentration and reduce the difference between individual altitudes.

It should come to one's attention that there is much larger increase of precipitation in July (about 22 mm) than in January and June to cause high dilution of the ion concentration in rainwater, but the total concentration gets larger than in June in the mountain. Even in seasons of relative large precipitation, the acid rain in the area is subject to intense influence from atmospheric pollution and has something to do with how well local atmosphere dissipates and atmospheric pollutants being transported from outside.

6.2 *Proportion of individual rainwater components to total concentration of ions*

The formation and acidity of acid rains are related with the conditions of atmospheric pollution, which depend mainly on the nature and concentration of pollutants coming into the precipitation and result from neutralization of the interactions between all acid and alkaline substances. As the Baiyun Mountain is affected by both local sources and atmospheric pollutants transporting from surrounding areas, the distribution of individual pollutants are made more complicated with the presence of topographic effect, playing a key role in the composition of precipitation. Tab.3 gives the proportions of different chemical compositions of precipitation to the total concentration of anions and cations for the three sites of observation in the Baiyun Mountain.

Tab.3 Proportions of different chemical compositions of precipitation to the total concentration of anions and cations

Serial No.	Sites of sampling	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Jan.	Admin. Bureau	3.2	18.7	17.2	60.9	13.4	23.2	7.2	52.2	4.1
Jan.	Zhi-qin building	3.3	14.8	24.7	57.2	21.5	24.6	3.8	45.5	4.7
Jan.	Cableway	2.3	22.3	27.1	48.2	15.4	39.4	3.0	34.8	7.4
Jun.	Admin. Bureau	5.1	15.1	17.2	62.6	4.1	22.8	5.2	61.8	6.0
Jun.	Zhi-qin building	5.8	15.9	18.4	59.9	4.9	23.9	6.0	59.1	6.1
Jun.	Cableway	5.8	14.3	19.8	60.1	6.9	27.2	11.0	49.3	5.6
Jul.	Admin. Bureau	4.9	26.7	19.2	49.2	6.7	32.8	4.4	53.9	2.1
Jul.	Zhi-qin building	4.3	23.3	23.9	48.5	5.3	40.9	4.6	46.7	2.4
Jul.	Cableway	5.8	20.6	25.6	48.0	5.7	36.4	5.2	51.1	1.7

Among the anions and cations in the rainwater of the mountain, SO_4^{2-} and Ca^{2+} take up predominant position. In the anions, SO_4^{2-}s take up between 48.0% and 62.6%, followed by NO_3^- and Cl^-, amounting to 17.2% – 27.1% and 14.3% – 26.7%, respectively. In the cations, Ca^{2+}, NH_4^+ and Na^+ take up 34.8% – 61.8%, 22.8% – 40.9% and 4.1% – 21.9%, respectively. According to monitoring results of chemical composition in precipitation published in Lushan in the late 1980's, the proportions of anions and cations to the total concentration are 65.4% (SO_4^{2-}), 41.3% (Ca^{2+}), 29.7% (NH_4^+), 16.4% (NO_3^-), 11.8% (Cl^-) and 10.9% (Na^+), respectively. Compared to the monitoring results for the area of Guangzhou, the proportion of SO_4^{2-} to the anions of precipitation of the mountain is apparently smaller while NO_3^- is larger; the proportion of Ca^{2+} to the cations is larger while the proportions of K^+ and Mg^{2+} are smaller. In contrast to the total level of acid rain in the city, the Baiyun Mountain obviously has its own particularity. As there is only small emission of SO_2 and thus lighter pollution as a result in the mountain area, SO_4^{2-} are mainly substances coming from afar. The high level of NO_3^- in the precipitation can be attributed to the fact that it is immediately affected by its release (such as NO_x et al.) from vehicles travelling nearby. The high level of Ca^{2+} in the mountain, in fact, relates much with large amount of dust being discharged by factories nearby or spread on the highways.

As shown in a lot of monitoring and measurement, SO_4^{2-} and NO_3^- are two main contributors to acidity while Ca^{2+} and NH_4^+ are two neutralizing agents of acidity, in the acid precipitation of China. From a comparison of proportions for four main ionic compositions in rainwater at the different sites of observation, we know that SO_4^{2-} and Ca^{2+} tend to decrease while NO_3^- and NH_4^+ tend to increase, with the increase of the mountain altitude. It shows that the latter two ions are increasing the acidity of precipitation in the upper part of the mountain.

6.3 *Enrichment factors in the ionic compositions of precipitation*

Acid rain forms when rainwater and other moisture-condensed substances scour gaseous, liquid and solid pollutants in clouds and wash and rinse them beneath clouds. In addition to the near-surface aerosol, the composition of precipitation is also affected by gaseous and upper-level atmospheric pollutants. To study the possible sources of the ionic compositions of precipitation, Wu et al. [8]'s method is based to calculate the enrichment factors taking the water-soluble ions as the system of reference, with the relatively stable F^- as the composition of reference. The results are listed in Tab.4. Relative to aerosol, it is F^- that is most enriched while NH_4^+ and Cl^- (in January) are slightly enriched. Tab.4 shows that the large enrichment factor for NO_3^- both up in the mountain and at the foot in January and June indicate that NO_3^- receive light influence from aerosol concerning the ionic compositions of precipitation in the area; the main sources are the gaseous nitric acid and nitrous acid or nitrate transported in the upper-level atmosphere. In addition, the less-than-1 enrichment factor for SO_4^{2-} and Ca^{2+} in the precipitation shows that they are somewhat related with aerosol but precipitation has relatively low cleansing rate for them. The enrichment factor is approaching 1 for K^+, indicating that its source is primarily aerosol related. The enrichment factor is larger in January than in June for Cl^- in the precipitation, suggesting the presence of enrichment to some degree due to industrial pollution in winter when aerosol of maritime salt is in its lighter season. In contrast, Cl^- is mostly affected by aerosol in summer when maritime salt plays a larger role at the time.

Tab.4 Enrichment factors for the ionic compositions of precipitation (relative to aerosol)

Time	Sampling sites	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Jan.	Admin. Bureau	4.75	12.83	0.23	0.96	5.57	1.57	0.51	0.14
	Zhi-qin building	3.66	15.33	0.20	1.33	4.37	0.66	0.38	0.12
Jun	Admin. Bureau	0.60	15.43	0.53	0.15	4.02	1.46	0.65	0.17
	Zhi-qin building	0.72	12.22	0.18	0.08	1.39	1.27	0.25	0.07

6.4 *Contribution of NO_3^- and SO_4^{2-} to the acidity of precipitation in the Baiyun Mountain*

Proportions of equivalent NO_3^- and SO_4^{2-} concentration reflect the magnitude of the contribution of the two anions to the rainwater acidity. The proportions of monthly mean concentration of NO_3^-/SO_4^{2-} for January, June and July at the three sites of the mountain are listed in Tab.5. The lowest proportion is 0.28, occurring at the mountain foot site of the administration bureau in January and June; the highest proportion is 0.56, appearing at the cableway site, in the upper part of the mountain in January. The mean is about 0.4, which is higher than the observation (0.36) made in the spring of 1986 in the mountain and much higher than the mean levels of 0.15 and 0.25 for the city of Guangzhou during the early 1980's and 1990's, respectively, approaching those in developed countries in Europe and the United States. With the development of economy in recent years, SO_4^{2-} remains the dominant acidity-causing factor but NO_3^- is catching up by enlarging its contribution to it and posing greater hazards to the Baiyun Mountain, which is relatively clean, than to the city proper.

Tab.5 also reveals that the proportion of NO_3^-/SO_4^{2-} generally increases with the rising of the altitude, with NO_3^- having greater effect on precipitation acidity at the Zhi-qin building and cableway up in the mountain than at the administration bureau at the foot of it. Of the 11 samples of severe acid rain (with pH less than 4) that are chemically assayed, the NO_3^-/SO_4^{2-} proportion is all greater than 1 (within a range of 1.2 – 1.99). The significant contribution of NO_3^- in acidifying precipitation in the mountain is one of the reasons for severe acid rain to appear. As severe acid rain is a huge threat to the ecosystem, special attention should be paid to control the release of NO_x in its surrounding area in attempts to mitigate the effect of acid rain on the ecosystem of the mountain and protect the natural resources there.

Tab.5 Statistics of the proportions of equivalent concentration of NO_3^-/SO_4^{2-} in the precipitation of Baiyun Mountain

sampling time	Sampling sites	NO_3^-/SO_4^{2-}
Jan.	Admin. Bureau	0.28
	Zhi-qin building	0.43
	Cableway	0.56
Jun.	Admin. Bureau	0.28
	Zhi-qin building	0.31
	Cableway	0.33
Jul.	Admin. Bureau	0.39
	Zhi-qin building	0.49
	Cableway	0.53
mean		0.40

7 CONCLUDING REMARKS

a. The mean pH value is 5.29, 4.88 and 4.83 for the three sites of observation at the administration bureau, Zhi-qin building and cableway, with acid rain taking place at rates of 58%, 85% and 91%, respectively and severe acid rain at rates of 19%, 32% and 39%, respectively. Gradient changes mark the acidity of precipitation and frequency of acid rain; pH values decrease with the increase of altitude and frequency of acid rain and severe acid rain increases with it.

b. As shown in the analysis of compositions of water-soluble ions of aerosol, alkaline aerosol in the near-surface layer is made up of generally the same compositions in winter at both of the sites in the upper and lower part of the mountain; the compositions are somewhat different at both altitudes in summer with much greater proportion of SO_4^{2-} in the upper part of the mountain. In spite of extremely low levels in the aerosol of the mountain, NO_3^- is found to be with obvious enrichment in precipitation, as shown in the enrichment analysis of ionic compositions in precipitation.

c. For the ionic compositions of precipitation in the Baiyun Mountain, SO_4^{2-} takes up the largest proportion in anions, followed by NO_3^-; Ca^{2+} takes up the largest proportion in cations, followed by NH_4^+. With the increase of altitude, the proportions of SO_4^{2-} and Ca^{2+} tend to decrease while those of NO_3^- and NH_4^+ tend to increase. It shows that in the upper part of the mountain NO_3^- and NH_4^+ have increasing effect on the precipitation acidity there.

d. As the Baiyun Mountain is directly affected by traffic on nearby highways, NO_3^- in precipitation there takes up a proportion larger than that for the area of Guangzhou and the proportion of equivalent NO_3^-/SO_4^{2-} increases with the rising of altitude, averaging at 0.40. It shows that NO_3^- plays an important role in the acidification of precipitation over the mountain, especially so with the increase of altitude.

The above analysis of the status of acid rain in the Baiyun Mountain has done based on the 8-month-long observations in 1999. For comprehensive reveals of long-term variation patterns of acid rain in the mountain, further and more detailed monitoring is needed.

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