

CHEMICAL COMPOSITION OF PRECIPITATION, THROUGHFALL AND SOIL SOLUTIONS AT TWO FORESTED SITES IN GUANGZHOU, SOUTH CHINA

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Abstract. Rain water at two forested sites in Guangzhou (south China) show high concentrations of SO_4^{2-} , NO_3^- and Ca^{2+} and display a remarkable seasonal variation, with acid rain being more important during the spring and summer than during the autumn and winter. The amount of acid rain represents about 95% of total precipitation. The sources of pollutants from which acid rain developed includes both locally derived and long-middle distance transferred atmosphere pollutants. The seasonal variation in precipitation chemistry was largely related to the increasing neutralizing capacity of base cations in rainwater in winter. Soil acidification is highlighted by high H^+ and Al^{3+} concentrations in soil solutions. The variation in elemental concentration in soil solution was related to nitrification (H^+ , NH_4^+ and NO_3^-) and cation exchange reaction (H^+ , Al^{3+}) in soil. The negative effect of soil acidification is partly dampened by substantial deposition of base cations (Ca^{2+} , Mg^{2+} and K^+) in this area.

Key words: acid deposition, forest ecosystem, Guangzhou, soil solution

1. Introduction

In China, the rapid economic growth has been accompanied by the increase in pollution with acid precipitation becoming one of major environmental problems. A representative example is Guangzhou in south China, where the acid rain accounts for more than 80% of total annual precipitation during the eighties (Chen *et al.*, 1990). However, only limited reports are available in international literature on precipitation and soil solution chemistry from long term monitoring sites in this region (Larssen *et al.*, 1998; Seip *et al.*, 1999). It is therefore highly urgent to assess scientifically the current status of precipitation and the ecological effects of acid deposition. For this purpose, the precipitation, throughfall and soil solution have been collected and analyzed during the period of April 1998 to March 1999 from two monitoring forested sites in Guangzhou. These data will be used to investigate the processes/factors responsible for chemical variation in precipitation and soil solution and to assess the response of forest ecosystem at Guangzhou to acid deposition.

2. Site description and Methods

The monitoring sites with Masson pine (*Pinus massoniana* Lamb) are located at



Baiyunshan (200 m altitude) at the center of Guangzhou city (31°55'N, 108°08'E) and at Longdong about 15 km north-east of Guangzhou. The climate in this region is subtropical and monsoonal with annually averaged temperature of 22 °C. Forest soil is red lateritic soil with granite bedrock.

Precipitation was collected with a standard rain gauge after every event outside of the monitoring sites. Throughfall water was collected using self-designed collectors with 2-3 replicates at each site. Soil solution was continuously collected using ceramic plates with fixed dimension at five soil depths (0, 20, 40, 60, 80 cm). After installation, the soil section was left for two months for re-equilibration prior to collection. The throughfall and soil solutions were sampled every two weeks for chemical analyses. Water samples were analyzed using flame atomic absorption spectrometer for cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Al^{3+}), ion exchange chromatograph for major anions (SO_4^{2-} , NO_3^- , Cl^-) and ion selective electrodes for NH_4^+ . Measurement of pH was conducted using a glass electrode pH meter (DF-807). Soil water fluxes were calculated on the basis of measured water volume. The annual and seasonal averages were calculated using the precipitation or water flux as weight.

3. Results

3.1. PRECIPITATION

The total annual amount of precipitation is 1625 mm during the monitoring period. pH values vary between 3.3 and 6.3, with an average of 4.38 (Table I). The frequency of acid rain (pH<4.5) is 80%. The amount of acid rain represents about 95% of total precipitation, indicating the severe environmental status at Guangzhou. The rainwater has high concentrations of SO_4^{2-} , NO_3^- and Ca^{2+} and shows a remarkable seasonal variation, with acid rain being more important in the spring and summer than in the autumn and winter (Table I).

3.2. THROUGHFALL

The concentrations of SO_4^{2-} , NH_4^+ , Ca^{2+} , Mg^{2+} and K^+ in throughfall water are higher than in precipitation (Table I). This is due to the washing out of dry deposits on vegetation and of ions released from vegetation. However, H^+ concentration in throughfall is lower than in rainwater, probably due to the neutralization of base cations by dry alkaline dust deposited and basic leachates from plants.

3.3. SOIL SOLUTIONS

The element concentration is much higher in soil solution than in precipitation

TABLE I
Compositions of precipitation, throughfall and soil solution at two forested sites in
Guangzhou (averaged, $\mu\text{eq/L}$)

	pH	H ⁺	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Cl ⁻	Al ³⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
Baiyunshan											
Precipitation											
spring	4.36	43.4	75.9	13.2	65.0	35.0	15.1	55.8	8.2	7.2	37.0
summer	4.21	61.8	293.9	1.9	52.4	34.1	13.5	97.3	14.3	10.1	31.3
autumn	5.12	7.6	48.1	11.1	122.3	41.1	13.0	220.3	20.0	12.3	29.2
winter	6.37	0.4	84.2	8.4	44.8	24.2	29.0	202.4	16.7	12.6	19.2
Annual average	4.39	40.7	200.0	7.5	64.2	33.8	15.3	105.4	12.0	9.1	30.0
Throughfall	5.56	2.7	837.8	8.8	349.3	49.3	19.1	319.1	82.9	125.9	73.0
Soil solution											
0 cm	5.64	2.3	1094.3	49.6	376.3	69.5	37.2	592.7	198.8	393.1	99.5
20 cm	3.75	179.8	718.2	50.8	113.6	47.5	170.8	305.6	57.1	65.2	86.2
40 cm	4.09	80.6	603.1	58.2	47.7	42.5	183.8	234.9	63.2	23.4	94.5
60 cm	4.14	72.3	625.6	38.7	71.6	45.8	176.2	227.2	70.8	43.7	88.0
80 cm	4.57	27.1	894.5	62.8	36.0	75.6	151.1	397.9	77.3	55.7	96.8
Longdong											
Precipitation											
spring	4.54	28.7	156.8	8.6	59.6	27.8	7.3	57.4	12.5	24.8	32.1
summer	4.13	73.6	126.1	6.0	68.9	27.3	20.3	56.3	6.3	4.4	15.6
autumn	4.83	14.9	121.9	5.3	33.9	32.1	7.8	58.5	7.5	15.9	46.5
winter	6.54	0.3	214.4	5.2	33.4	16.6	26.4	115.1	10.0	6.1	7.7
Annual average	4.37	42.3	138.9	6.8	63.6	27.2	15.7	58.5	8.5	11.7	25.8
Throughfall	5.53	3.0	413.9	10.1	153.6	31.5	18.4	115.9	28.6	53.5	39.0
Soil solution											
0 cm	4.61	24.7	1047	53.6	310.8	43.6	45.9	261.6	82.8	200.8	223.0
20 cm	3.66	220.1	278.4	84.9	40.6	40.2	187.5	128.8	29.5	24.7	72.9
40 cm	3.67	214.6	279.6	123.9	35.6	40.1	182.2	155.8	36.5	18.3	91.6
60 cm	4.09	81.6	131.9	131.1	97.9	35.7	119.4	102.7	21.2	42.2	89.8
80 cm	4.11	77.9	133.8	202.1	57.6	64.6	96.7	120.1	34.0	15.4	98.1

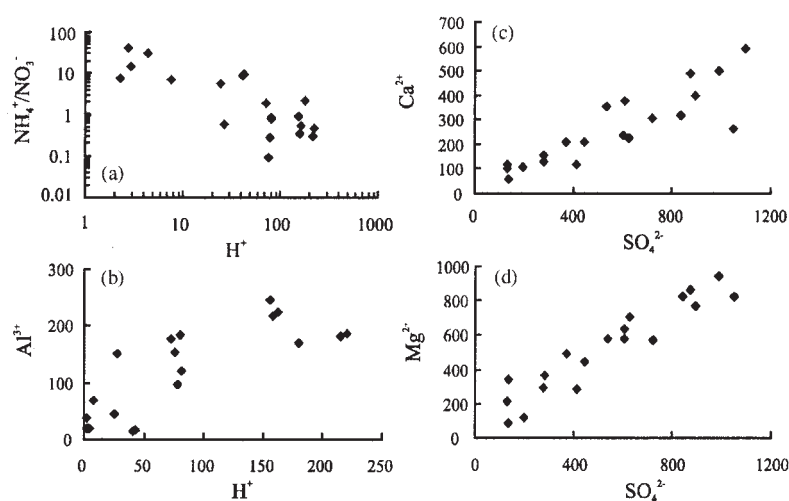


Figure 1. Diagram showing the correlation between major components ($\mu\text{eq/L}$) in precipitation, throughfall and soil solution: (a-b) H^+ vs $\text{NH}_4^+/\text{NO}_3^-$ and Al^{3+} ; (a-b) SO_4^{2-} vs Ca^{2+} and Mg^{2+}

(Table I). For instance, the enrichments of Al^{3+} and H^+ in soil solution relative to precipitation attain 15 and 4 times, respectively. Considerable chemical change in soil solution is observed from depth of 0 cm to 20 cm, whereas only a limited variation from 20 cm to 80 cm (except for NO_3^-). The $\text{NH}_4^+/\text{NO}_3^-$ ratio varies between 8 and 30 in precipitation and throughfall water, suggesting ammonium nitrogen as the principle form of N in the water before penetrating the soil. This ratio becomes considerably low in soil solution (Fig. 1a), indicating nitrate as the major form of N. There is marked positive correlation between SO_4^{2-} and base cations (Ca^{2+} , Mg^{2+} , K^+) in rainwater, throughfall and soil solution (Fig. 1c, d), suggesting the geochemical affinity of these components.

4. Discussions and Conclusions

4.1. ORIGIN OF CHEMICAL VARIATION OF PRECIPITATION

The rainwater at Guangzhou shows a chemical composition similar to that in southwest China (Zhang *et al.*, 1995b). The high SO_4^{2-} contents in precipitation from these two regions are largely related to coal combustion for the purpose of electricity generation and heating. Even if concentration of SO_4^{2-} in precipitation is high, pH of precipitation is relatively high, probably due to the neutralization of base cations (Galloway *et al.*, 1987). Concentrations of Ca^{2+} and other base cations are indeed very high in the precipitation (Table I). The exact origin of Ca is unclear at this stage but could be derived from road dust, cement factories and long-distance transported desert dust. Marine sources cannot be ignored for the precipitation chemistry at Guangzhou, especially for Na^+ and Cl^- .

It is interesting to note that the seasonal variation in chemistry of precipitation at Guangzhou is the reverse of what observed at Chongqing (SW China), where pH in rainwater being lower in winter than in summer (Zhang *et al.*, 1995b). This may imply the different mechanism of generation of acid rain in two areas. In the SW China, large cities are commonly situated along valleys. Limited air circulation in these regions is not favorable for the transport and diffusion of the locally emitted SO_2 . Consequently, these pollutants tend to accumulate in the lower atmospheric layer and enter the rainwater when precipitation is formed. This is supported by similar $\delta^{34}\text{S}$ between atmospheric SO_2 -aerosol and SO_2 -particles issued during coal combustion in SW China (Zhang *et al.*, 1995a). Therefore, the seasonal variation in precipitation chemistry in SW China may be directly related to the extent of local consumption of coal, which is greater in winter than in summer.

The source of pollutants from which acid rain develops at Guangzhou seems to be more complex. In this area, $\delta^{34}\text{S}$ of atmospheric SO_2 -aerosol is significantly lower than (by about 12‰) that of SO_2 -particles derived from coal combustion (Zhang *et al.*, 1995a). Therefore, in addition to the locally produced pollutants related to coal consumption, a source with low $\delta^{34}\text{S}$ is required in

order to account for the whole $\delta^{34}\text{S}$ range of precipitation at Guangzhou. In fact, the air circulation in the Pearl Delta region is strong. Long-middle distance-transported pollutants may also contribute in the formation of acid precipitation.

Ca^{2+} contents in rainwater in winter and autumn are significantly higher than in spring and summer. This is particularly true for the Baiyunshan site (Table I). It is likely that high pH in precipitation in winter is due to the increasing neutralizing capacity of base cations. Assuming that Ca^{2+} in rainwater was mainly contributed by alkaline dust, we attribute the seasonal variation in precipitation chemistry at Guangzhou to seasonal variation in weather and dry deposition. At Guangzhou, the majority of rainfall takes place in spring and summer and accounts for about 90% of annual precipitation. Soils are thus relatively wet and surface dusts are not easily incorporated into the air. Semi-continuous washing by rainfall also efficiently lowered the contents of alkaline particles in the atmosphere. This leads to the decrease in concentration of base cations in rainwater and the lowering of acid neutralizing capacity. In contrast, a high neutralizing capacity is expected for the rainwater in winter, because of high abundance of alkaline dust in atmosphere under dry weather.

4.2. EVIDENCE FOR AND MECHANISM OF SOIL ACIDIFICATION

It has been shown that soil acidification can lead to decrease of acid neutralizing capacity, losses of base cations from exchange sites and release of Al ions into soil solution as a consequence of H^+ -buffer processes (Matzner and Murach 1995). Perhaps, the most direct evidence for soil acidification is the decrease in soil pH. Some of these soil acidification symptoms have been noted at the studied area, pointing to current soil acidification.

In general, the H^+ input to the soil system consists of H^+ directly deposited by precipitation and of H^+ formed within the soil. As shown in Table I, H^+ concentration in soil solution at the upper soil layer is significantly higher than in precipitation and throughfall. Even with our underestimated flux of soil water, the flux of H^+ in soil solution is considerably higher than that in precipitation and throughfall. This suggests that the H^+ production mainly occurred at the upper soil layer and the amount of internally produced H^+ was more important than the external input. The lower NH_4^+ content in soil solution than in throughfall may be related to the uptake of this component by vegetation roots. However, this cannot be the primary cause at Guangzhou because it fails to account for the negative correlation between NO_3^- and NH_4^+ . Increasing H^+ along with the decreasing $\text{NH}_4^+/\text{NO}_3^-$ ratios (Fig. 1a) is broadly consistent with the nitrification of NH_4^+ in soils. This is particularly true at Longdong where NO_3^- content in soil solution is high and increases with soil depth. However, relatively low and rather stable NO_3^- concentration is noted in the soil solutions at Baiyunshan (Table I). Plant uptake of nitrate may be another factor besides

nitrification in governing nitrate chemistry in soil solution at this locality.

The H^+ concentration in soil solution decreases slightly with the soil depth (Table I), reflecting the consumption of H^+ in cation exchange and chemical weathering of primary minerals. In general, such a kind of exchange reaction would lead to the release of base cations and Al ions to soil solutions. This is widely considered as the mechanism of the soil change induced by acid deposition (Matzner and Murach, 1995). The Al concentration in soil solutions is much higher than in precipitation and in throughfall, thus supporting the hypothesis involving release of Al from soil into solution. Moreover, H^+ is positively correlated with Al^{3+} (Fig. 1b). It seems that the mobilization of Al was assisted and enhanced by the presence of H^+ , consistent with experimental results with simulated acid rain (Abrahamsen *et al.*, 1994). Because of the potential toxicity of Al ions to plant roots and soil organism (Ulrich, 1994), the increase in Al^{3+} in soil solution would leave negative impact on plants. However, the concentrations of base cations in soil solution are also high (Table I). The measured $Al^{3+}/(Ca^{2+}+Mg^{2+})$ molar ratios in soil solution are all less than the commonly accepted critical value above which forest damage occurs (Sverdrup and De Vries, 1994). It is possible that the substantial deposition of base cations at Guangzhou dampens to some degrees harmful effect of soil acidification.

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