



Chemical characteristics of precipitation at Nanping Mangdang Mountain in eastern China during spring

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Abstract

To study the characteristics of precipitation in eastern China, an automatic sampler was used to collect rainwater samples from 19 precipitation events at Mangdang Mountain, Nanping City, Fujiang Province, in the spring of 2009. We used ion chromatography to analyze the ionic components and concentrations, and inductively coupled plasma mass spectrometry (ICP-MS) to analyze element compositions and contents. The results demonstrated remarkable acidic characteristics: in more than 80% of precipitation events the pH was less than 5.6, with an average of 4.81. Mass concentration results showed SO_4^{2-} was the main anionic component (36.2% of the total anion mass), while NH_4^+ was the main cationic component (47.7% of the total cation mass) and main ion for acidity neutralization in the rainwater. Organic acid content accounted for 30.9% of total anion mass. The main trace metals were Ca, K, and Na. The $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio was 1.4, indicating that precipitation in this region was influenced by complex air pollution – the product of individual coal-burning combined with vehicle exhaust pollution. Correlation analysis of the chemical composition of the precipitation indicated that acidity in this region was determined by a combination of all acidic and neutralization ions rather than any single ion component. The results also showed that Na^+ and Cl^- contributions were mainly by seawater; Mg^{2+} by seawater and crustal materials; the NH_4^+ , K^+ , Ca^{2+} , NO_3^- and SO_4^{2-} by anthropogenic sources; the trace metals were from the Earth's crust; and organic acids were potentially from combustion of biomass.

Key words: chemical characteristics; enrichment factor; Mangdang Mountain; precipitation

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Introduction

Acid rain not only destroys soil, vegetation and aquatic ecosystems (Kim et al., 2000), but also has a serious impact on human health. As modern industries develop, the emission of acidic gases such as SO_2 into the atmosphere has continued to increase. Consequently, acid rain pollution has become a significant global environmental problem. Due to rapid economic growth, northeastern Asia is now the third largest acid rain area in the world, after Europe and North America. According to Zhou (1996) and Wang et al. (1997), China has the highest incidence of acid rain and is one of the largest affected areas in the world, particularly over four large areas: Central China, South-west China, Southern China, and Eastern China.

Precipitation chemistry is an important area of atmospheric acid precipitation research (Fujita et al., 2000;

Rastogi and Sarin, 2005). The chemical composition of the rainwater is the basis of evaluating acid levels, acid conversion and transport, and the effects on ecology, cultural relics, and materials. Chemical composition of precipitation can be affected by many factors, including anthropogenic emissions (Lara et al., 2001) and sea spray and terrestrial dust (Safai et al., 2004). In precipitation, the major inorganic ions NO_3^- and SO_4^{2-} can be transformed from their precursor gases, such as SO_2 and NO_x emitted from pollution sources (Seinfeld and Pandis, 2006). NH_4^+ primarily comes from fertilizers used in agriculture, biomass burning, livestock breeding and even natural activities (Topcu et al., 2002; Hu et al., 2003; Migliavacca et al., 2005). Other major elements (including Cl^- , Mg^{2+} , K^+ and Na^+) originate from natural sources such as sea spray, soils, and forest fires (Dordvić et al., 2005). Trace metals in precipitation are strongly affected by anthropogenic pollution sources, except for Fe, Al, and Mn which originate mainly from the earth's crust.

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Organic acid species come from primary biogenic and anthropogenic direct emissions and indirect production from precursors in the troposphere (Avery et al., 2006). Chemical characteristics of rainwater accurately reflect the quality of the local atmosphere, and are a reliable indicator for monitoring the influence of human activities on the atmosphere. These characteristics also help understand regional differences and the effects of climatic conditions. Chemical characteristics of precipitation in remote areas are especially significant for understanding the mechanisms of acid rain formation (Galloway, 1982).

Fujian Province is located in the southernmost region of East China, and borders Guangdong Province in South China. The consumption of fuels such as coal in this province is the lowest in China and major atmospheric pollutants (e.g. sulfur dioxide, nitrogen oxides and dust) are present at low levels. The atmospheric environment is good, and the annual average values of sulfur dioxide, nitrogen oxides and total suspended particulates meet the second grade of the Ambient Air Quality Standard of China. However, there is significant acid precipitation across the province (Zhao, 2004), particularly in the north-western region (Wu et al., 2009). The acidity and frequency of precipitation in spring and winter is also significantly higher than that in summer and autumn. Accordingly, the present study included the collection of rainwater samples during precipitation events in the Mangdang Mountain area of Nanping City in north-western Fujian Province.

The objective was to understand the acidity and chemical characteristics of precipitation in this region and determine the contribution of various sources to precipitation acidity. The overall aim was to provide a reliable objective basis for regional acid rainfall control and treatment research.

1 Materials and Method

1.1 Sampling site

From March 1 to April 12, 2009, precipitation sampling was carried out in the Mangdang Mountain, which is located in the natural reserves in north-western part of Nanping City, Fujian Province. The mountain is 15 km from Nanping City, covers 117 km² with an average elevation of 828 m and highest peak of 1363 m, and is located in a subtropical humid monsoon climate zone. The average temperature, humidity and wind speed were respectively 15.2°C, 85%, and 0.9 m/sec. Wind speed was low and the prevailing wind direction was north-east during sampling. Forests make up the main body of the vegetation ecosystem. Soil type is the Mountain Red and Yellow Soil, soil pH value ranged from 2.9 to 6.9 (average 4.7). There are no significant sources of man-made pollution on Mangdang Mountain, so this sampling site is representative for alpine area in the southeast, China.

1.2 Sample collection and analysis

A Precipitation Classification Automatic Sampler (APS-3A, Changsha Xianglan Scientific Instrument Co., Ltd.,

China) was used to make sublevel collection. The sampler consisted of a precipitation sampling bucket, dust sampling bucket, precipitation sensor and slideable cover plate. When the amount of rainfall was at the level of 0.2 mm/hr, the precipitation sensor detected the rainfall events and the precipitation sampling bucket opened until the rainfall ended, at which time it closed. This was determined as one sampling. Every sampling was conducted in several stages (usually 12). There were four setting levels for rainfall amount in every stage (1, 2, 3 and 4 mm), with 1 mm of rainfall amount equal to 70 mL of precipitation. The precipitation sampling bucket was changed to a larger one of 15 L in size at the last stage. The filter cloth, funnel, and precipitation collection polyethylene plastic bottle in the sampling instrument were cleaned with deionized water before each sample was collected to prevent sample contamination. After collection, a portion of the sample was immediately taken for pH determination (SG3, Mettler, Toledo, USA) and conductivity measurement (SevenEasy, Mettler, Toledo). The remainder was filtered using a 0.45-µm Millipore filter and sand core filter, then refrigerated below 4°C.

The samples were analyzed for ion components and organic acid content using ion chromatography (ICS-1500, Dionex Company, USA). For cation analysis, a CS12A cation analytical column was used with a cation Atlas[®] electrolytic suppressor (CAES) and 20 mmol/L of methanesulfonic acid (MSA) eluent, 110 mL/min flow rate, and 65 mA suppressor current. Anion analysis was carried out using an IonPac AS14 anion analytical column (anion self-regenerating suppressor (ASRS) 4 mm anion suppressor, eluent comprising 315 mmol/L of Na₂CO₃ and 110 mmol/L of NaHCO₃, flow rate 112 mL/min, suppressor current 30 mA). Inductively coupled plasma mass spectrography (Agilent 7500C, USA) was used for elemental composition analysis.

1.3 Sampling quality control and assurance

Sampling quality control and assurance were conducted during sampling collection and analysis, and the two processes were conducted strictly according to relevant technical specifications for acid deposition monitoring (Aas et al., 2003; China Environmental Science Press, 2002).

1.4 Data analysis

The pH value and component concentrations of each rainfall were calculated by Eqs. (1) and (2):

$$\overline{\text{pH}} = -\log[\text{H}^+] = -\log \left[\frac{\sum_{j=1}^n 10^{-\text{pH}_j} \cdot Q_j}{\sum_{j=1}^n Q_j} \right] \quad (1)$$

where, pH_j was pH value for the jth rainfall and Q_j (mm) was the amount of jth rainfall.

$$\bar{C}_i = \frac{\sum_{j=1}^n C_{ij} \cdot Q_j}{\sum_{j=1}^n Q_j} \quad (2)$$

where, \bar{C}_i ($\mu\text{eq/L}$) was the concentration of i th ion, C_{ij} ($\mu\text{eq/L}$) was the concentration of i th ion in j th rainfall. A total of 19 precipitation events occurred during the 42-day sampling period. The main ions measured were F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} and organic acids. Data analyses was carried out using SPSS (ver.18.0; SPSS Inc., USA) for Windows. Ion balance is an important parameter for evaluating precipitation data quality since it provides related information on both data analysis quality and possibility of ion measurement omitted. The relationship between total anion and cation concentration for all precipitation events during the sampling period are shown in Fig. 1, which show a significant linear correlation between them ($R^2 = 0.9486$). This indicates there was a very good anionic-cationic charge balance, and that no important components were omitted from the analysis. From this result we concluded that our sample collection and measurement methods were reliable.

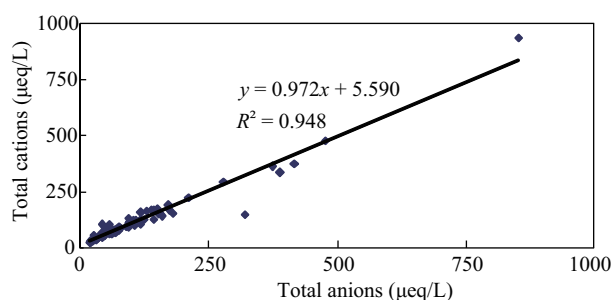


Fig. 1 Ion balance between anions and cations.

2 Results and discussion

For the 19 precipitation events occurred during the sampling period, average rainfall was 10.7 mm. The maximum rainfall was 22.2 mm, which occurred on 13 March, 2009, and minimum rainfall was 0.6 mm, which occurred on 6 April, 2009.

2.1 Precipitation pH values and conductivity

The pH of the rainwater ranged from 4.15 to 6.68 (average 4.81), lower than the pH of typical natural rainwater (5.6) (Seinfeld and Pandis, 2006). Eighty percent of acid precipitation events had $\text{pH} < 5.6$, 60% had $\text{pH} < 5.0$ (which has significant effect on environmental acidification), and 30% were strongly acidic with $\text{pH} < 4.5$ (Fig. 2). In view of the situation throughout the country, the degree of rainwater acidification in Mangdang Mountain is greater than that in northern China, and similar to that in southern China (Wang et al., 1996). Conductivity ranged from 3.07 to 101.6 $\mu\text{S/cm}$, with an average value of 20.01 $\mu\text{S/cm}$.

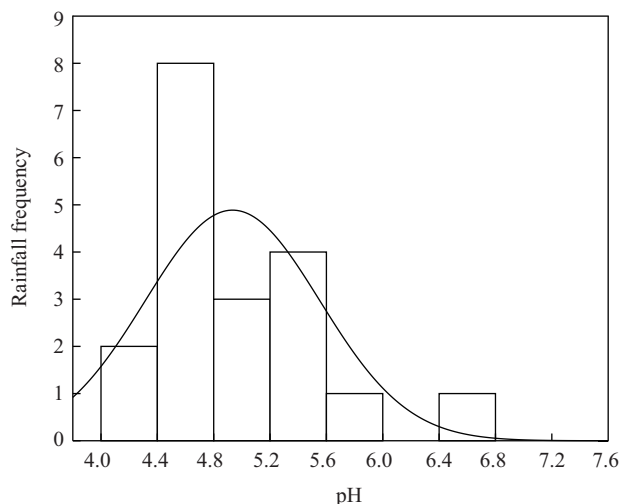


Fig. 2 Frequency distribution of precipitation pH value during sampling period.

This is slightly higher than the average conductivity of the precipitation at the global atmospheric background station in Waliguan Mountain (Tang et al., 2000) but lower than that in cities such as Beijing and Shenzhen (Yang et al., 2004; Niu et al., 2008). Precipitation conductivity is mainly contributed by water-soluble ions, the value being related to the total sum of anions and cations in the rainwater. Low precipitation conductivity is an indicator of good atmospheric environmental quality.

2.2 Chemical composition of the precipitation

The proportion of anions, cations, elements and organic acid in the rainwater are shown in Fig. 3. The most important anion component was SO_4^{2-} , accounting for 36.2% of the total anion mass, followed by organic acids (30.9%), NO_3^- (26.3%), Cl^- (5.8%) and F^- (0.8%) (Fig. 3a). Both NH_4^+ (47.7%) and Ca^{2+} (32.49%) were the major cation components (Fig. 3b), followed by Na^+ and Mg^{2+} (both 6.8%) and K^+ (6.2%).

The proportions of anions and cations ions were, in general, consistent with reported results from other locations in China, except for the contribution of organic acid to total anion content in which the results from this study were higher than those reported in previous research (Hu et al., 2005; Niu et al., 2008; Jiang et al., 2008). The anion content was lower than in urban areas in China, however, it was similar to results observed in some mountain areas in China. On the other hand, the anion content results in this study differ from those reported for some coastal areas abroad such as Okinawa, Japan, and New Jersey, USA (Table 1). The main organic acids were acetic and formic acid, accounting for 63.4% of the total organic anionic content (Fig. 3c). Succinic, adipic, malonic, propionic and methanesulfonic acids were also detected in the rainwater (Table 2). The organic acid content was the highest ever reported in China, and similar to results observed in North Carolina, USA, and Amazonas, Brazil. Of the trace elements (Fig. 3d), Ca accounted for 50.0% of the element mass, followed by K (17.2%) and Na (13.4%); Mg, Zn, Al, P and Fe ranged from 1.0% to 10.0%. The heavy metals Ni, Cu, Cd, Pb and Cr, all on the “black list” of pollutants, were

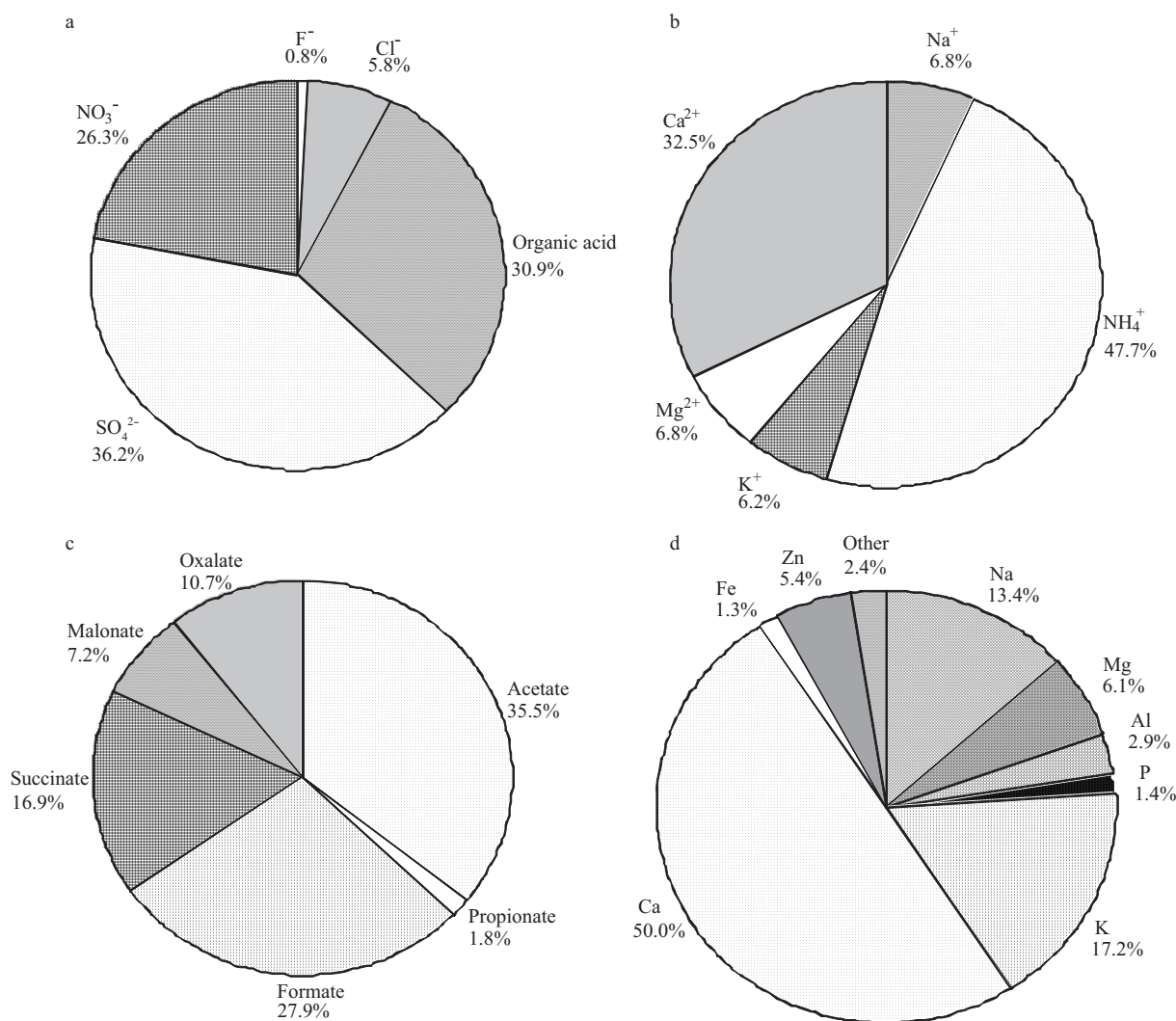


Fig. 3 Composition of anions (a), cations (b), organic acid (c) and elements (d) in precipitation.

also detected in small amounts: in combination with Ti, V, Mn, Co, As, Se, Mo, Ba, Tl, Th and U, their contribution to the total element mass was about 2.4%. This result was consistent with that from previous studies (Table 3).

2.3 $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio and acid-alkaline equilibrium in rainwater

The $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio in rainwater can indicate whether acidity is a consequence of human activity, and it can be

Table 1 Concentrations of inorganic ions in rainwater from Mangdang Mountain and comparison with other areas (unit: $\mu\text{eq/L}$)

Area	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Na^+	K^+	Mg^{2+}	$\text{SO}_4^{2-}/\text{NO}_3^-$	References
Mangdang Mountain	0.8	5.8	26.6	36.6	38.0	25.8	5.4	4.9	5.4	1.4	This study
Beijing	12.9	31.5	84.1	249	234	191	16.3	12.0	33.8	3.0	Yang et al., 2004
Nanjing	19.1	143	39.6	242	193	295	23	12.1	31.7	6.1	Tu et al., 2005
Fuzhou	5.26	21.4	24.9	96.9	78.1	65.3	2.61	4.1	2.5	3.9	Zhao, 2004
Shenzhen	18.7	24.5	23.6	66.1	30.7	59.4	14.4	5.9	10.7	2.8	Niu et al., 2008
Guangzhou	n.d.	4.6	44.9	149.8	57.8	82.8	13.0	5.9	6.9	3.3	Yang et al., 2005
Jinhua	11.54	10.29	36.98	116.91	96.96	56.06	7.46	5.28	4.38	3.2	Zhang et al., 2007
Lushan Mountain	2.2	6.7	21	66.3	38.7	26.1	n.d.	n.d.	3.4	3.2	Wang et al., 1996
Taishan Mountain	n.d.	13.3	30.8	111.5	80.9	49.9	14.4	7.3	5.4	3.6	Wang et al., 2006
Jinyun Mountain	n.d.	24.7	14.0	212.9	142.4	80.8	28.3	18.2	18.8	15.2	Wei et al., 2005
Waliguan Mountain	n.d.	6.1	8.3	24	45.5	34	8.7	3.8	12.1	2.9	Tang et al., 2000
Hong Kong	n.d.	27.8	13.2	43.1	n.d.	8.9	24.8	1.9	5.7	3.3	Tanner, 1999
Seoul, South Korea	n.d.	18.2	29.9	70.9	66.4	34.9	10.5	3.5	6.9	2.4	Lee et al., 2000
Okinawa, Japan	n.d.	351	7.0	53.9	9.5	25.2	308	9.4	63.9	7.7	Sakihama et al., 2008
Tinupati, India	4.7	33.9	40.8	128	20.4	151	33.1	33.9	50.5	3.1	Mouli et al., 2005
Ankara, Turkey	n.d.	20.4	29.2	48.0	86.4	71.4	15.6	9.8	9.3	1.6	Topcu et al., 2002
New Jersey, USA	1.1	10.7	14.3	19.0	24.4	3.0	10.9	1.3	1.6	1.3	Song and Gao, 2009

n.d. indicates not detected.

Table 2 Concentrations of organic acid in rainwater at Mangdang Mountain and comparison with other areas (unit: $\mu\text{eq/L}$)

Areas	Acetate	Formate	Propionate	Mesylate	Oxalate	Malonate	Succinate	Reference
Mangdang Mountain	9.9	7.9	1.1	0.2	3.6	2.8	5.3	This study
Beijing	4.6	4.6	n.d.	n.d.	1.2	n.d.	n.d.	Hu et al., 2005
Shanghai	0.1	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	Huang et al., 2008
Shenzhen	5.2	3.7	n.d.	0.2	3.2	0.03	0.1	Niu et al., 2008
Zunyi City	9.5	6.6	n.d.	n.d.	n.d.	n.d.	n.d.	Jiang et al., 2008
New Jersey, USA	4.4	3.5	n.d.	n.d.	1.4	0.6	n.d.	Song and Gao, 2009
North Carolina, USA	10.0	7.3	n.d.	n.d.	3.6	1.4	n.d.	Avery et al., 2006
Amazonas, Brazil	9.3	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	Williams et al., 1997

n.d. indicates not detected

Table 3 Concentrations of elements in precipitation at Mangdang mountain and comparison with other areas (unit: ppb)

Area	Ca	K	Na	Mg	Al	P	Fe	Mn	Cu
Mangdang Mountain	605.3	208	162.5	74.0	34.7	17	15.3	6.2	3.8
Nanjing	10.0	2693	927	257	6.5	n.d.	93.3	35.7	32.4
Northern Jordan	n.d.	n.d.	n.d.	n.d.	382	n.d.	92	2.1	3.1
New Jersey, USA	n.d.	n.d.	n.d.	n.d.	6.1	n.d.	4.6	n.d.	1.2
Area	Zn	Pb	Ba	Ni	Cd	Co	Cr	V	Reference
Mangdang Mountain	65.2	9.6	6.1	1.0	0.02	0.05	0.04	0.02	This study
Nanjing	245.8	51.8	n.d.	14.1	2.2	0.2	1.6	n.d.	Fan et al., 2009
Northern Jordan	6.5	2.6	n.d.	2.6	0.4	n.d.	0.8	4.2	Al-Momani, 2003
New Jersey, USA	4.9	0.39	n.d.	0.5	0.02	0.01	0.1	0.2	Song and Gao, 2009

n.d. indicates not detected.

used to evaluate the relative contributions of SO_4^{2-} and NO_3^- ions to the acidity. From Table 1 it can be seen that the $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio in this study was much lower than that in other areas of China and Asia, although it was similar to that reported in Ankara (Turkey) and New Jersey (USA). The elevated nitrate concentration and reduced sulfate-to-nitrate ratio are an indication of changes in compositions of atmospheric pollutants over recent years. From the 1990s, China has continually improved its energy structure by using clean energy sources, and SO_2 emissions have been well controlled. During this period, however, NO_x pollution has become more prominent due to rapid growth in motor vehicle numbers, resulting in enhanced atmospheric oxidization. The combination of coal-burning pollution and motor vehicle exhaust pollution has produced complex atmospheric pollution characterized by secondary particles such as sulfates, nitrates, ammonium salts and fine particulate organic matter.

Because of the significant contribution of organic acids to the total ion content in rainwater detected in this study, the influence of the organic acids was considered in the analysis of acid neutralization in the rainwater using the fractional acidity (FA) method, which initially proposed by Balasubramanian et al. (2001) and later modified by Song and Gao (2009). The FA equation was revised as follows:

$$\text{FA} = \frac{\text{H}^+}{(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Organic acid})} \quad (3)$$

The neutralization factor (NF) equation for describing the neutralizing ability of alkaline substances in rainwater was also revised correspondingly:

$$\text{NF}_{(X)} = \frac{X}{(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Organic acid})} \quad (4)$$

where, X is the relevant cation concentration.

The resulting FA in Mangdang Mountain was 24.5%, which means 75.5% of the acidity had been neutralized. Both NH_4^+ and Ca^{2+} were the main neutralizing media, accounting for 40.3% and 27.4%, respectively, to the neutralization. Additionally, Na^+ , K^+ and Mg^{2+} ions also contributed to acidity neutralization, accounting for 5.7%, 5.3% and 5.7%, respectively, indicating that NH_3 from man-made sources (Zunckel et al., 2003) and particulate CaCO_3 in the atmosphere had a neutralizing effect for the rainwater in the Mangdang Mountain area, as seen in the most other areas (Glavas and Moschonas, 2002; Al-Momani, 2003).

2.4 Correlation analysis and removal efficiency

To determine the sources of different anions and cations in the rainwater and their potential linkages, the main ion component relationships were calculated (Table 4).

The SO_4^{2-} and NO_3^- anions were highly correlated, possibly because they had the same emission source and similar chemical properties to their precursors SO_2 and NO_x . Both Mg^{2+} and Ca^{2+} demonstrated strong correlation, indicating that they may come from the same land-based source. The strong correlation between Mg^{2+} and Na^+ indicated that a marine source also contributed to the presence of Mg^{2+} ions. There was a strong correlation between Na^+ and Cl^- ions from a marine source. In addition, there were also strong correlation between Ca^{2+} and SO_4^{2-} , and between Ca^{2+} and NO_3^- , which were mainly caused by chemical reactions between H_2SO_4 and HNO_3 acids and the alkali carbonate Ca^{2+} in the atmosphere.

In general, the H^+ ion content in rainwater correlated strongly to the main acidic ions SO_4^{2-} and NO_3^- , but in the present study no obvious correlation was observed between H^+ and any other anions and cations. This indicated that the rainwater acidity in this region was a result of all

Table 4 Correlation of components in rainwater

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Organic acid
H ⁺	1	0.0018	0.4634	0.1182	0.0005	0.0054	0.0018	0.0873	0.0886	0.1101	0.1345
Na ⁺		1	0.1187	0.5045	0.8638	0.8210	0.2013	0.6001	0.6269	0.5935	0.0053
NH ₄ ⁺			1	0.5096	0.1586	0.1850	0.0604	0.3987	0.5072	0.5253	0.1064
K ⁺				1	0.6652	0.4606	0.5374	0.5506	0.5208	0.6000	0.2514
Mg ²⁺					1	0.7998	0.3830	0.5473	0.5261	0.5897	0.0335
Ca ²⁺						1	0.0922	0.5466	0.7139	0.7205	0.0026
F ⁻							1	0.2052	0.0573	0.0557	0.1406
Cl ⁻								1	0.7291	0.5034	0.0311
NO ₃ ⁻									1	0.7151	0.0075
SO ₄ ²⁻										1	0.0014
Organic acid											1

the acid-included ions and neutralization ions rather than any single ion component.

In the present study, the concentration of total cations, anions and trace metals showed a logarithmic decline with increase of precipitation volume, demonstrating the concentration/dilution effect of high precipitation rates. However, the total organic acid content did not show any significant change with increased volume (Fig. 4).

2.5 Source analysis of precipitation

2.5.1 Enrichment factor analysis

The enrichment factor method reveals important information about the elemental source of ions in the atmosphere and precipitant rainwater by comparing the ion concentration ratios in air and rainwater samples with the ion concentration in reference material. To estimate the contribution of marine and terrestrial sources in atmospheric precipitation in the present study, Na and Al were adopted as the reference elements for seawater and soil, respectively. The ion enrichment factor for atmospheric precipitation from both sources is calculated as follows:

$$EF_{\text{marine}} = [X/\text{Na}^+]_{\text{rainwater}}/[X/\text{Na}^+]_{\text{seawater}} \quad (5)$$

$$EF_{\text{soil}} = [X/\text{Al}]_{\text{rainwater}}/[X/\text{Al}]_{\text{soil}} \quad (6)$$

where, X is the ion or element in the rainwater; the X/Na⁺ proportion in seawater refers to the seawater component data in the previous study (Huang et al., 2008); and the X/Al proportion in soil refers to the results in China Soil Element Background Value (Environmental Monitoring of China, 1990).

Enrichment factor analysis showed the seawater enrichment factor for Cl⁻ in rainwater was low (0.68), indicating that its main source was seawater and it was a typical sea-salt ion. The seawater enrichment factor of Mg²⁺ was 4.59, which also indicated that it originated mainly from a marine source (Poissant et al., 1994). Such results are consistent with the strong correlation found between the values for Mg²⁺ and Na⁺ (Table 4). K⁺, Ca²⁺ and SO₄²⁻ were moderately enriched relative to seawater (their EF_{marine} value are 29.95, 100.10 and 22.39, respectively), indicating that these three ions may have originated from land-based and/or man-made sources in addition to seawater. The EF_{marine} value for NO₃⁻ was greater than 500 (EF_{marine} value 188,496.14), indicating that marine sources had only a slight influence on the presence of NO₃⁻ in rainwater

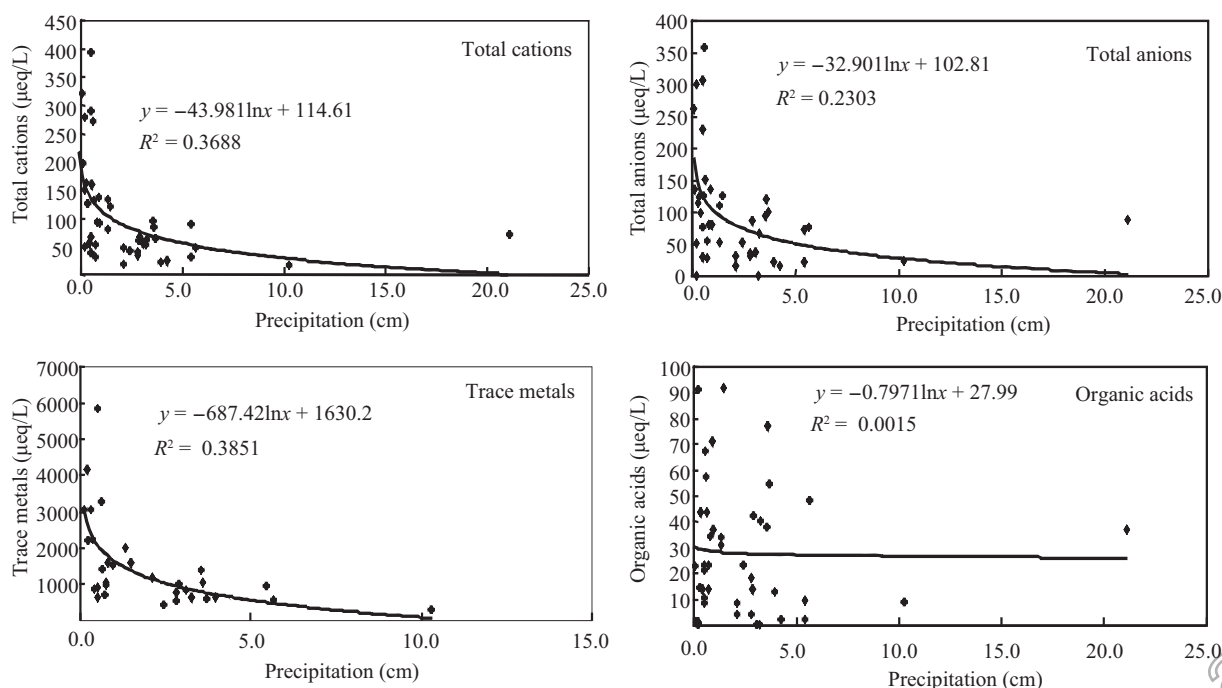


Fig. 4 Removal effect of precipitation volume on total cations, total anions, trace metals and organic acids.

Table 5 Contribution to rainwater ion components from different sources (%)

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Marine source	100.0	0.0	2.4	23.0	0.9	0.0	100.0	0.0	1.8
Crust source	0.0	0.0	0.1	77.0	3.5	0.0	0.0	0.0	1.2
anthropogenic source	0.0	100.0	97.5	0.0	95.6	100.0	0.0	100.0	97.0

Table 6 Correlation analysis between rainwater organic acids and other indicator component

	Acetate	Propionate	Formate	Mesylate	Succinate	Malonate	Oxalate
Na ⁺	0.003	0.001	0.002	0.05	0.002	0.140	0.020
NH ₄ ⁺	0.101	0.001	0.093	0.002	0.050	0.014	0.097
K ⁺	0.101	0.022	0.112	0.288	0.096	0.218	0.329
Mg ²⁺	< 0.001	0.007	0.001	0.167	0.017	0.176	0.105
Ca ²⁺	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.085	0.003
NO ₃ ⁻	0.009	0.005	0.007	0.001	< 0.001	0.021	0.006
SO ₄ ²⁻	< 0.001	0.009	< 0.001	< 0.001	0.002	0.018	0.015

(Poissant et al., 1994). Of the elements detected, only Na, Mg, K and Ca were moderately or extremely enriched relative to their concentration in soil (soil enrichment factors for Na, Mg, K and Ca in precipitation were 378.96, 90.09, 38.30 and 3388.30, respectively), which meant that they were derived from man-made or marine sources. All other detected elements originated from soil (their soil enrichment factors in precipitation were less than 1.0).

2.5.2 Source of inorganic components in precipitation

To understand the effect of different sources on inorganic components in precipitation, we analyzed the relative contribution of the sources to the components present in the rainwater. The SF (sea factor) refers to the proportion of ions from a marine source in rainwater, as normally the ocean is considered as the only source of Na⁺ (Huang et al., 2008; Zhang et al., 2007). The CF (crustal factor) represents the component contributed by crustal sources. It is generally considered that Mg²⁺ comes from marine and/or crustal sources (Huang et al., 2008). The crustal element content comes from the soil element background value in China. Man-made sources of ions are termed anthropogenic factors (AF).

These factors are calculated as follows:

$$SF_x = (X/Na^+)_{\text{seawater}} \times (Na^+/X)_{\text{rainwater}}$$

$$CF_x = (X/Mg^{2+})_{\text{seawater}} \times (Mg^{2+}/X)_{\text{rainwater}} \quad (7)$$

$$AF_x = 1 - SF_x - CF_x$$

Table 5 shows that Na⁺ and Cl⁻ were from marine source only; Mg²⁺ ions were mainly from crustal sources, although the contribution by the ocean cannot be ignored (23.0%). Marine and crustal sources made a minor contribution to K⁺, Ca²⁺ and SO₄²⁻. The NH₄⁺, F⁻ and NO₃⁻ ions came only from man-made sources which include local agricultural activities (such as fertilizing) and city development (such as burning of fossil fuel).

2.5.3 Potential source of organic components in precipitation

To better understand the source of organic acids and formation pathway, we conducted a correlation analysis

between rainwater organic acids and other indicator components (Table 6). Both K⁺ and NH₄⁺ were related to biomass burning, NO₃⁻ was an important component of motor vehicle exhaust emissions, SO₄²⁻ was an indirect indicator of anthropogenic sources, Na⁺ was a typical sea salt ion, and Ca²⁺ and Mg²⁺ were from soil.

Our results showed no significant correlation between organic acids and other indicator components. However, there were strong correlations between organic acid component and K⁺ and NH₄⁺. Jiang et al. (2008) proposed the ratio of formic and acetic acids in the precipitation (F/A) aq (in this study (F/A) aq = 1.58, F/A = 0.8), which indicated that the organic acids in precipitation were mainly from biomass burning in Mangdang Mountain, Fujian Province.

3 Conclusions

A study of the chemical characteristics of springtime precipitation in Mangdang Mountain, Fujian Province, South China was conducted. The rainwater was acidic with an average pH of 4.81 and average conductivity of 20.01 μS/cm. The relatively low conductivity indicated good atmospheric environmental quality. The major anion component was SO₄²⁻ (36.2% of the total anion mass), while NH₄⁺ was the main cation component (47.7% of total cation mass). The main trace metals in the rainwater were Ca (50.0% of total mass), K (17.2%) and Na (13.4%). Organic acids (including acetic, formic, succinic, adipic, malonic, propionic and methanesulfonic acids) were a significant component of the anions in the rainwater in the Mangdang Mountain area, and their percentages were higher than NO₃⁻ and lower than SO₄²⁻.

The SO₄²⁻/NO₃⁻ ratio of 1.4 suggested complex atmospheric pollution from combined coal-burning and motor vehicle exhaust. There was no obvious correlation between the rainfall acidity and either the anion and cation amounts, indicating that acidity was a combined result of all acidic and neutralizing ions and was not determined by any single ion in the rainwater: 75.5% of the acidity was neutralized by NH₄⁺, Ca²⁺, Na⁺, K⁺ and Mg²⁺; of these, NH₄⁺ and Ca²⁺ contributed most to acidity neutralization. Sources of rainwater pollution in the Mangdang Mountain area were: marine (mainly Na⁺ and Cl⁻), crustal (mainly Ti, V, Cr,

Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Ba, Tl, Pb, Th and U), man-made (mainly NH_4^+ , K^+ , Ca^{2+} , F^- , NO_3^- and SO_4^{2-}), and combustion of biomass (organic acids).

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