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Long-term trends in chemical composition of precipitation at Lijiang, southeast Tibetan Plateau, southwestern China

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ABSTRACT

1090 precipitation samples were collected between 1989 and 2006 from the Lijiang region, an internationally important tourist site in Yunnan province, southwestern China. All the samples were analyzed for pH, electrical conductivity, SO_4^{2-}, Cl^-, NO_3^-, Na^+, Ca^{2+}, Mg^{2+} and NH_4^+ concentrations. pH had a mean value of 6.08 and showed a slight increase as tourism developed between 1989 and 2006. SO_4^{2-} and Ca^{2+} were the dominant anion and cation, respectively. Most of the ions showed significantly increasing trends, especially Ca^{2+} and Mg^{2+}, with the exception of NH_4^+ that had a clearly decreasing trend. As a result, the neutralization capacity of Ca^{2+} increased significantly, and the precipitation NP/AP (neutralizing potential index/acidifying potential index) ratio increased. There was a significant correlation between the soil-derived cations Ca^{2+} and Mg^{2+}, and significant correlation of SO_4^{2-} with Ca^{2+} and Mg^{2+}. The sea-salt species Cl^- and Na^+ was not well correlated. Using Na^+ as a sea-salt tracer, non-sea-salt source fractions were calculated as SO_4^{2-}: 99.1%, Mg^{2+}: 92.6% and Ca^{2+}: 99.8%. Furthermore, about 95.4% of NO_3^- and 41.7% of SO_4^{2-} were contributed by anthropogenic sources, and 57.4% of SO_4^{2-} was contributed by soil/dust sources that had a remarkably strong relationship ($r=0.65$, $p<0.01$) with the number of tourists, suggesting that human activities in a tourism-oriented city increase atmospheric dust loading.

1. Introduction

Human activities are considered to have the most important influence on atmospheric chemistry (Munger and Eisenreich, 1983; Puxbaum et al., 1998; Lara et al., 2001; Zhang et al., 2007). Meanwhile, precipitation processes play a crucial role in the chemical transformation and removal of constituents that are important in determining air quality and rain acidity, in chemical reactions involving other components, and in the radiative balance in the Earth's atmosphere. Knowledge of these processes aids understanding of the relative contribution of different sources of atmospheric pollutants (Shrestha et al., 2002; Tang et al., 2005; Zhang et al., 2007; Das et al., 2011). Scavenging of atmospheric pollutants affects the chemical composition and pH of precipitation. Due to increased anthropogenic activities since the industrial revolution and associated urban development, the health of the environment is deteriorating in terms of increases of different types of contaminants and acidic species. Much attention has been paid to the study of the chemical composition of precipitation in order to understand the current status and level of acid rain (Okuda et al., 2005; Wang et al., 2008).

Numerous observations of precipitation have been published for North America and Europe, and the composition of atmospheric precipitation has been studied systematically (Keene et al., 1983; Munger and Eisenreich, 1983; Khwaja and Husain, 1990; Lim et al., 1991; Alastuery et al., 1999; Ito et al., 2002; Hontoria et al., 2003). In recent decades, the rapid development of heavy industry has led to an increased

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use of fossil fuels, causing increased emission of SO_2 and NO_x, which are the precursors of strong acids such as H_2SO_4 and HNO_3 (Lee et al., 2000). North America has been seriously affected by acid rain (Galloway et al., 1976; Cowling, 1982; Khwaja and Husain, 1990; Heuer et al., 2000; Ito et al., 2002), as has central Europe (Smirnioudi and Siskos, 1992; Al-Momani et al., 1995; Sanusi et al., 1996; Marquardt et al., 2001; Topcu et al., 2002) and the southern region of China (Wang, 1994; Ding et al., 1997; Zhang et al., 2007; Huang et al., 2008; Cao et al., 2009; Li et al., 2010).

Due to different natural environments and human activities, the composition of precipitation varies from site to site. As well as acid precipitation, alkaline precipitation has also been reported from around the world (Kulshrestha et al., 2003; Zhang et al., 2003b; Rastogi and Sarin, 2005; Zhao et al., 2008; Budhavant et al., 2011), and in particular over a great part of the Tibetan Plateau (Zhang et al., 2003a,b; Li et al., 2007). Lijiang is located in the southeast of the Tibetan Plateau. Because Lijiang has a low level of human activities and is far from industry, it was selected as an inland precipitation background site to research the global precipitation chemistry during 1987–1989 (Liu et al., 1993). Since 1990, Lijiang has gradually become a world famous tourist site, but there have been few recent reports of its precipitation chemistry. Moreover, although reports of acid rain in south China are increasing due to the region's rapid industrial growth, little attention has been paid to precipitation chemistry under developing tourism, with a notable lack of any long-term studies. Accordingly, we selected the Lijiang region as a study region for long-term precipitation chemistry monitoring to (1) understand the long-term trends of precipitation pH, conductivity and chemical composition; (2) identify the possible sources of the various components of precipitation; and (3) assess the influence of developing tourism on the atmospheric environment. The study was based on precipitation data collected during the period 1989–2006 at Lijiang City.

2. Experimental methods

2.1. Study area

The Lijiang region (100.25°E, 26.86°N) is an intermontane basin situated at a mean elevation of 2393 m in the northwest of Yunnan Province, southwest China (Fig. 1). There are several tourist cities around Lijiang, such as Diqing Tibet Autonomous Prefecture (Shangri-La) to the north, Dali to the south and Nujiang Lisu Autonomous Prefecture to the west. The one exception is Panzhihua City, which is a heavy industrial city to the east. The climate is dominated by the southwesterly summer monsoon (from May to October) and is controlled by the southern branch of the westerly jet in winter (from November to the following April). Consequently, the whole year is dominated by westerlies, leading to very little transport of pollutants from the industrialized Panzhihua City area to Lijiang. The annual mean temperature and mean annual precipitation are 12.6 °C and 900 mm, respectively. 90% of the annual precipitation falls during the summer monsoon months (from June to September), and the vapor source for monsoon rainfall is mainly the Indian Ocean (Pang et al., 2006).

Tourism began to develop in Lijiang in 1990. Since 1996, tourism has seen steady growth, and the region has now become world famous because of the Old Town of Lijiang, which was listed as a World Heritage site in 1997. Lijiang is a historic and cultural city of great value and importance (UNESCO World Heritage Centre 1997). The nearby Mt. Yulong, a typical monsoonal temperate glacial area, is the southernmost mountain in mainland Eurasia that has modern glaciers. Tourism is now the mainstay of the Lijiang region economy. According to Lijiang Statistics Yearbook, Fig. 2 shows the variations of the percents of three industries, it can be see that Lijiang transforms from an agricultural city (mainly primary industry) to a tourist city (mainly tertiary industry) between 1990 and 2006, and in order to develop tourism, secondary industry related to heavy pollution has developed slowly. Moreover, the number of tourists visiting the area annually was 0.84 million in 1995, increasing to almost 4.6 million in 2006 (Fig. 5-h).

2.2. Sampling and analyses

Precipitation sampling was carried out using a funnel collector about 15 m above the ground and 1.5 m above the roof of the Lijiang Environmental Monitoring Station building. In order to avoid contamination, the funnel and collector were cleaned before sampling. The collected precipitation was divided into two parts: one for analyzing pH and conductivity, and the other for ion analysis. Details of the sampling and pretreatment procedures followed those adopted at the Shenzhen Environmental Monitoring Station and described by Huang et al. (2008). The annual rainfall and sample size (1090 samples totally) at Lijiang during 1989–2006 are shown in Fig. 3. Data on annual tourist visits and the percent of different industries during 1990 to 2006 were obtained from the Lijiang Statistical Yearbook.

The pH of precipitation was measured in the laboratory at a temperature of approximately 25 °C with an acidometer (Type: pH-2, Shenzhen, China). The electric conductivity was measured using a conductivity meter (Type: DDS-II, Shanghai, China). Analysis of cations (NH_4^+, Mg^{2+}, Na^+ and Ca^{2+}) and anions (Cl-, SO_4^{2-} and NO_3^-) was carried out initially with an atomic absorption spectrophotometer (Type: PE-2380, Massachusetts, USA) and subsequently by ion chromatography (Type: Dionex-300, Sunnyvale, Canada).

Data quality was checked by calculating the ionic balance. According to the United States Environmental Protection Agency (USEPA), the acceptable range for ionic imbalance in precipitation samples is 15–30% for samples having ionic concentration $>100\ \mu eq \cdot L^{-1}$, and 30–60% for samples having ionic concentration $>50–100\ \mu eq \cdot L^{-1}$ (Rastogi and Sarin, 2005; Zhang et al., 2007). All the samples in this study met the quality criteria based on ionic balance. The difference and ratio between mean cations ($Na^{2+} + Ca^{2+} + Mg^{2+} + NH_4^+$) and mean anions ($Cl^- + SO_4^{2-} + NO_3^-$) were $24.26\ \mu eq \cdot L^{-1}$ and 1.50, respectively. The observed anion deficiency was mainly attributable to the HCO_3^-/CO_3^{2-} in the precipitation. The correlation coefficient between Ca^{2+} and ΔC (total cation equivalents minus total anion equivalents) was 0.90 ($p<0.01$), suggesting that the ΔC mainly represented the HCO_3^-/CO_3^{2-} (Wake et al., 1992; Williams et al., 1992; Li et al., 2006; Zhao et al., 2008). Moreover, as pointed

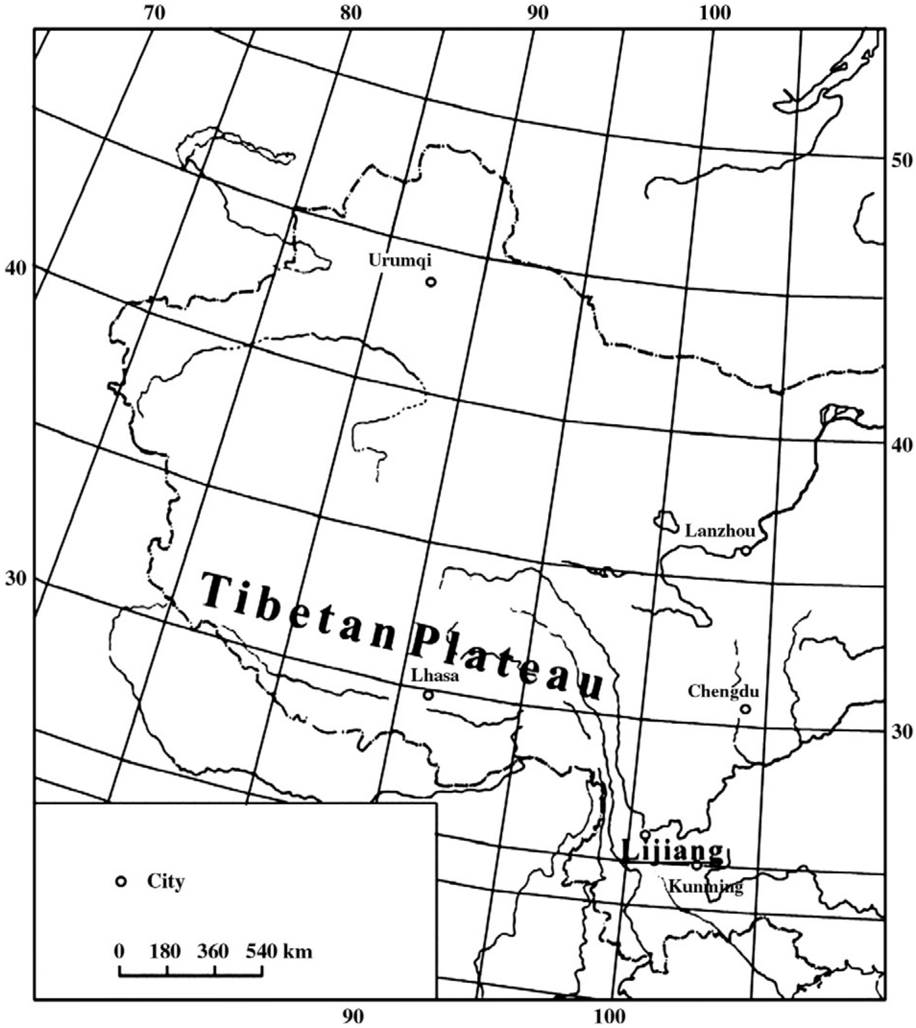

Fig. 1. Location of Lijiang.

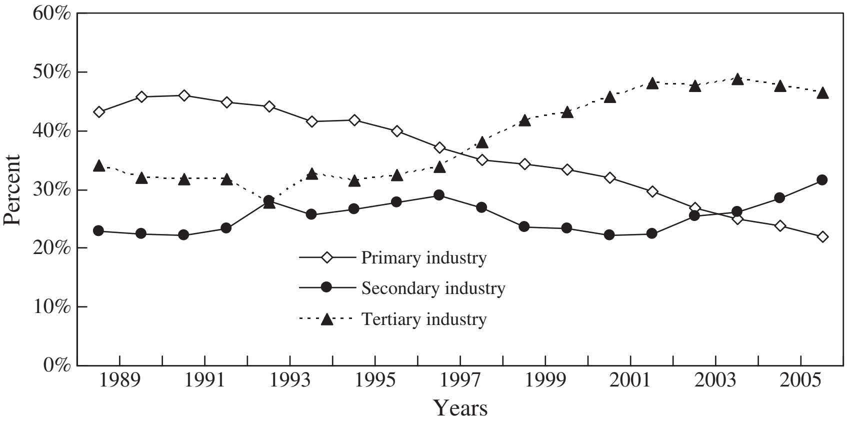

Fig. 2. Variations of percent of different industries (Primary industry mainly refers to agriculture; Secondary industry mainly refers to heavy industry, and tertiary industry main refers to service industry).

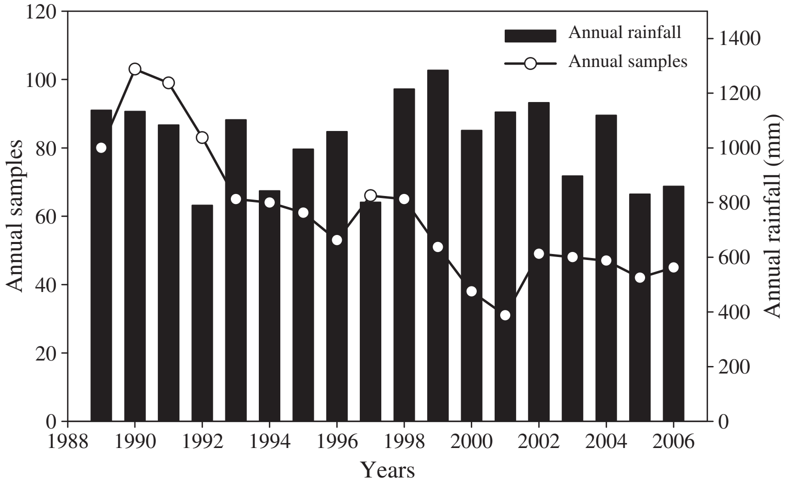

Fig. 3. Annual precipitation and sampling number at Lijiang during 1989–2006.

out by Liu et al. (1993), organic acids, in particular formic and acetic acids, contribute 44% of the acidity of precipitation; these acids were not detected in the present study.

3. Results and discussion

3.1. pH and electrical conductivity

The pH value of unpolluted rainwater at equilibrium with atmospheric CO_2 is 5.60. With the exception of 1994 (5.25) and 1995 (4.99), the annual mean pH values in our samples were all greater than 5.60, with an overall mean of 6.08. Due to differences in the acidic constituents and neutralizing capacity, many places in South China, especially around Lijiang, are classified as acid rain regions (Table 1). For example, average pH values have been measured as 4.78 in Chongqing city during 1996–2002 (Zhou et al., 2003), 5.25 in Kunming city during 1998–2002 (Wang, 2003), and 5.02 in Chengdu city during 1995–2003 (Mei et al., 2005). However, the precipitation in Lijiang city is relatively alkaline in comparison with these cities, but similar to the pH values published at other sites on the Tibetan Plateau (Table 1). From Table 1 we can see that the mean pH value of our samples was closest to that of Waliguan, which is the background monitoring station in the hinterland of the Tibetan Plateau, and was smaller than the values observed at Nam Co and Lhasa. Zhang et al. (2003a) pointed out that the alkaline precipitation over the Tibetan Plateau was not due to the low atmospheric pCO_2, but rather to the neutralization of acidity by airborne dust aerosols that are derived from the surface soil. In our samples, the correlation coefficients of pH with Ca^{2+} and Mg^{2+} were 0.48 ($p = 0.05$) and 0.46 ($p = 0.05$), but the correlation coefficients of pH with SO_4^{2-} and NO_3^- were only 0.28 and 0.21. Similar situations are also found in other regions (Rastogi and Sarin, 2005; Li et al., 2007).

The mean pH value at Lijiang was 5.00 during 1987–1989 (Table 1), indicating weakly acid precipitation. However, the alkaline precipitation identified in this study may be due to an increase in alkaline species inputs into the atmosphere since 1990, especially since the temporal variations of annual pH values show an increasing trend (Fig. 4). This trend contrasts with observations from Qinghai Province (China), Shenzhen city (China) and Pune (India), where the pH value declined significantly due to fast industrial development during the periods of 1980–1990, 1986–2006 and 1984–2002, respectively (Zhang et al., 2003b; Huang et al.,

Table 1
Chemical composition in precipitation at various sites (μeq L^{-1}).

Variable				Tibetan Plateau			South China			
	This wok		Lijiang[a] (1987–1989)	Lhasa[b] (1987–1988, 1997–1999)	Nam Co[c] (2005–2006)	Waliguan[d] (1997)	Chongqing[e] (1996–2002)	Kunming[f] (1991–2000)	Chengdu[g] (1995–2003)	Shenzhen[h] (1986–2006)
	Average	Range								
pH	6.08	4.99–6.80	5	8.36	6.59	6.38	4.78	5.25	5.02	5.02
EC[i]	14.17	9.00–28.00	5.26		19.7	14.58				25.52
SO_4^{2-}	32.64	16.67–79.17	8.15	2.5	15.5	24	448.16	108.84	291.14	74.3
NO_3^-	3.63	0.65–7.58	1.92	2	10.37	8.3	47.05	15.4	52.31	22.1
Cl^-	11.56	0.85–32.68	3.69	21.2	19.17	6.1	52.87	31.97	38.89	37.9
NH_4^+	11.36	1.11–55.00	5.67	21.9	18.13	45.5	170.02	44.9	173.53	35.2
Ca^{2+}	50.19	14–218.50	4.45	150.3	65.58	34	358.66	111.08	241.14	77.7
Mg^{2+}	7.73	1.67–34.17	1.58	5.7	7.43	12.1	43.49	44.07	27.87	9.7
Na^+	2.54	0–11.74	0.96	89	15.44	8.7	24.4	28.13	19.66	40.3
$\Sigma^+ + \Sigma-$	119.65	50.05–346.41	26.42	292.6	151.62	138.7	1144.65	384.38	844.55	297.2

[a]Liu et al. (1993); [b]Zhang et al. (2003b); [c]Li et al. (2007); [d]Tang et al. (2000); [e]Zhou et al. (2003); [f]Wang (2003); [g]Mei et al. (2005); [h]Huang et al. (2008); [i]unity of EC is $s \cdot cm^{-1}$.

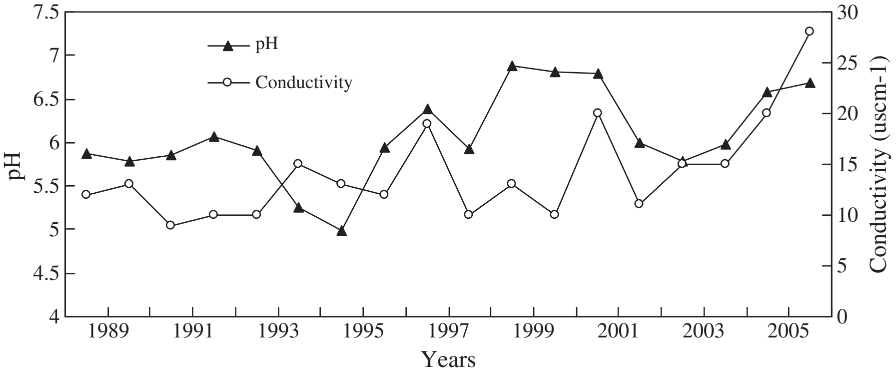

Fig. 4. Temporal variation of pH value and conductivity in precipitation at Lijiang during 1989–2006.

2008; Safai et al., 2004). This result reveals that Lijiang, as a city based on tourism, inputs more alkaline constituents to the region's precipitation than that input by industrialized cities.

The electrical conductivity was attributed mainly to the total soluble ions. The average conductivity in this study was 14.20 μs·cm^{-1}, which was nearly three times higher than the conductivity reported during 1987–1989 (Liu et al., 1993). However, it is close to that measured at Waliguan, which represents the background value of the northern Tibetan Plateau, slightly lower than that of Nam Co located on the central Tibetan Plateau, and nearly half of that at Shenzhen City which is a metropolis. These comparisons show that although the number of constituents in the precipitation increased after 1989, precipitation is still clean at Lijiang.

3.2. Chemical composition of precipitation

3.2.1. Temporal variations

The sequence of the mean concentrations (volume-weighted average) of ionic species in precipitation at Lijiang city during 1989–2006 was: $Ca^{2+} > SO_4^{2-} > Cl^- > NH_4^+ > Mg^{2+} > NO_3^- > Na^+$. Ca^{2+} and SO_4^{2-} were the dominant cation and anion, respectively. Fig. 5 (a–g) shows the annual variation of detected ionic constituents in precipitation at Lijiang city during 1989–2006. Although solar energy is used commonly at Lijiang, the main energy source is gas and coal, which are consumed by local residents, most hotels and motor vehicles. In particular, since 1990 an increasing number of tourists visiting Lijiang city has led to increased anthropological emissions into the atmosphere. These changes have led to an increasing trend in mean annual concentrations of SO_4^{2-} ($r = 0.41$, $p = 0.09$). The increasing trend of SO_4^{2-} was clearer than that of NO_3^- ($r = 0.29$, $p = 0.23$), and the concentration of SO_4^{2-} was greater than that of NO_3^- in this study. These results indicate that NO_3^- plays a less important role in acidification at Lijiang city than that of SO_4^{2-}. Meanwhile, all the detected anions showed increasing trends, and Cl^- showed a weak (but not significant) increasing trend ($r = 0.11$; $p = 0.6$).

It is interesting that, among the detected ions, only the concentration of NH_4^+ showed a clearly decreasing trend ($r = -0.49$, $p = 0.03$) (Fig. 5-g). This may be due to two factors. Firstly, most of the emission of NH_4^+ from soil is from the nitrogen fertilizers used in agricultural. Local farmers and herders are becoming increasingly engaged in tourism, thus reducing agricultural activities and associated NH_4^+ emission. A similar pattern was also found at Shenzhen (Huang et al., 2008). Secondly, the soil type in the Lijiang region is mainly red soil, which is acidic and releases little NH_3 to the air.

In contrast to NH_4^+, the other cations all showed an increasing trend during 1989–2006, especially the concentrations of Mg^{2+} and Ca^{2+} which displayed significant increases with time ($r = 0.70$, $p = 0.001$; $r = 0.67$, $p = 0.002$, respectively). These changes reflect urban expansion. Increasing tourism in Lijiang and rapid urbanization has led to increased open areas and construction sites, which act as sources of carbonate-rich soil/dust particles. This process is evident in the limestone quarry in the hillside close to Lijiang city. At the same time, deforestation for building by local residents and decreasing annual precipitation has indirectly contributed to increased atmospheric dust loading.

3.2.2. Chemical composition during different stages of development

Based on the different stages of tourism development, we divided the study period into three shorter periods to allow discussion of the chemical composition in more detail (Table 2). Period I represents the natural precipitation chemistry of the Lijiang region. During this period, the total ionic abundance ($\sum^+ + \sum^-$) was only 26.41 μeq·L^{-1}, which is far less than the values listed in Table 1, and similar to values found at high altitude (Hidy, 2003). The ionic sequence in Period I was $SO_4^{2-} > NH_4^+ > Ca^{2+} > Cl^- > NO_3^- > Mg^{2+} > Na^+$. SO_4^{2-} and NH_4^+ were the dominant anion and cation, respectively, similar to the chemical composition of natural precipitation and indicating that the precipitation chemistry at Lijiang during Period I represented the natural or background state. There was little tourism (and no official tourism statistics) in Lijiang prior to 1989.

During 1989–1996 (Period II), tourism began to develop in Lijiang, and the annual number of tourist visits reached 368,600. At the same time, the total ionic abundance as well as the ionic concentrations of each individual ion all increased relative to Period I, and of particular note was the concentration of Ca^{2+} which increased by more than a factor of 5. During Period II, SO_4^{2-} and Ca^{2+} became the dominant anion and cation, and the ionic order shifted to $Ca^{2+} > SO_4^{2-} > Cl^- > NH_4^+ > Mg^{2+} > NO_3^- > Na^+$. It can be seen that

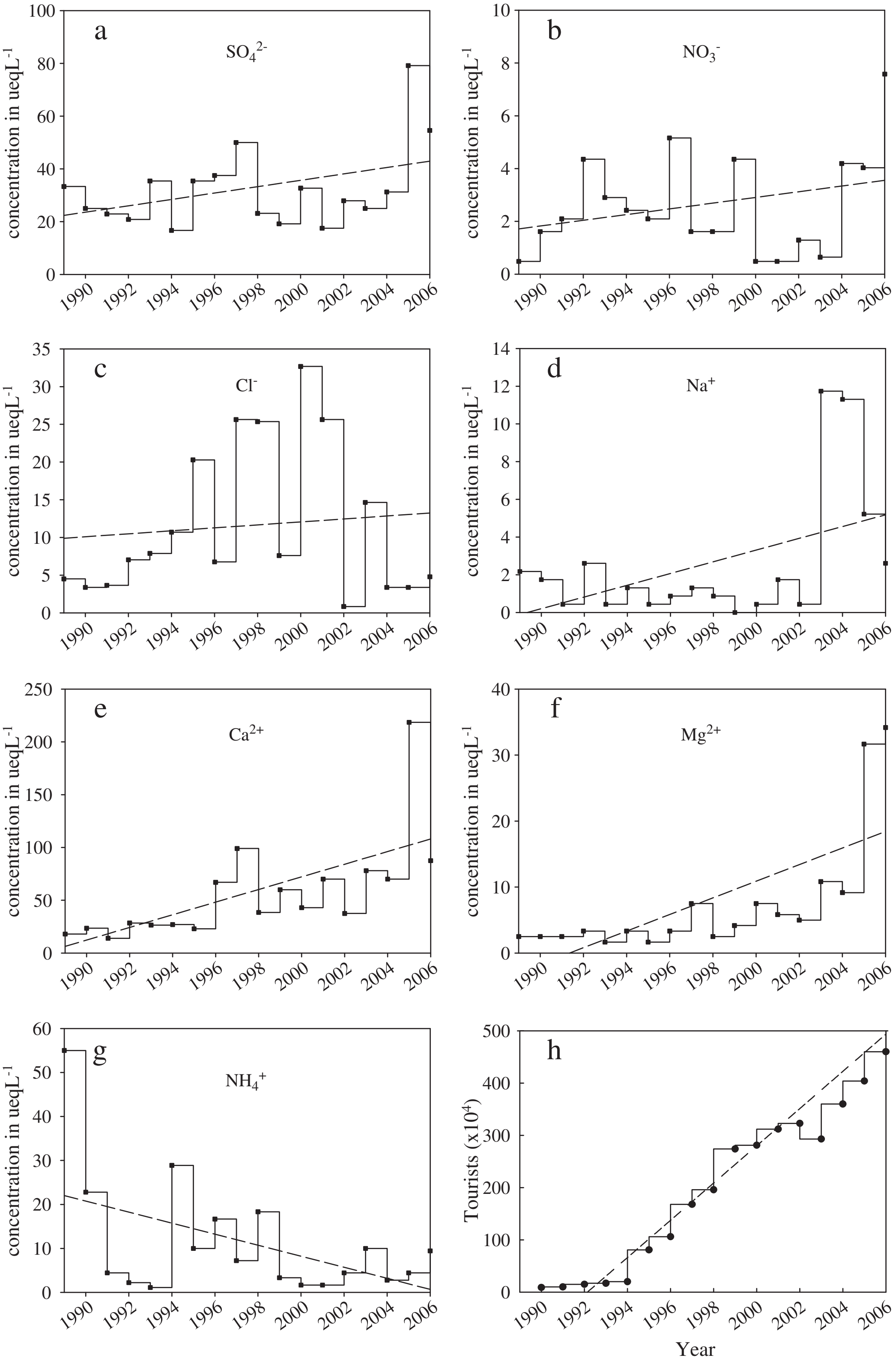

Fig. 5. Temporal variation of ionic concentrations (a–g) in precipitation during 1989–2006 and annual tourists (h) during 1990–2006 at Lijiang.

Table 2
Compare of average concentration in precipitation at various periods (μeq L^{-1}).

Periods (year)	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	Total ionic concentration	Yearly tourists ($\times 10^4$)
I (1987–1989)	8.15	1.92	3.69	5.67	4.45	1.58	0.96	26.41	–[a]
II (1989–1996)	28.39	2.64	8.03	17.64	28.44	2.60	1.25	88.99	36.86
III (1997–2006)	36.04	2.63	14.39	6.33	80.20	11.83	3.57	155.00	307.1

[a] Means no data.

the concentration of Ca^{2+} exceeded the concentration of SO_4^{2-}, and that the concentration of Mg^{2+} exceeded the concentration of NO_3^-, suggesting that the input of dust to the atmosphere was greater than emissions from industrial sources.

During Period III, the annual number of tourist visits rose sharply to 3.07 million, which is around 9 times greater than in Period II, indicating that the scale of tourism in Lijiang had expanded considerably. Meanwhile, the total ionic abundance during Period III was nearly twice that of Period II, and the concentration of each ion had again increased relative to the previous period, with the exception of NO_3^-. The ionic order in Period 3 was $Ca^{2+} > SO_4^{2-} > Cl^- > Mg^{2+} > NH_4^+ > Na^+ > NO_3^-$. Although the dominant anion and cation were the same as in Period II, the concentration of Ca^{2+} was twice that of SO_4^{2-}, and the concentration of Mg^{2+} exceeded that of NH_4^+. Comparing the ionic concentration and order of Period 3 with those in Period I, we can see that the total ionic concentration in Period III was nearly six times that in Period I, with the greatest increases seen in Ca^{2+} and Mg^{2+} (increases of more than 18 and 7 times, respectively). Overall, by examining the ion concentrations and order during each of the three periods, it can be seen that ion concentrations, especially those of crustal origin, have increased in tandem with the expansion of tourism.

3.3. Neutralization capacity

Neutralization factors (NF) were used to evaluate the neutralization of precipitation by crustal components and NH_4^+, and were calculated by the following equation (Possanzini et al., 1988):

$$(NF)_X = [X]/\left\{[NO_3^-] + \left[nssSO_4^{2-}\right]\right\} \qquad (1)$$

where $X = NH_4^+$, non-sea-salt (nss) Ca^{2+} or nss Mg^{2+}.

Table 3
Neutralization factor at different areas.

Area	NH_4^+	Ca^{2+}	Mg^{2+}	Reference
Lijiang	0.32	1.63	0.20	This work
Delhi	0.91	0.25	0.02	Parashar et al., 1996
Pune	0.66	1.64	0.43	Parashar et al., 1996
Pune	0.18	1.21	0.19	Safai et al., 2004
Ahmedabad	0.7	1.8	0.1	Rastogi and Sarin, 2005
Jinhua	0.64	0.38	0.03	Zhang et al., 2007

The nss fraction ion concentrations were calculated by:

$$NSS_x = X - R * M \qquad (2)$$

where X denotes ions, NSS_x denotes the non-sea-salt source fraction of the ions, M is the sea-salt tracer ion concentration, and R is the ratio X/M of standard seawater. The rules for selecting a sea-salt tracer ion are as follows (Church et al., 1982; Keene et al., 1986):

(a) If the quantity ratios of $C1^-/Na^+$ and $Mg^{2+}/Na^+ \geq$ corresponding values of standard sea-water ($C1^-/Na^+ = 1.17$, $Mg^{2+}/Na^+ = 0.23$), Na^+ is the sea-salt tracer ion;
(b) If the quantity ratios of Na^+/Cl^- and $Mg^{2+}/Cl^- \geq$ corresponding values of standard sea-water ($Na^+/Cl^- = 0.86$, $Mg^{2+}/Cl^- = 0.20$), Cl^- is the sea-salt tracer ion;
(c) If the quantity ratios of Na^+/Mg^{2+} and $Cl^-/Mg^{2+} \geq$ corresponding values of standard sea-water ($Na^+/Mg^{2+} = 4.40$, $Cl^-/Mg^{2+} = 5.13$), Mg^{2+} is the sea-salt tracer ion.

The concentrations of ions in standard seawater are given by Brewer et al. (1975) and Qin (1995). The selected sea-salt tracer ion in this study was Na^+. According to Eq. (1), the NF values for NH_4^+, Ca^{2+} and Mg^{2+} with an average value are 0.32, 1.63, and 0.20, respectively (Table 3), suggesting that the main neutralizing component in precipitation at Lijiang was Ca^{2+}. The average NF value of Ca^{2+} was as high as the values observed at Pune (Parashar et al., 1996) and Ahmedabad (Rastogi et al., 2005). Temporal variations in NF values for NH_4^+, Ca^{2+} and Mg^{2+} (Fig. 6) show that the neutralization capacity of Ca^{2+} increased, following the increasing trend of Ca^{2+} concentration in the precipitation samples. However, the neutralization capacity of NH_4^+ declined, because of the decreasing trend of NH_4^+ concentrations in the precipitation samples.

In general, the main neutralization components in rain are considered to be NH_4^+ and nss Ca^{2+}. The neutralization capacities of those two ions showed contrary trends in our results. In order to assess the neutralization capacity variations and the balance between alkalinity and acidity, the ratio of NP to AP was computed as:

$$NP/AP = \left[NH_4{}^+ + nss\ Ca^{2+}\right]/\left[nssSO_4{}^{2-} + NO_3{}^-\right] \qquad (3)$$

The increasing trend of this ratio (Fig. 6) indicates that the neutralization capacity was rising, corresponding to the increasing trend in pH values. The main neutralization

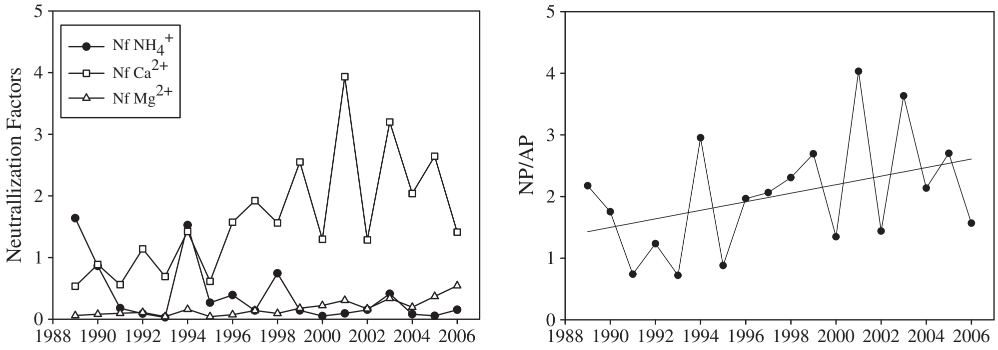

Fig. 6. Variation of NFs for NH_4^+, Ca^{2+} and Mg^{2+} in precipitation at Lijiang during 1989–2006 (a); and variation of NP/AP in precipitation at Lijiang during 1989–2006 (b).

component at Lijiang was Ca^{2+}, as was also found at Pune during 1984–2002 (Safai et al., 2004) and at Shenzhen during 1986–2006 (Huang et al., 2008), but the NP/AP and pH values in those two regions have been declining. There are some industrial zones around Pune, and vehicles, small-scale industries and rapidly growing construction activity are widespread within the city. Shenzhen has a large number of chemical industries, motor industries and power plants. However, Lijiang is primarily a tourist city, with an industrial structure that is totally different to that at Pune and Shenzhen. Thus, our results may suggest that inputs from tourism contribute more neutralization components to atmospheric precipitation, but without increasing the acidifying components supplied by other industries at Lijiang during 1989–2006.

3.4. Determination of chemical sources

3.4.1. Correlation coefficients

In order to identify associations between ions in precipitation, as well as possible sources of pollutants, correlation coefficients between ions in the rainwater were calculated (Table 4). Significant correlations between SO_4^{2-} and Ca^{2+} ($r = 0.80$) and between SO_4^{2-} and Mg^{2+} ($r = 0.78$) were noted. There also was a strong correlation between NO_3^- and Mg^{2+} ($r = 0.54$). These results suggest that acid pollutants might be absorbed on the surface of particulate matter and react with cations Ca^{2+} and Mg^{2+}, and that the common source of these ions is natural dust or soil. Similar results have been reported from India (Safai et al., 2004), Nanjing, China (Tu et al., 2005) and Shenzhen, China (Huang et al., 2008).

pH was mainly correlated with Ca^{2+} and Mg^{2+} ($r = 0.48$ and 0.46, respectively; Table 4). This indicates that the pH was controlled by alkaline earth elements and could explain why the precipitation in this region was not acidic. A significant correlation was found between Ca^{2+} and Mg^{2+} ($r = 0.78$), similar to the temporal trend found in 1986–2006 (Fig. 5), suggesting a common crustal source species of the two ions.

Cl^- and Na^+ are normally considered to have a marine source, especially in monsoonal regions. Na^+ was calculated to be the sea-salt tracer ion in this study, but there was no significant correlation between Cl^- and Na^+. Also, Cl^- and Na^+ did not have a significant correlation with most of the other ions. Huang et al. (2008) considered that this pattern indicates that most of the other ions came from anthropogenic and crustal sources. In our samples, Cl^- had an increasing trend with time, and displayed several individual peaks that were asynchronous with those of other ions (Fig. 5). The average Na^+/Cl^- ratio was 0.22, much lower than that in seawater (0.86), suggesting that precipitation was enriched in Cl^-. Thus, the data may indicate that the Cl^- in precipitation at Lijiang had complex sources (both marine and anthropological).

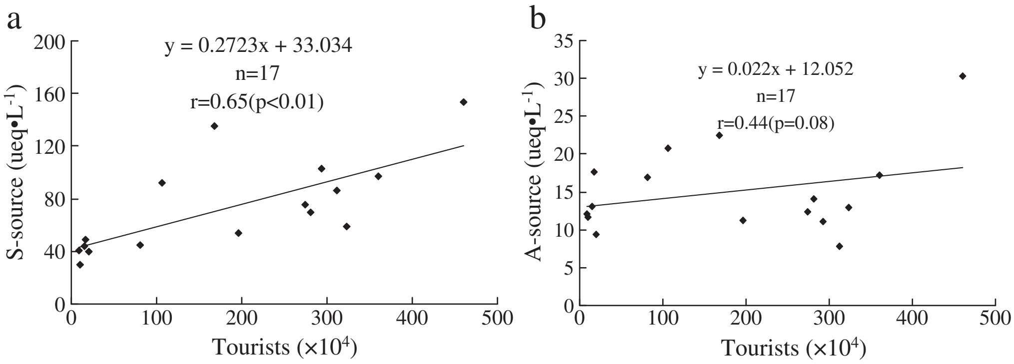

Fig. 7. Relationship among yearly tourists, S-source (a) and A-source (b).

Table 4
Correlation coefficients for the pH and ionic constituents of precipitation at Lijiang.

	pH	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+
pH	1.00							
SO_4^{2-}	0.28	1.00						
NO_3^-	0.21	0.39	1.00					
Cl^-	0.17	−0.13	−0.48a	1.00				
NH_4^+	−0.40	−0.10	−0.24	−0.17	1.00			
Ca^{2+}	0.48a	0.80b	0.31	−0.04	−0.29	1.00		
Mg^{2+}	0.46a	0.78b	0.54a	−0.19	−0.20	0.78b	1.00	
Na^+	−0.05	0.13	0.06	−0.18	−0.08	0.37	0.33	1.00

[a]Significant at 0.05 level; b significant at 0.01 level.

3.4.2. Contributions of sources

Using Eq. (2), the calculated non-sea-salt source percentages of Cl^-, SO_4^{2-}, Mg^{2+} and Ca^{2+} were 74.3%, 99.1%, 92.6% and 99.8%, respectively. These results indicate that non-sea sources played an important role in determining the ionic composition of our samples. As discussed above, the source vapor contributing to precipitation at Lijiang was mainly derived from the Indian Ocean, but the shortest linear distance from Lijiang to the nearest coast exceeds 1000 km. Consequently, when the vapor is transported, continuous exchanges and reactions between terrestrial material and the atmosphere alter the chemical composition, such that the composition of our samples was different from that in sea water. For example, the reaction between sea salt particles and H_2SO_4 can cause the enrichment of Cl^- in precipitation and depletion in aerosol (Hitchcock, 1980; Shrestha et al., 1997). This can explain the Cl^- enrichment in our samples.

Due to the very low concentration of NO_3^- in sea water, the NO_3^- detected in precipitation is considered to have been only from soil and anthropogenic sources. According to Horn and Adams (1966), Safai et al. (2004), and Huang et al. (2008), SO_4^{2-} is derived from sea water, soil and anthropogenic sources. The contribution of NO_3^- and SO_4^{2-} from soil can be calculated using the ratio of NO_3^- or SO_4^{2-} to Ca^{2+}. In our study, about 95.4% of the NO_3^- was contributed by anthropogenic sources. Approximately 41.7% of the total SO_4^{2-} was from anthropogenic sources, while 57.4% was contributed by soil sources and only 0.9% came from marine sources. The results indicate that: (1) the soil source contribution of SO_4^{2-} was higher than that of anthropogenic sources, in contrast to previous reports (Zhang et al., 2007; Huang et al., 2008), suggesting that emissions from the tourism industry supply less SO_2 to the air than other industrial sources; (2) SO_2 from tourist activities (vehicular emissions) could have formed SO_4^{2-} which reacted with crustal components like Ca and Mg to form sulfates, explaining the significant correlation between SO_4^{2-} with Ca and Mg; and (3) the anthropogenic source contribution of NO_3^- is much larger than the anthropogenic source contribution of SO_4^{2-}.

In order to understand the tourism industry's influences on chemical components in precipitation, we define A-source as the sum of 95.4% NO_3^- and 41.7% SO_4^{2-}, and S-source as the sum of 99.8% Ca^{2+}, 92.6% Mg^{2+} and 57.7% SO_4^{2-}. These source terms can be compared with the variations of annual tourist visits in the Lijiang region during 1990–2006 (Fig. 7), yielding correlation coefficients between yearly tourists and either A-source or S-source of 0.44 and 0.65 ($p = 0.01$), respectively. This shows that annual number of tourist visits has a remarkably strong relationship with the presence of ions from soil/dust sources in precipitation samples. The relationship can be explained as follows. Firstly, due to developing tourism, there is no heavy industry in Lijiang district. Therefore, pollutants such as NO_x and SO_2 related to industrial production do not increase noticeably with number of tourists. Secondly, in order to accommodate the increasing number of tourists, urban expansion is required, bringing more construction industries and altering the landscape. Consequently, tourism also indirectly increases dust transport from the soil to the air, leading to a significant increasing trend of Ca^{2+} and Mg^{2+} in precipitation, and a gradually increasing neutralization capacity of the air. This is in contrast to other cities, where rising emissions of acid gases tend to increase the acidity of precipitation.

4. Conclusions

A study of the chemical composition of precipitation was carried out at Lijiang City in the southwest region of China during the period 1989 to 2006. Although the Lijiang region was considered to be a suitable site for monitoring the background precipitation chemistry more than 20 years ago, this study represents the first report on the precipitation chemistry after the development of tourism in the area, and the following important results have been obtained.

(1) pH shows an increasing trend, and an average pH of 6.08 during 1989–2006. Compared with the pH value of 5.00 during 1987–1989 before development of tourism, the increased pH indicates greater alkaline species inputs into the air following the development of tourism. SO_4^{2-} and Ca^{2+} were the dominant anion and cation, respectively, in our samples. Meanwhile, electrical conductivity and most of the detected ions also show an increasing trend, especially Ca^{2+} and Mg^{2+}, with the exception of NH_4^+ which showed a very clear decreasing trend.

(2) The increasing total ion concentrations were found to occur in tandem with increasing tourist numbers, and the increased concentration was mainly attributed to input of crustal components. The main neutralizing component was Ca^{2+} and the neutralization capacity of Ca^{2+} increased markedly during 1989–2006. This led to an increasing trend in NP/AP, which is opposite to the trend reported from some industrial cities, and suggests that developing tourism at Lijiang, had increased the neutralization capacity of precipitation.

(3) Significant correlations between Mg^{2+}, Ca^{2+} and between acid anions (SO_4^{2-}, NO_3^-) were found, but Cl^- and Na^+ was not well correlated. Using Na^+ as a sea-salt tracer, the non-sea-salt percentages of SO_4^{2-}, Cl^-, Mg^{2+} and Ca^{2+} were 99.1%, 74.3%, 92.6% and 99.8%, respectively. These figures indicate that SO_4^{2-}, Ca^{2+} and Mg^{2+} are essentially derived from non-marine sources. Furthermore, about 95.4% of NO_3^- was contributed by anthropogenic sources, while 41.7% and 57.7% of the total SO_4^{2-} were from anthropogenic and soil sources, respectively.

(4) The number of annual tourist visits has a remarkably strong relationship with the concentration of ions derived from soil/dust sources, suggesting the human activities in a tourism-oriented city increase atmospheric dust loading rather than emitting acid gases as is the case with heavy industries. This is the reason why the concentrations of Ca^{2+} and Mg^{2+}, the neutralization capacity of precipitation, and the pH value all increased.

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