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Seasonal variations of carboxylic acids and their contributions to the rainwater acidity: A case study of Guiyang and Shangzhong, China

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Low molecule weight carboxylic acids are ubiquitous and important chemical constituents in the troposphere. Seven carboxylic acids in the rainwater of Guiyang and Shangzhong were simultaneously determined by ion chromatography from April 2006 to April 2007. Formic, acetic and oxalic acids were found to be the predominant carboxylic acids. Their volume weighted average concentration (VWA) in the rainwater of Guiyang were 14.24 μmol/L, 9.35 μmol/L and 2.79 μmol/L, respectively; as compared to 4.95 μmol/L, 1.35 μmol/L and 2.31 μmol/L in the rainwater of Shangzhong. In Shangzhong it is witnessed that the concentrations of these acids were higher in the summer than in the winter and direct emissions from vegetations or soils may account for the main provenance of the acids. This is, however, not the case in Guiyang, where the concentrations of the carboxylic acids were higher during the non-growing season than during the growing season. The relatively weak scavenging affected by scarce and little rainwater as well as the particles accompanied with the rainfall may have some effect on the carboxylic acids during the wintertime in Guiyang. Carboxylic acids in the rainwater of Guiyang were estimated to account for 18.7% to the free acidity, where formic, acetic and oxalic acids accounted for 7.9%, 4.7%, 6.1%, respectively. In Shangzhong, the 3 primary carboxylic acids represented 58.1% to the free acidity where formic, acetic and oxalic acids represented 25.1%, 7.5%, 25.5%, respectively. Carboxylic anions accounted for 6.6% (1.7%–19.2%) to the total anions in the rainwater of Guiyang. Carboxylic anions represented 13.2% (0.5%–92.2%) to the total anions in the rainwater of Shangzhong. These results indicated that carboxylic acids were the important contributors to the rainwater acidity, especially in remote regions.

rainwater, acid rain, ion chromatogram, carboxylic acids, seasonal variation

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Low molecule weight carboxylic acids are ubiquitous and important chemical constituents in the troposphere [1]. Major carboxylic acids include formic, acetic, propionic, oxalic, lactic and pyruvic acids, however, formic, acetic and oxalic acids are the predominant carboxylic acids and contribute 75% to the total carboxylic acids [2,3]. Furthermore, they contribute significantly, 13%–65%, to the rainwater acidity in some regions of the world [4]. The presence of formic and acetic acid in the atmosphere can influence the pH-dependent chemical reactions in clouds [5]. Primary and secondary sources have been suggested as their major sources in the atmosphere. Primary sources include the direct emission from vehicles [6], biomass burning [7], plants [8], soils [9], oceans [3], and ants [10]. Secondary sources include the photochemical reaction of unsaturated hydrocarbons in the atmosphere [11]. The formaldehydes oxidation with OH radical in the aqueous phase was also investigated as the important source for formic acid in the atmosphere [12]. During the past decades, much attention has been paid to the carboxylic acids in the troposphere, which allows a better understanding of their distributions in the gas, aqueous and aerosol phases, and their sources and sinks

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[3]. Recently, carbon isotope has been used to trace the origin of carboxylic acids and remarkable progress has been made [13]. The researches on the carboxylic acids have been focused on their concentration levels, ice-core record and organic aerosol in the atmosphere since the 1980s based on the acid rain study in China, but little on the contributions of the carboxylic acids to the rainwater acidity.

Guizhou Province is one of the most serious areas of acid rain in China and is typical of the Karst topographic feature. The ecosystem in this region is fragile and irreversible after being disturbed. So it makes sense to carry out the work on the formation and the possible reasons of the acid rain in such a region. In previous work [14], the average pH of the rainwater in Guiyang was measured as 4.53 and the frequency of acid rains was 86%. Lowe pH value in the rainwater may be due to the presence of natural H_2SO_4, or anthropogenic emission of H_2SO_4 and HNO_3, or carboxylic acids. Therefore, 2 distinct sites have been selected for the determination of carboxylic acids: one is the anthropogenic dominated area, Guiyang and the other is the less anthropogenic dominated area, Shangzhong. And the rainwater in both sites has been collected for 13 months to measure the seven carboxylic acids as well as major anions and cations. The purpose of this paper is to report the concentration levels and seasonal variations of these carboxylic acids in the rainwater, to evaluate the possible sources of these species and their contributions to the rainwater acidity on the basis of the comparison of the two distinct sites.

1 Experimental

1.1 Sample location

Guiyang (26°34′N, 106°43′E), the capital of Guizhou Province, which is located in southwest China, is one of the most polluted cities with the most density of population in the urban and the industry and traffic develop quickly. And the city lies in a wide karst valley basin with all mountains around and it is hard for the diffusion of the pollution in the atmosphere. The rainwater samples in Guiyang were collected on the roof of doctoral dormitory in Guiyang Institute of Geochemistry of the Chinese Academy of Sciences, which is about 200 m higher than the ground and the surrounding buildings. The site is located in the center of Guiyang with no specific or point pollution sources and can represent the normal state of the city. Shangzhong (26°16′N, 108°40′E) lies in the southeast of Guizhou Province, 200 km away from Guiyang, approximately 60% of which is covered with trees. And there are neigher intense traffic vehicles nor big factories within a radius of 50 km. In contrast with Guiyang, Shangzhong is little influenced by the anthropogenic forces and can represent the rural condition.

1.2 Sample collection and analysis

The samples in Guiyang were collected with 1.5 m × 2 m polyethylene bottles, which had been cleaned with acid (2–3 mol/L HCl) and thoroughly rinsed with Milli-Q water (18.2 MΩ) before use. In order to minimize the contamination from the particulate material, special attention should be paid to opening the sampler as soon as rainfall set on. The collector was mounted on the iron stand, about 1.5 m high above the ground. An automatic sampler (from Changsha Company) was taken to collect the rainwater in Shangzhong, while rainwater was collected on an event basis from April 2006 to April 2007 in both sites. And 144 samples in Guiyang and 47 samples in Shangzhong were collected.

The pH and conductivity of the samples were analyzed after collection. The residual samples were frozen to –18°C until analysis [15]. Carboxylic acids and major anions were simultaneously determined by the Dionex ICS-90 ion chromatography. The separation column was AS11-HC (AG11-HC as guard column) and the gradient eluent KOH was generated form reagent free controller (RFC-30). The relative standard deviations (RSD%) of the method were below 5%. Quantitative recoveries of spiked samples ranged from 80% to120% [16].

2 Results

2.1 The characteristic composition of carboxylic acids in the rainwater

As illustrated in Table 1, 7 carboxylic acids in the rainwater of Guiyang and Shangzhong were all monocarboxylic acids except oxalic acid (dicarboxylic acid) and pyruvic acid (oxcarboxylic acid). Formic, acetic and oxalic acids were found to be the most abundant and predominant carboxylic acids. The overall VWA concentrations of formic and acetic acids were 14.24 μmol/L and 9.35 μmol/L in Guiyang (N=143), which were higher than that in Shangzhong: 4.95 μmol/L and1.35 μmol/L respectively (N=47). The separability between lactate and [F^-] is weak because of the similar polarity for two species. As a result, the concentration of lactate is difficult to determine accurately and the determined concentration of lactate in few samples in Guiyang was 7.17 μmol/L. Methanesulfonatic acid was the lowest carboxylic acids, and the concentration was 0.12 μmol/L in Guiyang and 0.10 μmol/L in Shangzhong Town. The mean pH of the rainwater of Guiyang was 4.4, with 80% of the samples being acidic (pH <5.6). The degree of the acid rain is relatively high, in particular, it is worth noting that the strong acid rain (pH <4) accounted for half of the total rain samples. In contrast to Guiyang, the mean pH of the rainwater in Shangzhong was 5.8, and almost no acid rain was observed.

Table 1 The concentration level of major carboxylic acids, precipitation and pH in the rainwater of Guiyang and Shangzhong

	Guiyang		Shangzhong	
	Range	VWA	Range	VWA
Lactate (μmol/L)	0.28–48.82	7.17	0.10–4.73	1.00
Acetate (μmol/L)	0.17–67.26	9.35	0.02–7.33	1.35
Proponate (μmol/L)	0.01–1.35	0.18	0.00–0.18	0.12
Formate (μmol/L)	0.04–139.43	14.24	0.04–36.47	4.95
MSA (μmol/L)	0.04–0.79	0.12	0.01–0.22	0.10
Pyruvate (μmol/L)	0.04–11.76	0.69	0.06–3.14	1.47
Oxalate (μmol/L)	0.16–41.27	2.79	0.16–13.37	2.31
Precipitation (mm)	0.1–80.0	6.1	0.5–61.0	6.9
Conductivity (μs/cm)	10.02–1028.00	248.31	10.02–1028.00	213.75
pH	2.49–6.92	4.4	5.00–6.50	5.83

2.2 The seasonal variations of the carboxylic acids in the rainwater

The VWA of the carboxylic acids in the rainwater of Shangzhong are presented in Figure 1. In general, the concentration of carboxylic acids changed in the order of spring (March to May) > summer (June to August) > winter (December to February next year) > autumn (September to November). Carboxylic acids exhibited significantly enhanced concentration levels during the growing season (April to September). The concentrations of formic and acetic acids were roughly 8 and 10 times higher during the growing season than that during the non-growing season, and the concentration of oxalic acid was threefold during the growing season compared to that during the non-growing season. The turning points of the seasonal variation were March and September, respectively. However, carboxylic acids showed the opposite seasonal variations in Guiyang, as shown in Figure 2, formic and acetic acid was quite higher during the non-growing season than that during the growing season. The concentration of formic acid during the non-growing season was about four times higher than that during the growing season. For acetic and oxalic acids, the concentrations were double during the nongrowing season. Specific seasonal variations of carboxylic acids followed in the order of spring > winter > autumn > summer, and the turning points of seasonal variation were May and November respectively.

3 Discussions

3.1 Factors influencing the seasonal variations of carboxylic acids in rainwater

The seasonal variations of carboxylic acids in rainwater had been abuntantly investigated in the past decades. The first observation was made by Keene and Galloway [5] through the Global Precipitation Chemistry Project. They hypothesized that the primary or the secondary emission from vegetation could contribute to the higher concentrations of these species during the growing season. Talbot et al. [17] determined the concentrations of formic and acetic acid in the rainwater over a 15-month time period at eastern Virginia. The results showed that carboxylic acids followed an obviously increase (about 3–5 times) during the growing-season compared to that during the non-growing season. As indicated above, the emissions from vegetation [8] or soils [9] could be the predominate sources of carboxylic acids in Shangzhong. The growth of vegetation fluctuated seasonally

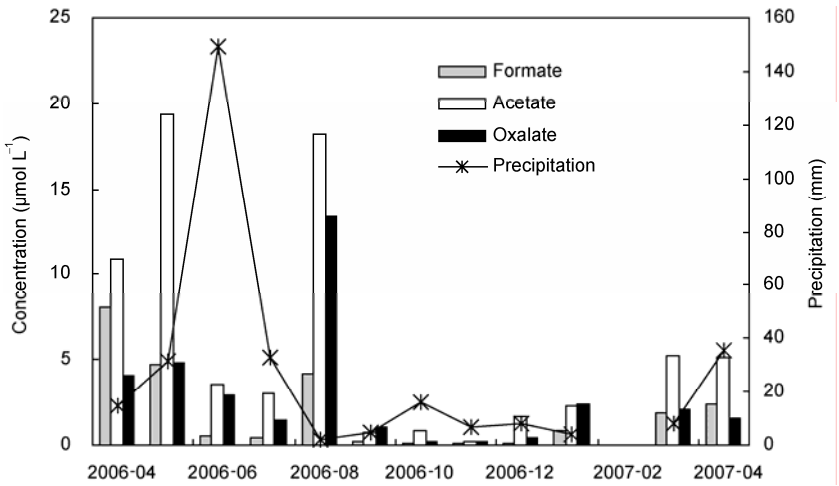

Figure 1 The seasonal variation of the concentrations of the carboxylic acids and the precipitation in Shangzhong.

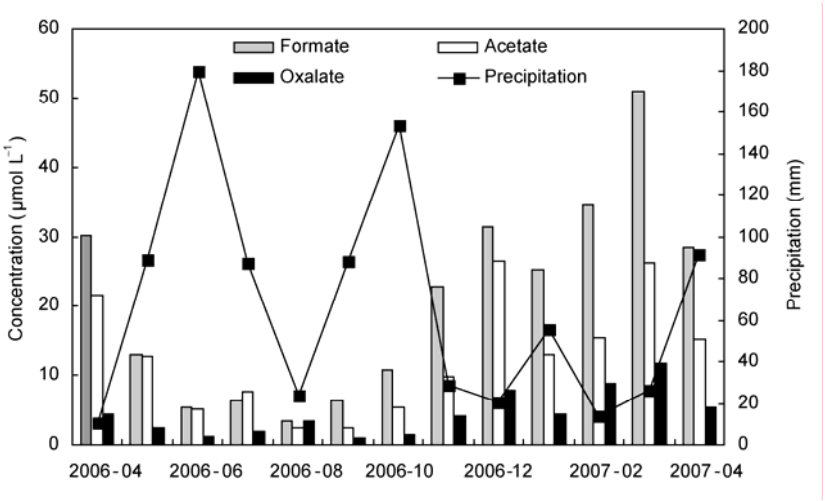

Figure 2 The seasonal variation of the concentrations of the carboxylic acids and the precipitation in Guiyang.

with temperature changes in Shangzhong and so did the concentrations of carboxylic acids. Filella et al. [18] found that acid emission by the Norway spruce (*Picea abies*) increased with temperature, but reached saturation at 30°C. By contrast with Shangzhong, the concentration levels of formic, acetic and oxalic acids in Guiyang during the non-growing season were higher than that during the growing season by 70%, 174% and 139%, respectively. Obviously, such a seasonal variation suggested that biogenic emissions were not the primary sources for carboxylic acids in Guiyang. Particles, rain amount and pH of the rainwater may be the leading factors for such seasonal variations, so we shall discuss them one by one below.

First of all, the interference of particles is the inevitable factor during the collection of rainwater. For Guiyang, especially after November, due to the heavy use of coal- fired heating and the reduced numbers of the rainfall, small rain amount (less than 1 mm) and longer duration of the rain time, the concentrations of the particulate matters in the atmosphere were higher than that during the summertime. That is to say, the particulate matters were easily deposited into the collected samples during the winter. Chapman EG [19] found that the mean concentrations of the carboxylic acids in sedimented samples were significantly higher than those in non-sedimented samples in the spring in Wisconsin. The difference may be caused by the presence of carboxylic acids in the sedimented particles and the influence of the accompanying meteorological conditions. In order to eliminate the influence of the particulate matters, the samples with rain amount < 5 mm and longer rainfall duration were excluded from the seasonal variations (Figure 3). It is amazing that the seasonal variation is almost just like before, which indicates that particulate matters were not the primary reason for the higher carboxylic acid concentrations during the wintertime in Guiyang [20].

Rainfall amount is another factor that may affect the concentrations of the carboxylic acids. The carboxylic acids in Guiyang were mainly incorporated into the rainwater during the below-cloud process [21]. It means that the carboxylic acids always decreased with increased rainfall so these species are mainly controlled by dilution. As shown in Figure 2, the higher rainfall during the growing season compared to that during the non-growing season caused such seasonal variation. After May in Guiyang, the precipitation increased significantly, and the larger rainfall enhanced the leaching of the trace species in the atmosphere, the concentrations of the carboxylic acids in the rainwater were reduced by the purification of the air pollutants. However, during the dry season after November in Guiyang, the frequency of the rainfall reduced, much rainfall was less than 1 mm and continued for a longer time, so the pollutants in the atmosphere could not be timely and effectively removed and the organic pollutants were prone to accumulate, as a result the concentrations of the carboxylic acids in the rainwater increased. Similar results were presented by Kumar et al. [22] in Agra of India, they speculated this seasonal variation may result not only from a variation in the nature and strength of the sources of the two acids but also from the higher rainfall per event as well as higher rain depth in the monsoon (460 mm) compared to winter (60 mm). As a result, the eluviation and the dilution effect were the important reasons for the lower carboxylic acids concentrations in the summer than that in the winter in Guiyang. However, changes of the rainfall cannot explain the seasonal variations of the carboxylic acids in the rainwater of Shangzhong.

Last but not least is the effect of pH in the rainwater on the concentrations of the carboxylic acids. As is shown in the following formula, carboxylic acids are weak acids and the ionization equilibrium is posed between RCOOH(aq) and $RCOO^-$. Assume the pH of the rainwater increases, then much more $[H^+]$ will be produced to compensate the decreased $[H^+]$ through the ionization equilibrium in rainwater. As a result, much more RCOOH(g) will dissolve into the rainwater to equalize the decreased RCOOH(aq) through

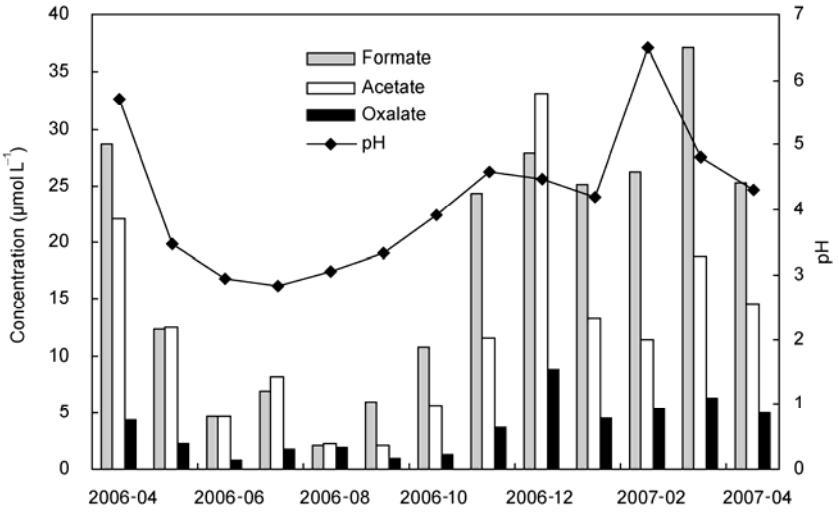

Figure 3 The seasonal variation of the concentrations of carboxylic acids (rainfall amount > 5mm) and pH in the rainwater of Guiyang.

reaction (I). So the total carboxylic acids will increase with the increasing pH. So the higher volume weighted pH of the rainwater during the non-growing season compared to that during the growing season in Guiyang favors the transfer of carboxylic acids from the atmosphere to the rainwater, which leads to the enhanced concentration levels during the non-growing season as shown in Figure 3. The seasonal variation of pH in the rainwater of Shangzhong was not obvious so it cannot explain the seasonal variation of the carboxylic acids.

$$\mathrm{RCOOH(g)} \overset{\text{(I)}}{\rightleftharpoons} \mathrm{RCOOH} \overset{\text{(II)}}{\rightleftharpoons} \mathrm{RCOO^- + H^+}$$

In summary, the seasonal variation of carboxylic acids in Guiyang was not the result of the vegetation emissions or the particulate matters but the reflection of the relatively heavy scavenging effect of precipitation and higher pH in rainwater during the summertime.

3.2 The contribution of the carboxylic acids to the rainwater acidity and its chemical composition

(i) To the rainwater acidity. In order to calculate the contribution of the carboxylic acids to the free acidity, the total carboxylic acids (the amount of the carboxylic anions plus the undissociated acid) in the rainwater were determined by Ion Chromatography (IC). Assuming that all of the measured carboxylic anions are contributed by acid forms, the maximum contribution of these measured carboxylic ions to the free acidity of the rainwater can be calculated via the expression as advised by Keene [23].

Maximum contribution

$$= \left(\frac{K_f C_f}{[H^+]+K_f} + \frac{K_a C_a}{[H^+]+K_a} + \frac{K_{o1} C_o [H^+] + K_{o1} K_{o2} C_o}{[H^+]^2 + K_{o1}[H^+] + K_{o1} K_{o2}} \Big/ [H^+] \right) \times 100\%.$$

The expression was applied to the rainwater with pH not higher than 5, where $[H^+]$ is the free hydrogen ion concentration (mol/L), C_f, C_a, C_o in the equation are IC-measured quantities of the total carboxylic acids (mol/L), and K_f, K_a, K_{o1}, K_{o2} represent dissociation constants for formic acid, acetic acid and oxalic acid. Their values are 1.78×10^{-4} mol/L, 1.75×10^{-5} mol/L, 5.9×10^{-2} mol/L and 6.4×10^{-5} mol/L, respectively [15].

As illustrated in Table 2, the mean contribution of formic acid to the free acidity was 7.9% (ranging from 0% to 97.2%) because of the highest concentration level and higher dissociation constant among the 3 carboxylic acids. Acetic acid contributed 4.7% to the free acidity and ranged from 0% to 98.4%. It is remarkable that oxalic acid was demonstrated to be an important contributing compound to the acidification of the rainwater, representing 6.1% (ranging from 0% to 89.4%) of the free acidity because of the highest dissociation constant among the 3 carboxylic acids. As a whole, 3 major carboxylic acids contribute 18.7% to the free acidity and ranged from 0.1% to 75.8%. In Shangzhong, the respective figures for formic acid, acetic acid and oxalic acid to the free acidity were 25.1% (ranging from 7.2% to 48.1%), 7.5% (ranging from 3.1% to 14%), 7.5% (ranging from 6.1% to 42.1%) and the total contribution of carboxylic acids was 58.1% with a range from 18.1% to 97.3%. These figures clearly demonstrated the importance of the carboxylic acids to the acidification of the rainwater, especially in remote regions.

Table 2 indicates that several samples have calculated results closed to 100%. Possible explanation relates to carboxylate present in rainwater. This part of the carboxylate will not only fail to provide ionization $[H^+]$, but also consume part of the hydrolysis of $[H^+]$, make calculations on the high side. So the calculation poses the maximum contribution to the free acidity. Samples with pH$\leqslant$5, as well as remote samples with low concentrations of alkaline substances, will get better results via this calculation method.

Table 2 The contribution of carboxylic acids to the free acidity in rainwater in Guiyang and Shangzhong

		Acetate		Formate		Oxalate		Major carboxylic anions	
		Range	VWA	Range	VWA	Range	VWA	Range	VWA
Contribution to free acidity	Guiyang	0%–98.4%	4.7%	0%–97.2%	7.9%	0%–89.4%	6.1%	0.1%–75.8%	18.7%
	Shangzhong	3.1%–14.0%	7.5%	7.2%–48.1%	25.1%	6.1%–42.1%	25.5%	18.1%–97.3%	58.1%

(ii) To the chemical composition of the rainwater. Acid rain is caused by the acidic gases SO_2, NO_x, HCOOH and CH_3COOH which dissolve into the rainwater and make it unusually acidic. As a result, specific acid contribution to the total free acidity is calculated by the following expression [20]:

$$HX\%=[X]/\sum \text{anions},$$

where $[X]=2[\text{nss-}SO_4^{2-}]$(non-sea-salt SO_4^{2-}), $[\text{nss-}Cl^-]$(non-sea-salt Cl^-), $[NO_3^-]$, $[HCOO^-]$, $[CH_3COO^-]$, $HOOCCOO^-$, $^-OOCCOO^-$.

$$\sum \text{anions}=2[\text{nss-}SO_4^{2-}]+[\text{nss-}Cl^-]+[NO_3^-]+[HCOO^-]+[CH_3COO^-]+[HOOCCOO^-]+[^-OOCCOO^-].$$

As illustrated in Figure 4, the carboxylic anions account for 6.6% (ranging from 1.7%–19.2%) to the total anions of the rainwater of Guiyang with others coming from inorganic anions. Approximately 81.4% of the total anions was dominated by $\text{nss-}SO_4^{2-}$, and the less important NO_3^- accounted for 11.3% to the total anions in rainwater. Similar to oxalate, $\text{nss-}Cl^-$ only accounted for 0.7% to the total anions. In Shangzhong, the contribution of the carboxylic anions to the total anions was much higher, the mean value was 13.2% (ranging from 0.5%–92.2%), $\text{nss-}SO_4^{2-}$ was similarly predominated anions and accounted for 64.4% to the total anions, NO_3^- and $\text{nss-}Cl^-$ accounted for 19% and 3.3% respectively. As discussed in 3.2 (i) the similar conclusion can be drawn, carboxylic anions were important chemical constituents in rainwater, especially in the remote regions. Their contributions were much higher than those of $\text{nss-}Cl^-$ and less important than those of NO_3^-.

4 Conclusions

There are distinctively different anthropogenic activities between Guiyang and Shangzhong. Carboxylic acids in the rainwater of the two sites were simultaneously determined and the main conclusions are as follows:

(i) Formic, acetic and oxalic acids were the predominant carboxylic acids at the two sites. The concentration levels of the carboxylic acids in Guiyang were higher than those in Shangzhong. In Shangzhong it is witnessed that the concentrations of these acids were higher in the summer than in the winter. Direct emissions from growing vegetations or soils may account for the main provenance of the acids in the rural area. This is, however, not the case in Guiyang, where the concentrations of the carboxylic acids were found higher during the non-growing season than during the growing season. The seasonal variation of the acids indicated the relatively weak scavenging effect of precipitation and higher pH in rainwater which enhanced the concentrations of the carboxylic acids during the wintertime.

(ii) From the contributions of the carboxylic acids to the free acidity and total anions of the rainwater, it can be concluded that carboxylic acids were important components of the rainfall and their contributions to the rainwater acidity could not be ignored. Especially in the remote Shangzhong region, carboxylic acids which made major contributions to the rainwater acidity preponderated over incarboxylic acids. Although $SO_4^{2-}$and NO_3^- were major species, the carboxylic acids accounted for 1.7%–19.2% of the total anions in the rainwater of Guiyang. Therefore, carboxylic acids were also important for the constitution and the acidity of the rainwater

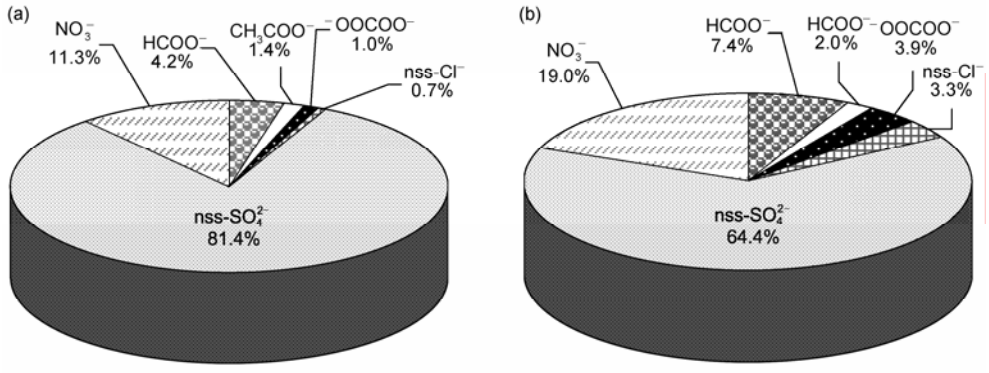

Figure 4 The constitution of the major anions in the rainwater of Guiyang (a) and Shangzhong (b).

in urban areas.

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