Urban and rural observations of carboxylic acids in rainwater in Southwest of China: the impact of urbanization

Gang Xu · Xinqing Lee · Yingchun Lv

Abstract Seven carboxylic acids in rainwater were simultaneously determined using ion chromatography for 13 months in two different sites, Guiyang and Shangzhong, southwest of China. Results showed formic, acetic and oxalic acids were the three predominant carboxylic acids. Their volume-weighted average concentrations were 14.24, 9.35, 2.79 µmol/L in Guiyang and 4.95, 1.35, 2.31 µmol/L in Shangzhong, respectively. A distinctive diurnal pattern in carboxylic acid concentrations (daytime>nighttime, t test, $p<0.05$) was observed during the growing season in Guiyang. Shangzhong witnessed higher concentration of these acids during the growing season than that during the non-growing season. Direct emissions from growing vegetation or soils probably account for the main provenance of the acids in the rural area. However, the opposite trend were found in Guiyang and the anthropogenic sources during the non-growing season were the main reason. By comparison of our result with the previous data about 20 years ago, we calculated that at least 42% of acetic acids and 69% of formic acid originated from the anthropogenic sources in Guiyang. Furthermore, the ratio of formate/acetate in gas phase larger than 1 suggest the oxidation of unsaturated hydrocarbons from the human activity and/or natural sources were the main origin of carboxylic acids in Guiyang. While The F/A ratio in gas phase was less than 1 in Shangzhong which indicate the direct emissions from biogenic sources. Oxalic acid was in similar amounts in both sites, indicating the common source of the acid.

Keywords Carboxylic acids · Formic acid · Acetic acid · Rainwater

1 Introduction

As the important components of organic compounds in atmosphere, carboxylic acids have received increasing attention in recent years due to their effects on environment and climate

G. Xu · Y. Lv (✉)
Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China
e-mail: yclv@yic.ac.cn

G. Xu · X. Lee
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,
Chinese of Academy of Sciences, Guiyang 550002, China

change (Khare et al. 1999). Researches found that carboxylic acids could be responsible for up to 64% of the rainwater acidity in remote areas (Galloway et al. 1982) and up to 30% of the acidity of wet deposition in polluted areas (Peña et al. 2002). The existence of carboxylic acids on the atmospheric aerosol surface can alter the chemical and physical properties of the aerosol and enhance its capability as cloud condensation nuclei (Kawamura et al. 2007). Furthermore, the presence of formic and acetic acids in atmosphere can influence the pH-dependent chemical reactions in clouds (Keene and Galloway 1988). Extensive measurements of carboxylic acids have been conducted in gas phase, aqueous phase (rainwater, fog, cloud.) and in aerosol (Millet et al. 1997; Khare et al. 1999; Löflund et al. 2002), which suggest primary and secondary sources are the major sources of carboxylic acids in atmosphere. Primary sources include the direct emission from vehicles (Kawamura et al. 1985), soils (Sanhueza and Andreae 1991), oceans (Graedel and Eisner 1988), ants as well as biomass burning (Hartmann et al. 1989). Secondary sources are the photochemical reaction of unsaturated hydrocarbons in atmosphere (Sanhueza et al. 1995). Kinetic studies assure that carboxylic acids can be the products of the reaction of ozone with olefins such as ethene, propene, and butene which are ubiquitous in the atmosphere but are predominantly anthropogenic in origin (Atkinson 1990; Orzechowska and Paulson 2005). The formaldehyde oxidation with OH radical in aqueous phase has been investigated as an important source for formic acid in atmosphere (Chameides and Davis 1983; Jacob. 1986).

In spite of the important role of carboxylic acids in atmosphere, few studies have been performed on the variation of carboxylic acids in rainwater in southwest of China. Therefore, Guiyang and Shangzhong as the representation of the urban area and the rural area were selected in our study. The rainwater in both sites had been collected for 13 months continuously to measure the seven carboxylic acids as well as the major anions and cations. The purposes of this paper are to report the concentration levels of carboxylic acids in rainwater; to examine their diurnal, seasonal and temporal variations; and to evaluate the possible sources of these species by comparison of the two distinctive sites.

2 Experiments

2.1 Sample sites

Guiyang (26°34′,106°43′), the capital of Guizhou Province, southwest of China, is one of the most polluted city with the most population density in the urban and the city industry and traffic develope rapidly. It lies in a wide Karst valley basin with all mountains around so the diffusion of the pollution in atmosphere is difficult. The rainwater samples in Guiyang were collected on the roof of the doctoral dormitory in the Chinese Academy of Sciences (CAS) Institute of Geochemistry, where is about 20 m above the ground and higher than the surrounding buildings. This site is located in the center of the Guiyang with no specific or point pollution sources around and can represent the normal state of the city (Fig. 1). About 200 km away from Guiyang, Shangzhong (26°16′, 108°40′) lies in the southeast of Guizhou Province and approximately 60% of the town is covered with trees. Moreover, there are few vehicles and no cities or factories within a radius of 50 km. Compared to Guiyang, Shangzhong is little influenced by the anthropogenic forces and can represent the rural condition.
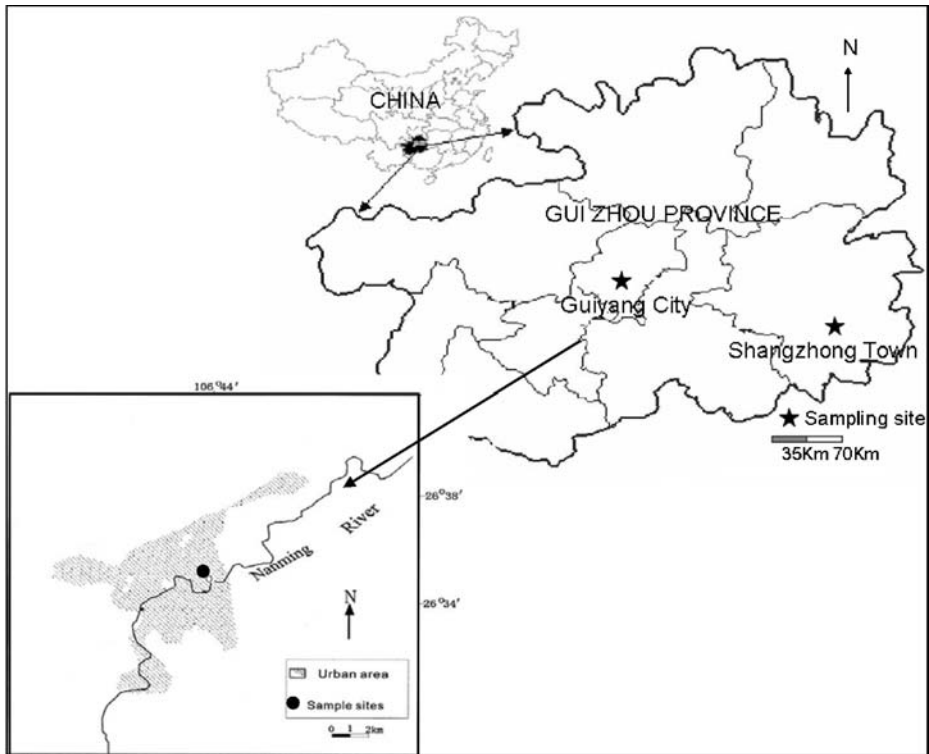
Fig. 1 Map of the sampling sites

2.2 Sample collection and analysis

The samples in Guiyang were collected with 1.5 m×2 m polyethylene container, which had been cleaned with 2–3 N HCl and thoroughly rinsed with Milli-Q water (18.2MΩ) before using. In order to minimize the contamination of the particulate matter, special attention were paid to open the sampler as soon as the onset of rainfall. The collector was installed on an iron stand, about 1.5 m high above the building ground. An automatic sampler (APS-2B, Changsha Company) was used to collect the rainwater in Shangzhong. And 144 samples in Guiyang and 47 samples in Shangzhong were collected on an event basis from April 2006 to April 2007. The rainwater samples and the blank sample with deionized water were frozen to −18°C until analysis (Karlsson et al. 1999; Fornaro and Gutzb 2003). Blank tests and stability tests performed for these samples show no detectable peaks.

In situ we measured the pH and conductivity with a PIONneer 65 multiparameter instrument (Radiometer Co.). Back in laboratory, the carboxylic acids and major anions were simultaneously determined using Dionex ICS-90 ion chromatography equipped with AS11-HC seperation column and AG11-HC guard column. The gradient eluent of KOH was generated form reagent free controller (RFC-30). The linear correlation coefficients of calibration curve were in the range of 0.9995~0.9999. The relative standard deviations (RSD%) were below 5%. Quantitative recoveries of spiked samples ranged from 80% to 120%. Concentrations of major cations were measured with Flame atomic absorption spectrophotometric method and the analytical reproducibility was below 5%.

3 Results and discussions

3.1 Characteristic composition of carboxylic acids in rainwater

3.1.1 Concentration levels of carboxylic acids in rainwater

As illustrated in Fig. 2, seven carboxylic acids with diverse functional groups were found in rainwater at two sites: formic, acetic, oxalic, pyruvic, propanic, methanesulfonic and lactic acid. Most of them were short chain monocarboxylic acids except oxalic, pyruvic and Methanesulfonic acids.

Formic, acetic and oxalic acids were the most abundant and predominant carboxylic acids in rainwater in southwest of China which is consistent with previous studies (Khare et al. 1999). The overall volume-weighted average (VWA) concentrations for formic and acetic acids were 14.24 μmol/L and 9.35 μmol/L in Guiyang, which were significantly higher than 4.95 μmol/L and1.35 μmol/L in remote Shangzhong. In addition, the data in Guiyang were higher than that reported in Xiamen as 5.7 μmol/L for formic acid and 2.9 μmol/L for acetic acid, southeast of China (Yu et al. 1998). This can be explained by the difference of the geographical location of the two sampling sites. Unlike our work, the Xiamen studies were performed in the coastal site, which contain lower carboxylic acids concentrations in storms than the continental rain events (Khare et al. 1999). In general, the acids in Guiyang fell within the range found in contaminated rainwater in the global urban regions as summarized by Khare et al. (1997a, b) and were in good agreement with values of Sao Paulo of Brazil (formic:17.0 μmol/L, acetic:8.9 μmol/L) (Fornaro and Gutzb 2003). The values of formic and acetic acids at remote Shangzhong were in good agreement with the previous studies at rural sites, lower than those measured in Katherine, Australia (formic:4.2 μmol/L, acetic acid 10.5 μmol/L) and higher than that in Central Virginia (formic:0.3 μmol/L, acetic acid 0.6 μmol/L) (Khare et al. 1997a, b). The different levels of formic and acetic acids in Guiyang and Shangzhong indicates that the acids had regional sources. The higher concentrations of the acids in urban areas implied the importance of anthropogenic sources because the values at Shangzhong were only about 34.8% and 14.4% of that at Guiyang. However, the fairly similar results were found for the oxalic acid values in Guiyang (2.79 μmol/L) and Shangzhong (2.31 μmol/L), which indicates little influence from anthropogenic activity and the similar sources at both sites. Main sources of oxalic acid were thought to be photochemical oxidation of anthropogenic, biogenic and oceanic emissions (Kawamura et al. 1996; Ervens et al. 2004). Because of the chemical stability, oxalic acids can accumulated in atmosphere and may be transported to other

Fig. 2 Volume-weighted mean concentrations of carboxylic acids in rainwater in Guiyang and Shangzhong from April 2006 to April, 2007
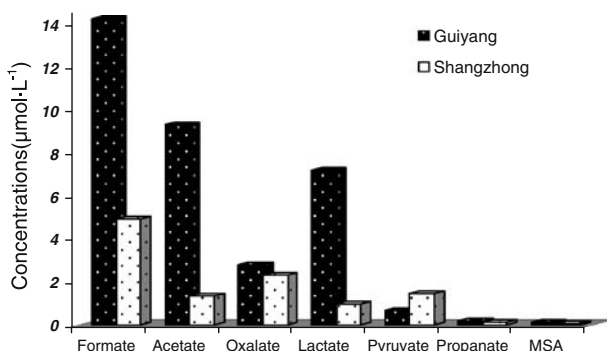
regions (Chebbi and Carlier 1996). Limited studies have been carried out with rainwater pyruvic acid. Avery et al. (2001a, b) reported the pyruvic acid concentration as low as 0.19 μmol/L in Wilmington rainwater. However, very high concentrations of the pyruvic acid in Guiyang and Shangzhong were observed as 0.69 μmol/L and 1.47 μmol/L, respectively. The predominant source of tropospheric pyruvate is closely related to the atmospheric reaction of isoprene (Talbot et al. 1995). And propanic acid was detected in over 50% of rain events with VWM concentration of 0.18 μmol/L in Guiyang and 0.12 μmol/L in Shangzhong, respectively. Lactate and [F⁻] have a poor peak resolution due to their similar polarity. And lactic acid is susceptibly contaminated during sample collection and analysis. So much more work are needed to be carried out to address this issue.

Methanesulfonic acid (MSA) was the lowest carboxylic acids in rainwater, the measured VWM concentration was 0.12 μmol/L in Guiyang and 0.10 μmol/L in Shangzhong, respectively. The exclusive source for MSA is related to the oxidation of DMS which is mainly produced (98%) by algae in sea. Therefore, it is interesting and valuable to report high concentration levels of the acid in continental sites in southwest of China. This fact may be attributed to small DMS emissions from terrestrial environment (Ayers and Gillett 2000).

Although pyruvic propanic methanesulfonic and lactic acids were also determined in trace levels, there were more than 50% of the measurements below the detection limits, therefore they were excluded from further discussion in the following parts.

3.1.2 Diurnal variations

Many studies have been conducted to understand the diurnal variations of the acids in gas phase (Talbot et al. 1988). However, to the best of our knowledge, few studies have been addressed to their diurnal cycles in rainwater (Avery et al. 2001a, b). To investigate the diurnal variations of the carboxylic acid in rainwater, samples in each site were separated into two groups: daytime (6:00~18:00) group and nighttime (18:00~6:00) group. Events were excluded from the classification if they occurred during the two-time period. Compared to that at nighttime rain during growing season, the concentrations of the acids at daytime rain were higher (t test, $p < 0.05$). Formic, acetic and oxalic acids concentrations at daytime events were approximately doubled that at nighttime events (Fig. 3). This may attribute to the increased photochemical production of these species in the atmosphere and
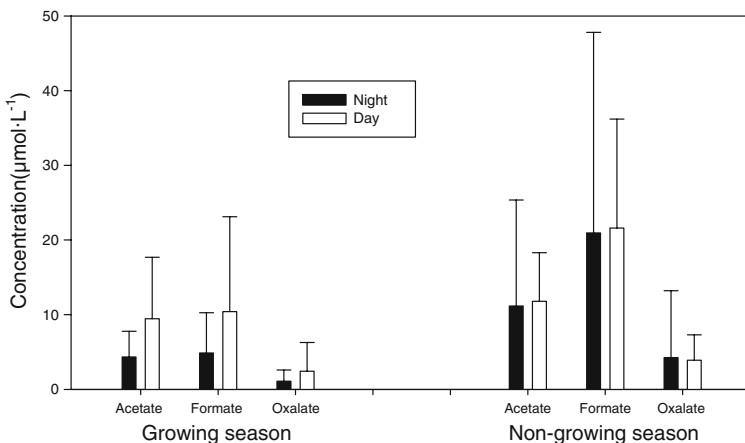

Fig. 3 Diurnal variation of carboxylic acids in rainwater in Guiyang from April 2006 to April, 2007

directly emissions by fossil fuels combustion and cooking activities which occur with more frequency at daytime (Sakugawa and Kaplan 1993). The dry deposition and dew at nighttime accelerate the deposition of carboxylic acids to the ground, which may also result in the lower concentrations of the acids at nighttime (Khwaja. 1995). However, no pronounced diurnal cycles were observed during non-growing season (Fig. 3) because the non-growing season was characterized by low temperature and low solar radiation time and intensity which do not favor the production of the acids by photochemical reactions at daytime (Sanhueza et al. 1995).

3.1.3 Seasonal variations

In general, the acids followed the trends of significantly enhanced levels during the growing season (Fig. 4). Formic, acetic and oxalic acids were roughly 8, 10 and 2 times higher than that during the non-growing season, respectively. The seasonal variations of carboxylic acids in rainwater point to the importance of vegetation emissions (Kuhn et al. 2002). The seasonal study of formic and acetic acids in rainwater was firstly made by Keene and Galloway (1986). They hypothesized that the biogenic emissions from vegetation could contribute to the higher concentrations of these species during the growing season over continents. Shangzhong is representative of the rural area in Guizhou Province because there are no cities or factories within a radius of 50 km and approximately of 60% of the sampling site are surrounded with trees. It was estimated the anthropogenic activity could be insignificant in this area. As a result, the seasonal variations of carboxylic acids indicate the biogenic emissions from vegetation dominated the sources of carboxylic acids in this site which was consistently with previous studies (Talbot et al. 1990; Kuhn et al. 2002; Peña et al. 2002).

However, the remarkable opposite seasonal pattern of carboxylic acids were observed in Guiyang (Fig. 5). The concentrations of formic, acetic and oxalic acids during non-growing season were higher than that during growing season by 70%, 174% and 139%, respectively. Obviously, such seasonal variations suggest that biogenic emissions were not the primary sources of the carboxylic acids in this site. The carboxylic acids in Guiyang were mainly incorporated into the rainwater during the below-cloud process because a negative correlations ($p < 0.05$) were observed between the carboxylic acid concentrations and rainamount. The higher rainamount during the growing season compared to that during the non-growing season seemed to cause such seasonal variation (Fig. 5). After May, the precipitation increased significantly in Guiyang, and the larger rainfall enhanced the washout of the trace species in the atmosphere (Kumar et al. 1996), so the concentrations of the carboxylic acids in the rainwater were reduced by the purification of the air pollutants.

Fig. 4 Volume-weighted monthly concentrations of formate, acetate, oxalate and precipitation in rainwater in Shangzhong from April 2006 to April, 2007
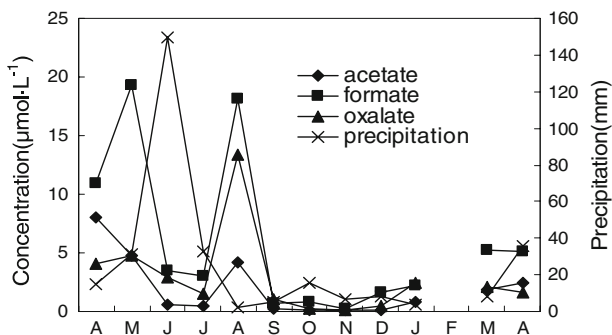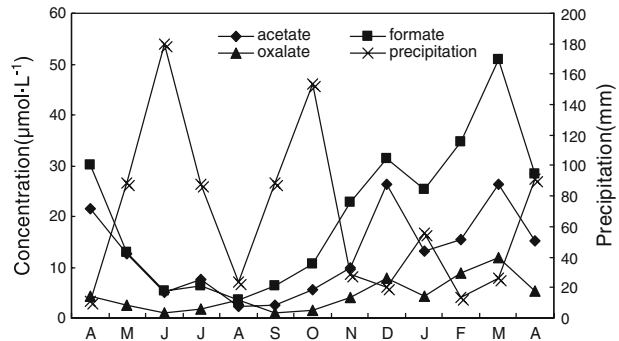
Fig. 5 Volume-weighted monthly concentrations of formate, acetate and oxalate and precipitation in Guiyang from April 1, 2006 to April 30, 2007

However, during the dry season after November in Guiyang, the frequency of the rainfall reduced, the pollutants in the atmosphere were prone to accumulate, thus the concentrations of the carboxylic acids in the rainwater increased. Similar results were also found in Hong Kong, southeast of China (Tanner and Law 2003). They speculated this seasonal variation may result not only from a variation in the nature and strength of the acids sources but also the higher rainfall per event as well as higher rain depth in the monsoon compared to winter (Kumar et al. 1996). As a result, the eluviation and the dilution effects were the main reasons for the seasonal variation of the carboxylic acid concentrations in Guiyang. However, changes in the rainfall cannot explain the seasonal pattern of the carboxylic acids in Shangzhong (Fig. 4).

3.1.4 Temporal variations

Industrial activities are considered as the most important driving forces in the ongoing process of atmospheric chemistry in urban region. The significant higher concentrations of carboxylic acids in rainwater in urban sites than that in rural sites suggest the importance of anthropogenic sources. However, as the biogenic emissions are different between rural and urban sites, it is still difficult to access the importance of anthropogenic versus biogenic inputs of carboxylic acids to rainwater by comparing concentrations from various urban and rural locations (Avery et al. 2001a, b). Avery et al. (2001a, b) proposed an approach to assess the relative importance of anthropogenic and biogenic emissions. It is to compare the temporal data from a single site which has undergone extensive changes in either anthropogenic or biogenic sources (Avery et al. 2001a, b).

Guiyang can serve as an ideal location for such study because this site has undergone extensively urbanization and rapid industrial expansion since the first determination of formic and acetic acids conducted approximately 20 years ago (Chen et al. 1991). For example, the total city population increased by 137% from 1.5 million in 1989 to 3.5 million in 2005, and the industrial output increased by 824% from 7.7 billion yuan in 1989 to 71.4 billion yuan in 2005(Guizhou Statistical Yearbook). From these data, we can see that tremendous social and economic changes have taken place from 1989 to 2005 in Guiyang. On the contrary, the biological production of carboxylic acids in rainwater is of relatively little variation during the past 20 years because the population growth or industrial expansion always associate with the decline of forests and lands for development.

From the data in our study, we can see that the mean concentrations of formic and acetic acids had increased dramatically since the previous work at this site between 1989 and

1990 by Chen et al. (1991) (Fig. 6). Formic acid increased from 5.83 μmol/L to 18.84 μmol/L while acetic acid approximately doubled from 6.3 μmol/L to 10.8 μmol/L. The increased concentrations of formic and acetic acids in rainwater in Guiyang likely reflect the impact of extensive population growth and industrial expansion. Assume all the carboxylic acids were biogenic origin in previous work by Chen et al. (1991), it can be calculated that 42% of acetic acids and 69% of formic acid were from anthropogenic sources in Guiyang during our study period.

The ratio of formate to acetate (F/A) (based on linear regression analysis) varied from 0.79 (Durana et al. 1992) to 3.47 (Keene and Galloway 1986) in rainwater around the world. In the past 20 years, the F/A ratio had increased from 0.82 to 1.8. These changes likely reflect the increased photochemical source strengths in atmosphere (Khwaja. 1995). Back in the 1980's the correlation of these species with the growing season and their diurnal cycles indicated the direct vegetation sources. Twenty years later, researches show that the secondary sources are very important and perhaps dominate in some locations (Fisseha et al. 2009). In addition, the F/A ratio in rainwater is expected to be more complicated than that in the gas phase because it is affected by the pH of rainwater. The pH of the rainwater had decreased from 4.1 to 3.3 since 1989 in Guiyang. Because of the 10 times larger acid dissociation constant of HCOOH than CH_3COOH, higher hydronium concentration can favor the release of CH_3COOH rather than HCOOH from the rainwater. Additionally, the oxidation of HCHO could increase HCOOH concentration and thus contribute to the higher $HCOOH/CH_3COOH$ ratio (Fornaro and Gutzb 2003). On the other hand, more HCOOH dissociates to formate ion at higher pH values, and the fast oxidation of formate ion by HO radicals in the aqueous phase (Jacob. 1986) would contribute to lower $HCOOH / CH_3COOH$ ratios. Finally, with the application of natural gas in vehicles, carboxylic acid concentrations from the vehicles significantly decreased, and only formic acid was detected in exhaust gas under experimental conditions (Zervas and Tazerout 2000). As a result, the F/A ratio increased than ever before.

3.2 Possible sources of carboxylic acids in rainwater

3.2.1 Correlation analysis with specific species

A correlation analysis of carboxylic acid concentrations with other spices parameters was conducted with SPSS 13.0. K^+ was selected as biomass burning indicator (Chow 1995); NO_2^- for traffic emissions; SO_4^{2-} or MSA for secondary formation of different mechanism (Huang et al. 2005); Mg^{2+} for sea salt (Keene and Galloway 1986) and Ca^{2+} for soils emissions (Taylor 1964); NH_4^+ for agricultural activities (Huang et al. 2005).

Fig. 6 Temporal variation of carboxylic acids in rainwater in Guiyang for the past 20 years (Data of carboxylic acids for 1988~1989 came from Chen et al. (1991))
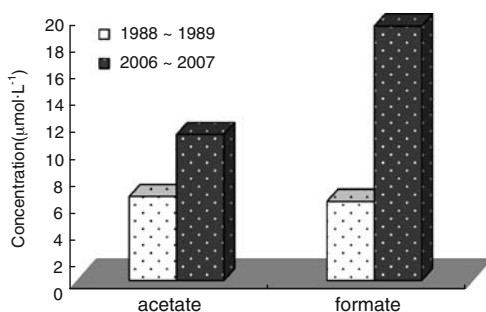
Table 1 Correlation analysis with other chemical spices

		NO_2^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+
Guiyang	acetate	0.424**	0.287**	−0.078	−0.130	0.028	−0.160	0.142
	formate	0.701**	0.625**	0.393**	0.303**	0.583**	0.226**	0.475**
	oxalate	0.741**	0.693**	0.440**	0.315**	0.648**	0.287**	0.696**
Shangzhong	acetate	0.306*	0.467**	0.385*	0.293	0.103	−0.01	0.289
	formate	0.265	0.329*	0.383*	0.328*	0.164	0.047	0.241
	oxalate	0.180	0.192	0.121	0.152	0.213	0.020	0.057

(**$p<0.01$; *$p<0.05$)

From the linear correlation in Table 1, we can see the origin for the carboxylic acids in Shangzhong was simple and single. The positively relationship between carboxylic acids and SO_4^{2-}, Ca^{2+} indicate the secondary formations in atmosphere and soil emissions were the major sources. But as to Guiyang, the sources become more complicated, natural and anthropogenic origin could affect the carboxylic acids concentrations in rainwater.

3.2.2 The contribution of carboxylic acids from primary or secondary sources

Various investigators have examined the utility of the F/A ratio in the gas phase or in rainwater as an indicator of the relative contribution of direct emissions and secondary formation in the gaseous phase. If the origin is mainly from direct emissions, the F/A is lower than one and if the secondary source dominates the origin, the F/A is larger than one. The ratio of F/A from different sources are illustrated in Table 2.

The F/A ratio in liquid phase is more complicated than that in gas phase and they are dictated by the Henry constants and dissociations of formic and acetic acids as well as pH of liquid water. As a result, the F/A ratio for aqueous phase cannot be used directly to evaluate the relative importance of primary sources and secondary sources, but the calculated corresponding F/A ratio in the gas phase can be used for such evaluation. The F/A ratios in rainwater and gas phase are shown in Table 3. To see more detailed calculation in literature (Helas et al. 1992). The F/A ratios in rainwater in both sites are larger than 1. The F/A ratio in gas phase was less than 1 in Shangzhong which indicate the direct emissions from biogenic sources. On the contrary, the gas phase F/A ratio is more than 1 in Guiyang which may be caused by secondary sources in the atmosphere (Jordan et al. 2009).

Table 2 The F/A ratio for gas phase from different sources

Sources	F/A	References
Primary sources	<1	
Biomass burning	0.1~0.5	(Talbot et al. 1988)
	0.2~0.4	(Hartmann et al. 1991)
Vehicular emissions	0.4~0.6	(Talbot et al. 1988)
	0.3~0.5	(Grosjean 1992)
Vegetation (tropical forests)	0.6	(Talbot et al. 1990)
Vegetation emissions	0.4	(Servant et al. 1991)
Secondary sources	>1	(Talbot et al. 1988)

Table 3 The F/A ratio in rainwater and gas phase in Guiyang and Shangzhong

	Guiyang		Shangzhong	
	Growing	Non-growing	Growing	Non-growing
F/A (rainwater)	2.09	1.53	3.48	1.36
F/A (calculated for gas phase)	2.53	1.85	0.59	0.23

The unsaturated hydrocarbons (olefins, isoprene) are important factor to control the concentrations of carboxylic acids in the atmosphere which may originate from biogenic or anthropogenic sources (Lee et al. 2006).

4 Conclusions

Guiyang and Shangzhong were selected in this study for the urban and rural observation of low-molecule-weight carboxylic acids in rainwater in southwest of China. The main conclusions are as follows:

(1) Formic, acetic and oxalic acids were the three predominant carboxylic acids at the two sites. Their volume weighted average concentration (VWA) were 14.24 μmol/L, 9.35 μmol/L and 2.79 μmol/L in Guiyang, 4.95 μmol/L,1.35 μmol/L and 2.31 μmol/L in Shangzhong, respectively.

(2) Carboxylic acids in rainwater in Guiyang demonstrated obviously diurnal, seasonal (include Shangzhong) and temporal variations. The carboxylic acids concentrations in rainwater in Guiyang were higher at the daytime compared to that at the nighttime during growing season. It is worth to note that different seasonal pattern was observed in the two sites with higher concentrations of the acids during the growing season in Shangzhong. Direct emissions from growing vegetation may account for the main provenance of the acids in the rural area. In Guiyang, the higher concentration level of the acids may result from the little frequency and small rainamount of the rainfall during the non-growing season. Concentrations of formic and acetic acids in rainwater in Guiyang had increased dramatically since the earlier work conducted at the same place about 20 years ago. According to the approach of Avery et al. (2001a, b), we calculated that 42% of acetic acids and 69% of formic acid were from the anthropogenic sources. Because we assume all of the carboxylic acids were biogenic origin in previous study, so the actual fraction of anthropogenic acids may be even higher.

(3) From correlation results, it was estimated the origins for carboxylic acids in Shangzhong were simple and single which mainly originated from the direct biogenic or soil emissions. By contrast, the sources of carboxylic acids in Guiyang were more complicated and anthropogenic activities can affect the distribution of carboxylic acids in atmosphere. The ratios of F/A larger than one for gas phase indicate that the secondary formation of carboxylic acids was vital to the atmosphere in Guiyang and the direct emissions from vegetation, vehicles or biomass burning were unimportant.

References

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: a review. Atmos. Environ. **24**(1), 1–41 (1990)

Avery, G.B., Tang, Y., Kieber, R.J., Willey, J.D.: Impact of recent urbanization on formic and acetic acid concentrations in coastal North Carolina rainwater. Atmos. Environ. **35**(19), 3353–3359 (2001a)

Avery, G.B., Willey, J.D., Kieber, R.J.: Diurnal variations in major rainwater components at a coastal site in North Carolina. Atmos. Environ. **35**, 3927–3933 (2001b)

Ayers, G.P., Gillett, R.W.: DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry. J. Sea Res. **43**(3–4), 275–286 (2000)

Chameides, W.L., Davis, D.D.: Aqueous-phase source of formic acid in clouds. Nature **304**(4), 427–429 (1983)

Chebbi, A., Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources and sinks: a review. Atmos. Environ. **30**(24), 4233–4249 (1996)

Chen, Z.L., Wang, Y.B., Lu, M.Q.: The role of atmospheric organic compounds in the formation of acid rain. Environ. Chem. **10**(1), 1–13 (1991), in Chinese with English abstract

Chow, J.C.: Measurement methods to determine compliance with ambient air quality standards for suspended particles. J. Air Waste Manage. Assoc. **45**(5), 320 (1995)

Durana, N., Casado, H., Garcia, C., Ezcurra, A., Lacaux, J.P., Encinas, D.: Organic acids in precipitation in the Basque Country (North of Spain). Atmos. Res. **28**, 93–101 (1992)

Ervens, B., Feingold, G., Frost, G.J., Kreidenweis, S.M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. J. Geophys. Res. **109**, D15205 (2004)

Fisseha, R., Saurer, M., Jäggi, M., Siegwolf, R.T.W., Dommen, J., Szidat, S., Samburova, V., Baltensperger, U.: Determination of primary and secondary sources of organic acids and carbonaceous aerosols using stable carbon isotopes. Atmos. Environ. **43**(2), 431–437 (2009)

Fornaro, A., Gutzb, I.G.R.: Wet deposition and related atmospheric chemistry in the Sao Paulo metropolis, Brazil: part 2-contribution of formic and acetic acids. Atmos. Environ. **37**, 117–128 (2003)

Galloway, J.N., Keene, W.C., Likens, G.E., Miller, J.M.: The composition of precipitation in remote areas of the world. J. Geophys. Res. **87**(C11), 8771–8786 (1982)

Graedel, T.E., Eisner, T.: Atmospheric formic acid from formicine ants: a preliminary assessment. Tellus **40**, 335–339 (1988)

Grosjean, D.: Formic acid and acetic acid: emissions, atmospheric formation and dry deposition at two southern California locations. Atmos. Environ. **26**(18), 3279–3286 (1992)

Hartmann, W.R., Andreae, M.O., Helas, G.: Measurements of organic acids over central Germany. Atmos. Environ. **23**(7), 1531–1533 (1989)

Hartmann, W.R., Santana, M., Hermoso, M., Andreae, M.O., Sanhueza, E.: Diurnal cycles of formic and acetic acids in the northern part of the Guayana shield, Venezuela. J. Atmos. Chem. **13**(1), 63–72 (1991)

Helas, G., Bingemer, H., Andreae, M.O.: Organic acids over equatorial Africa results from DECAFE-88. J. Geophys. Res. **97**(D6), 6187–6193 (1992)

Huang, X.-F., Hu, M., He, L.-Y., Tang, X.-Y.: Chemical characterization of water-soluble organic acids in PM2.5 in Beijing, China. Atmos. Environ. **39**, 2819–2827 (2005)

Jacob, D.J.: Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. J. Geophys. Res. **91**, 9807–9826 (1986)

Jordan, C., Fitz, E., Hagan, T., Sive, B., Frinak, E., Haase, K., Cottrell, L., Buckley, S., Talbot, R.: Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences. Atmos. Chem. Phys. **9**, 4677–4697 (2009)

Karlsson, S., Wolrath, H., Dahlen, J.: Influence of filtration, preservation and storing on the analysis of low molecular weight organic acids in natural waters. Water Res. **33**(11), 2569–2578 (1999)

Kawamura, K., Ng, L.-L., Kapian, I.R.: Determination of organic acids (C1–C10) in the atmosphere, motor exhausts, and engine oils. Environ. Sci. Technol. **19**, 1082–1086 (1985)

Kawamura, K., Steinberg, S., Kaplan, I.R.: Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern California wet precipitations: comparison of urban and nonurban samples and compositional changes during scavenging. Atmos. Environ. **30**(7), 1035–1052 (1996)

Kawamura, K., Narukawa, M., Li, S.M., Barrie, L.A.: Size distributions of dicarboxylic acids and inorganic ions in atmospheric aerosols collected during polar sunrise in the Canadian high Arctic. J. Geophys. Res. **112**(D10), 10–18 (2007)

Keene, W.C., Galloway, J.N.: Considerations regarding sources for formic and acetic acids in the troposphere. J. Geophys. Res. **91**(D13), 14466–14474 (1986)

Keene, W.C., Galloway, J.N.: The biogechemical cycling of formic and acetic acids through the troposphere: an overview of current understanding. Tellus **40B**, 322–334 (1988)

Khare, P., Satsangi, G.S., Kumar, N., Kumar, K.M., Srivastava, S.S.: HCHO, HCOOH and CH3COOH air and rain water at a rural tropical site in north central India. Atmos. Environ. **31**(23), 3867–3875 (1997a)

Khare, P., Satsangi, G.S., Kumar, N., Kumari, K.M., Srivastava, S.S.: Surface measurements of formaldehyde and formic and acetic acids at a subtrpical semiarid site in India. J. Geophys. Res. **102** (D15), 18997–19006 (1997b)

Khare, P., Kumar, N., Kumari, K.M., Srivastava, S.S.: Atomspheric formic and acetic acids: an overview. Rev. Geophys. **37**(2), 227–248 (1999)

Khwaja, H.A.: Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site. Atmos. Environ. **29**(1), 127–139 (1995)

Kuhn, U., Rottenberger, S., Biesenthal, T., Ammann, C., Wolf, A., Schebeske, G., Oliva, S.T., Tavares, T.M., Kesselmeier, J.: Exchange of short-chain monocarboxylic acids by vegetation at a remote tropical forest site in Amazonia. J. Geophys. Res. **107**(D20), 8069 (2002)

Kumar, N., CKULShrestha, U., Saxena, A., Khare, P., Kumar, K.M., Srivastava, S.S.: Formate and acetate levels compared in monsoon and winter rainwater at Dayalbagh, Agra (India). J. Atmos. Chem. **23**, 81–87 (1996)

Lee, A., Goldstein, A.H., Keywood, M.D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N.L., Flagan, R.C., Seinfeld, J.H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes. J. Geophys. Res. **111**, D07302 (2006). doi:10.1029/2005JD006437

Löflund, M., Kasper-Giebl, A., Schuster, B., Giebl, H., Hitzenberger, R., Puxbaum, H.: Formic, acetic, oxalic, malonic and succinic acid concentrations and their contribution to organic carbon in cloud water. Atmos. Environ. **36**(9), 1553–1558 (2002)

Millet, M., Wortham, H., Sanusi, A., Mirabel, P.: Low molecular weight organic acids in fogwater in an urban area: Strasbourg (France). Sci. Total Environ. **206**, 57–65 (1997)

Orzechowska, G., Paulson, S.E.: Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under dry and humid conditions using SPME. J. Phys. Chem. A. **109**, 5358–5365 (2005)

Peña, R.M., García, S., Herreroa, C., Losada, M., Vázquez, A., Lucas, T.: Organic acids and aldehydes in rainwater in a northwest region of Spain. Atmos. Environ. **36**, 5277–5288 (2002)

Sakugawa, H., Kaplan, I.R.: Measurements of H2O2, aldehydes and orgnic acids in Los Angeles rainwater: their sources and deposition rates. Atmos. Environ. **27B**(2), 203–219 (1993)

Sanhueza, E., Andreae, M.O.: Emission of formic and acetic acids from tropical savanna soils. Geophys. Res. Lett. **18**(9), 1707–1710 (1991)

Sanhueza, E., Figueroa, L., Santana, M.: Atmospheric formic and acetic acids in Venezuela. Atmos. Environ. **30**(10/11), 1861–1873 (1995)

Servant, J., Kouadio, G., Cros, B., Delmas, R.: Carboxylic monoacids in the air of mayombe forest (Congo): role of the forest as a source or sink. J. Atmos. Chem. **12**(4), 367–380 (1991)

Talbot, R.W., Beecher, K.M., Harriss, R.C., Cofer, R.W.: Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. J. Geophys. Res. **93**, 1638–1652 (1988)

Talbot, R.W., Andreae, M.O., Berresheim, H., Jacob, D.J., Beecher, K.M.: Sources and sinks of formic, acetic, and pyruvic acids over Central Amazonia: 2. Wet Season. J. Geophys. Res. **95**, 16799–16811 (1990)

Talbot, R.W., Mosher, B.W., Heikes, B.G., Jacob, D.J., Munger, J.W., Daube, B.C., Keene, W.C., Maben, J.R., Artz, R.S.: Carboxylic acids in the rural continental atmosphere over the eastern united states during the shenandodh coud and photochemistry experiment. J. Geophys. Res. **100**(D5), 9335–9343 (1995)

Tanner, P.A., Law, P.T.: Organic acids in the atmosphere and bulk deposition of Hong Kong. Water Air Soil Pollut. **142**, 279–297 (2003)

Taylor, S.R.: Abundance of chemical elements in the continental crust: A new table. Geochim. Cosmochim. Acta. **28**, 1273–1285 (1964)

Yu, S., Gao, C., Cheng, Z., Cheng, X., Cheng, S., Xiao, J., Ye, W.: An analysis of chemical composition of different rain types in Minnan Golden Triangle region in the southeastern coast of China. Atmos. Res. **47–48**, 245–269 (1998)

Zervas, E., Tazerout, M.: Organic acids emissions from natural-gas-fed engines. Atmos. Environ. **34**(23), 3921–3929 (2000)