

Organic acids in cloud water and rainwater at a mountain site in acid rain areas of South China

Xiao Sun¹ · Yan Wang¹ · Haiyan Li¹ · Xueqiao Yang² · Lei Sun³ ·
Xinfeng Wang³ · Tao Wang⁴ · Wenxing Wang³

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Abstract To investigate the chemical characteristics of organic acids and to identify their source, cloud water and rainwater samples were collected at Mount Lu, a mountain site located in the acid rain-affected area of south China, from August to September of 2011 and March to May of 2012. The volume-weighted mean (VWM) concentration of organic acids in cloud water was 38.42 $\mu\text{eq/L}$, ranging from 7.45 to 111.46 $\mu\text{eq/L}$, contributing to 2.50 % of acidity. In rainwater samples, organic acid concentrations varied from 12.39 to 68.97 $\mu\text{eq/L}$ (VWM of 33.39 $\mu\text{eq/L}$). Organic acids contributed significant acidity to rainwater, with a value of 17.66 %. Formic acid, acetic acid, and oxalic acid were the most common organic acids in both cloud water and rainwater. Organic acids had an obviously higher concentration in summer than in spring in cloud water, whereas there was much less discrimination in rainwater between the two seasons. The contribution of organic acids to acidity was lower during summer than during spring in both cloud water (2.20 % in summer vs 2.83 % in spring) and rainwater (12.24 % in summer vs 19.89 % in spring). The formic-to-acetic acid ratio (F/A) showed that organic acids were dominated by primary

emissions in 71.31 % of the cloud water samples and whole rainwater samples. Positive matrix factorization (PMF) analysis determined four factors as the sources of organic acids in cloud water, including biogenic emissions (61.8 %), anthropogenic emissions (15.28 %), marine emissions (15.07 %) and soil emissions (7.85 %). The findings from this study imply an indispensable role of organic acids in wet deposition, but organic acids may have a limited capacity to increase ecological risks in local environments.

Keywords Organic acids · Cloud water · Rainwater · Sources · Mount Lu

Introduction

Organic acids are abundant and ubiquitous in the atmosphere (Paulot et al. 2010; Chebbi and Carlier 1996), and organic acids in the gas phase, in the aqueous phase, and in aerosols have been observed (Alier et al. 2014; Li et al. 2015) (Keene and Galloway 1988; Khare et al. 1999). High polarity and hygroscopicity impel organic acids in the atmosphere to become a cloud condensation nucleus (Sun and Ariya 2006). And significant effect of oxalic acid on cloud condensation nucleus activity of mineral dust aerosols was reported via laboratory experiments (Gierlus et al. 2012). Clouds continuously absorb organic acids from the gaseous phase and aerosols when floating in the atmosphere. During the process of scavenging below clouds, rain drops further adsorb organic acids from the gaseous phase and aerosols and thus considerably affect organic acids in rainwater (Sun et al. 2010). In many nonurban environments, organic acids were identified as important contributors to rain acidity (Akpo et al. 2015; Kawamura et al. 2001; Pena et al. 2002); the contribution rate even reached 80–90 % (Kawamura et al. 1985; Talbot et al.

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✉ Yan Wang
wy@sdu.edu.cn; wangyan405@gmail.com

¹ School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

² Shandong Academy of Environmental Science, Jinan 250013, China

³ Environment Research Institute, Shandong University, Jinan 250100, China

⁴ Department of Civil and Environmental Engineering, the Hong Kong Polytechnic University, Hong Kong, China

1988). Therefore, it was significant to monitor and to research organic acids in wet depositions, including cloud water and rainwater.

Monocarboxylic acid, such as formic and acetic acids (Avery et al. 1991; Nolte et al. 1997; Paulot et al. 2011), and dicarboxylic acid such as oxalic acid (Legrand et al. 2005; Sellegri et al. 2003) constitute the most abundant organic acids in the atmosphere. Formic acids and acetic acids have been detected for several decades in the atmosphere in a variety of international environments, such as rural (Laouali et al. 2012; Xu et al. 2009), urban (Song and Gao 2009; Zhang et al. 2011) and marine areas (Gioda et al. 2011). Some reports have examined organic acids in China in recent years; for example, the concentration levels of organic acids in Beijing (Hu et al. 2005) and Shenzhen (Huang et al. 2010) were investigated. Sources of organic acids in the atmosphere are not completely determined, but it is recognized that sources of organic acids include direct and secondary sources (Carlton et al. 2007; Paulot et al. 2011; Tan et al. 2010). The former comprises direct emissions from biogenic emission, fossil fuel combustion, automobile emission, biomass burning, and meat cooking operation (Cheng et al. 2013; Wu et al. 2015; Ying and Kuo 2013), whereas the latter comprises the photochemistry oxidation of precursors from natural and artificial sources (Carlton et al. 2007; Chebbi and Carlier 1996; Khare et al. 1999; Tan et al. 2010). The formic-to-acetic acid ratio (F/A) was broadly applied in previous research to determine the sources of organic acids as primary emissions or secondary formations (Carlton et al. 2007; Khare et al. 1997a; Tan et al. 2010). Positive matrix factorization (PMF) analysis has been extensively used as a quantitative source apportionment tool of $PM_{2.5}$ and PAHs (Khan et al. 2015; Sofowote et al. 2015), but it is uncommon to use PMF to analyze the sources of organic acids.

Southern China has become the third largest acid rain-prone region worldwide after Europe and North America, and acid rain considerably influences the environment and human health (Galloway and Likens 1976; Menz and Seip 2004; Wang and Wang 1995). Mount Lu, a high-elevation site located in this acid rain-affected area away from local emissions, was selected as the monitoring site of this study. The analysis of organic acids in cloud water and rainwater simultaneously would provide a better understanding of the characteristics and transformation mechanism of organic acids. This study covered content levels, acidity contribution, and discrimination between summer and spring and identified the source of organic acids in cloud water and rainwater at Mount Lu. The concentration of organic acids in total suspended particulate (TSP) was tested to auxiliarily explain the difference in organic acids in rainwater between summer and spring. F/A was implemented to determine whether organic acid was generated from primary discharge or secondary formation, and PMF

analysis was conducted to determine potential emission sources of organic acids.

Materials and methods

Site description

Mount Lu (29° 35' N, 115° 59' E; 1165 m a.s.l.) is situated on the eastern edge of the middle reaches of the Yangtze River, approximately 400 km from the Yangtze River Delta, a larger national industrial hub. The site is approximately 500 km from the East China Sea and 700 km from South China Sea, respectively, and is thus affected by the sea to some extent.

Located in an area of the comprehensive broad-leaved forest and subtropical coniferous forest preserved at the Lushan natural reserve, with a good biodiversity of more than 2000 species of wild plant, the sampling site was situated on the summit of Mount Lu, far away from residents and tourists. An automatic weather system from the meteorological station was used to record air temperature, humidity, wind speed and direction, and precipitation amount. At Mount Lu, cloud or fog events frequently occur because of the advection of frontal systems and the rising topography, which leads to moist air masses moving upward. More than 190 cloudy and foggy days are reported annually. As part of the East Asian monsoon system, this region experiences obvious seasonal variation and plentiful rainfall. Mount Lu is characterized by frondent plants, intense solar radiation, high temperatures, a low frequency of fog and prevailing southeast winds in summer. On the contrary, it is characterized by plants in the bud, low temperature, temporary illumination, faint solar radiation, and prevailing northwest winds in spring. Considering its unique topographic conditions, monsoonal climate, and high elevation, Mount Lu is therefore an excellent location at which to conduct atmospheric chemistry measurements and to study regional pollution transport.

Sampling collection

The entire atmospheric observation was conducted during August 22–September 24, 2011 and March 19–May 19, 2012. A total of 118 cloud water samples were collected during the monitoring period with a Caltech Active Strand Cloud Collector (CASCC) designed by California Institute of Technology, USA. Ambient air that contains cloud droplets/fog droplets is inhaled into the CASCC by a fan, and the droplets are impacted on vertical 508- μ m Teflon strands. The theoretical lower 50 % size cut for this sampler was 3.5 μ m (drop diameter). Once a cloud event occurred, cloud water sample was immediately collected into a pre-cleaned, high-density 500-ml Teflon bottle. Sampling interval for a single cloud event was ranged from 2 to 3 h, but longer or

shorter sampling periods were used on some cases to ensure the volume of each sample not less than 200 ml. In addition, 49 precipitation events were sampled using a pre-cleaned, high-density polyethylene (HDPE) rain sampler with a diameter of 50 cm in a HDPE bucket, in accordance with the technical specifications required for the monitoring of acid depositions (China Meteorological Administration 2003). The rainwater sample collection began at the start of the rain events till the events ended if duration of rainfall was less than 24 h. If it rained for more than 24 h, another rainwater sample collection would begin when the time period of collecting reached 24 h. Moreover, the sampler was capped and sealed after sampling to avoid the effect of dry deposition. One hundred eighteen valid TSP samples were obtained and stored in the dark at $-20\text{ }^{\circ}\text{C}$ before laboratory analysis. TSP samples were collected on glass fiber filters ($203\times 254\text{ mm}$, FP2063-810, HI-Q Environmental Products Company, San Diego, USA) employed in a TSP impactor (HVT-4300AFC) with a high flow rate of $1\text{ m}^3/\text{min}$. For exploring the variation of species in TSP before and after the rain (cloud), one TSP sample was collected at the time of expected rain (cloud) and after rain (cloud). Sampling time period was 40 min to 3 h. Before sample collection, the filters were heated at $500\text{ }^{\circ}\text{C}$ for 3 h, subsequently balanced at $25\text{ }^{\circ}\text{C}$ and a relative humidity of 50 % for 24 h and weighed using a Sartorius CP2P analytical balance with a sensitivity of $1\text{ }\mu\text{g}$ before and after sampling.

Chemical analysis

After collection, the samples of cloud water and rainwater were filtered through $0.45\text{ }\mu\text{m}$ pore-size membrane filters and separated into several aliquots. Then, the pH value was immediately determined on aliquots of samples on site using a pH meter, and the rest of the samples were reserved in a refrigerator under $4\text{ }^{\circ}\text{C}$ prior to further analysis in the laboratory. To avoid the loss of organic acids due to biodegradation, chloroform was added to the organic acid samples as a preservative.

Aqueous aerosol extracts were prepared by shaking a portion of the loaded filters vigorously for 1 h in Nanopure water ($18.0\text{ M}\Omega\text{ cm}$) with an ultrasonic vibrator. Sample solutions then were filtered through $0.2\text{ }\mu\text{m}$ ether acetate filter paper. A half-sample filter was extracted with 25 ml portions of water.

Selected organic acids (formic acid, acetic acid, oxalic acid, methane sulfonic acid, propionic acid, lactic acid, and butyric acid) in cloud water and rainwater samples and in aerosol extracts were simultaneously quantified by an ion chromatography system (ICS-2500, Dionex, USA) within 2 weeks. The ion chromatography system was equipped with a Dionex IonPac AS11-HC analytical column and solution of NaOH as eluent at a rate of 1.2 ml/min . The linear correlation coefficients of the calibration curve were stable in the range of 0.9994–0.9998.

PMF

EPA PMF 3.0 software was used to identify to the major emission sources of organic acids in cloud water at Mount Lu. The data matrix was decomposed into two categories, factor contributions and factor profiles, with a residual matrix by PMF, which was a multivariate factor analysis model (Paatero and Tapper 1994). The PMF model was described briefly and built on the following Eq. (1):

$$X_{ij} = \sum_{k=1}^p A_{ik} F_{kj} + R_{ij} \tag{1}$$

where X_{ij} is the concentration of the j_{th} congener in the i_{th} sample of the original dataset, p is the number of factors, A_{ik} is the contribution of the k_{th} factor to the i_{th} sample, F_{kj} is the fraction of the k_{th} factor arising from congener j and R_{ij} is the residual for each sample species.

The PMF calculation minimizes object function Q with the adjusted values of A_{ik} , F_{kj} and p and the estimate of uncertainty (S_{ij}). Q is defined by Eq. (2):

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{X_{ij} - \sum_{k=1}^p A_{ik} F_{kj}}{S_{ij}} \right)^2 \tag{2}$$

Two input files were required by PMF, one containing concentration values and one containing either uncertainty values or parameters for calculating uncertainty for each sample. The uncertainty values were estimated for two cases: when the concentration of the specie (X) is less or equal to the method detection limit (MDL) (Eq. (3)) and when the concentration of the specie is greater than the MDL (Eq. (4)) (Adam et al. 2007):

$$\text{Unc} = \frac{5}{6} \text{MDL} \tag{3}$$

$$\text{Unc} = \sqrt{(\text{Error fraction} \times \text{concentration})^2 + (\text{MDL})^2} \tag{4}$$

Species that have a signal-to-noise (S/N) ratio ranging from 0.2 to 2 and missing or values below a MDL greater than 50 % were considered weak variables. Different numbers of factors were run in the default robust mode (strong species) as the input of the model to decrease the influence of extreme values on the PMF solution, and the f_{peak} parameter was utilized to control rotational ambiguity (Paatero et al. 2002). In this study, the model was run at numbers of factors from 3 to 8 to get the optimal number of factors, determined by the slope of the Q value vs the number of factors. For each run, the stability and reliability of the output were checked according to the Q value, correlation coefficients between predicted and observed concentrations, and residual analysis. The frequency distributions of the scaled residuals as well as changes in the Q value must be at a minimum or stable. If the analysis is

properly weighted, the Q value should be approximately equal to the theoretical Q value. The theoretical Q value can be estimated by Eq. (5) (Callén et al. 2014):

$$Q_{(\text{Theoretical})} = (\text{samples} \times \text{strong species}) + (\text{samples} \times \text{weak species})/3 - (\text{samples} \times \text{factors estimated}) \quad (5)$$

Results and discussion

Composition and concentration levels of organic acids

The concentration of seven organic acids (formic acid, acetic acid, oxalic acid, methane sulfonic acid (MSA), propionic acid, lactic acid, and butyric acid) were detected in 118 cloud water samples and 49 rainwater samples collected at Mount Lu from August 22 to September 24, 2011 and March 19 to May 19, 2012. Figure 1 summarizes the content levels of these seven organic acids in cloud water and rainwater. The total concentration of the analyzed organic acids in cloud water varied from 7.45 to 111.46 $\mu\text{eq/L}$, with a VWM concentration value of 38.42 $\mu\text{eq/L}$. The VWM concentrations were 10.82 $\mu\text{eq/L}$ for formic acid, 9.29 $\mu\text{eq/L}$ for acetic acid and 9.90 $\mu\text{eq/L}$ for oxalic acid; these three organic acids occupied the top three values in cloud water, whereas propionic acid ranked last, with a VWM value of 1.38 $\mu\text{eq/L}$. The total concentration of the analyzed organic acids in rainwater ranged from 12.39 to 68.97 $\mu\text{eq/L}$, with a VWM concentration value of 33.39 $\mu\text{eq/L}$. Moreover, formic acid, acetic acid, and oxalic acid were the three most abundant carboxylic acids in rainwater; their VWM concentrations were 11.20, 10.21, and

5.07 $\mu\text{eq/L}$, respectively. Propionic acid was the most indigent carboxylic acid in rainwater; its VWM concentration was 1.18 $\mu\text{eq/L}$.

The VWM concentration of organic acid in cloud water was similar to that of rainwater, but the variation range of the former was larger, as shown in Fig. 1. The VWM concentration of oxalic acid in cloud water was twice as much as that in rainwater which was related to the fact that oxalate tended to have higher concentrations in smaller drops and droplet size of cloud drops was far less than that of rain drops (Bator and Collett 1997; Hoag et al. 1999).

The major composition and concentration levels of organic acids in cloud water and rainwater in this station and the reported data sets of representative various environments (including mountain sites, tropical ecosystems, rural areas, urban areas, and marine environments) are listed in Table 1 for comparison. The sum of the concentration of the four typical organic acids (formic acid, acetic acid, oxalic acid, and methane sulfonic acid) in the cloud water of Mount Lu was close to those of the forest ecosystems of Taiwan (Ying and Kuo 2013) but lower than those of Mount Heng (Wang et al. 2011). A higher sum of the concentration of the four typical organic acids at Mount Lu than in Puerto Rico (Gioda et al. 2011), a sampling site related to marine environments, was observed due to Mount Lu's more polluted air masses and more discharge sources from plants. The concentrations of formic acid and acetic acid were both lower than that at Mount Heng but higher than that in Puerto Rico. However, the concentration of formic acid at Mount Lu was higher than that of Taiwan but the concentration of acetic acid at Mount Lu was lower than that of Taiwan. The concentration of oxalic acid at Mount Lu was comparable with the concentration of oxalic acid in Taiwan and Mount Heng but was higher than that in Puerto Rico.

The sum of the concentration of the four typical organic acids in rainwater at Mount Lu was close to that of Mount Mangdang (Cheng et al. 2011) and the forest ecosystem of Taiwan (Ying and Kuo 2013) because of the homologous natural environments of these three sampling sites located in natural protection areas with lush vegetation. An obviously higher sum of the concentration of the four typical organic acids in rainwater was observed at Mount Lu than in Shenzhen (Huang et al. 2010) and New York (Song and Gao 2009). Among these four organic acids, acetic acid and oxalic acid showed similar concentration levels with the sum of these four organic acids. However, the concentration of formic acid was higher than most of the sampling sites listed in Table 1. To a large extent, the discrepancies in the composition and concentration levels at different sites indicated different sources of carboxylic acid associated with different geographical locations of the sampling sites. To sum up, sum of the concentration of the four typical organic acids in wet deposition at Mount Lu was comparable to those of other mountain sites

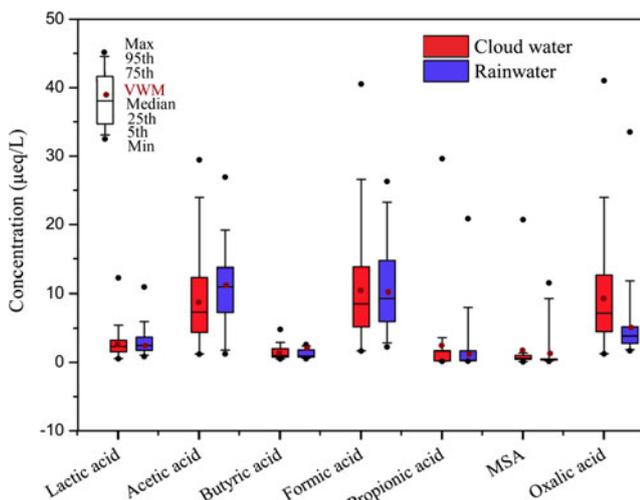


Fig. 1 Concentrations ($\mu\text{eq/L}$) of major organic acids in cloud water and rainwater over the sampling period

Table 1 VWM concentrations ($\mu\text{eq/L}$), fluxes ($\text{g m}^{-2} \text{year}^{-2}$; within the brackets) of major organic acids, corresponding contributions of organic acids to the total acidity and pH in cloud water and rainwater in different representative atmospheric environments

Location	Category	PH	Formic acid	Acetic acid	Oxalic acid	MSA	Sum	OA/TAC (%)	OA/TFA (%)	References
Mountain site										
Mount Lu	Cloud	3.81	10.83	9.29	9.90	2.71	32.73	6.70	2.50	This study
Mount Lu	Rain	4.44	10.21	11.20	5.07	2.41	28.89	27.89	17.66	This study
Mount Heng	Cloud	3.80	19.65	16.04	10.22	3.41	49.32	7.93	3.53	Wang et al. (2011)
Mount Heng	Rain	4.35	14.30	16.46	3.31	2.92	36.99	24.50	16.78	Wang et al. (2011)
Mangdang Mountain	Rain	4.81	7.90	9.90	3.60	0.20	21.60	23.46	18.42	
Urban										
Shenzhen, South China	Rain	4.56	2.26	0.55	1.15	–	3.96	3.64	2.86	Huang et al. (2010)
Anshun	Rain	4.67	8.77	6.93	5.68	–	21.38	15.00	8.1	Zhang et al. (2011)
Newark US East Coast	Rain	4.60	4.44	3.56	1.36	–	9.36	13.09	14	Song and Gao (2009)
Rural										
Shangzhong	Rain		4.95	1.35	2.31	0.10	8.71		58.1	Xu et al. (2009)
São Paulo State, Brazil	Rain	4.96	7.80	5.00	2.40	–	15.20	42.80	39.83	Coelho et al. (2011)
Tropical and subtropical ecosystem										
Agoufou, Africa	Rain	6.28	4.50 (6.7)	3.90 (7.4)	2.20 (1.5)	–	10.60	17.80	17.57	Laouali et al. (2012)
Balbina, Amazonia	Rain	4.90	0.45	5.20	0.25	–	5.90	29.70	19.87	Pauliquevis et al. (2012)
Taiwan	Cloud	–	5.74	15.80	13.20	–	34.74	–	–	Ying and Kuo (2013)
Taiwan	Rain	–	2.79	6.94	5.64	–	15.38	–	–	Ying and Kuo (2013)
Marine environment										
Puerto Rico	Cloud	5.50	1.00	5.40	1.00	2.10	9.50	1.71	1.18	Gioda et al. (2011)
Puerto Rico	Rain	5.30	0.20	5.80	0.00	0.38	6.38	4.28	3.2	Gioda et al. (2011)

OA/TAC proportion of organic acids accounted of total anionic content, *Sum* sum of concentration of four typical organic acids (formic acid, acetic acid, oxalic acid, and methane sulfonic acid), *OA/TFA* contribution of organic acids to total free acidity

and forest ecological systems but higher than those of urban and marine sites.

Contribution to acidity and wet deposition flux

Mount Lu is located in the south of the Yangtze River in China, where the acid rain phenomenon is serious. In this study, the pH values varied from 2.94 to 5.47 for all cloud samples, with a VWM pH value of 3.81, and rainwater samples showed a similar pH range, with a VWM pH value of 4.44. In addition to inorganic acids such as nitric acid and sulfuric acid, it was agreed that the effect of organic acids on the acidity of wet deposition in forest ecological system with lush vegetation (Avery et al. 2001; Fornaro and Gutz 2003) was non-negligible. As shown in Table 1, the total contribution of organic acids to the acidity in rainwater at Mount Lu was much higher than the total contribution to cloud water (17.66 vs 2.50 %), which was attributed to the limited solubility of weak organic acids associated with the higher amount of dissociated hydrogen ions (lower pH) and with the more abundant inorganic acidic species in cloud water (Wang et al. 2011).

Because the contribution of organic acids to acidity in cloud water is low, this study will not discuss it in detail. Nonetheless, the contribution of organic acid to acidity was significant in rainwater. The average contributions to acidity of formic, acetic, and oxalic acids were 8.08, 3.48, and 3.96 % in rainwater, respectively. The contribution of acetic acid to acidity was low, which was not consistent with its high concentration levels. This contribution is evidenced by the fact that the dissociation constant of acetate was small, and thus, it is difficult to knock off hydrogen ions. As indicated in Table 1, the contribution of organic acid to acidity in rainwater at Mount Lu was comparable to the contributions of Mount Heng, Mount Mangdang, and a forest ecological system in Taiwan (Ying and Kuo 2013). However, compared to the contribution of organic acid to acidity in urban sites of China, like Shenzhen (approximately 2 %) (Huang et al. 2010), their contribution at Mount Lu was higher. The high concentrations of organic acids and the contribution levels of organic acids to acidity at Mount Lu suggested that organic acid was an indispensable component of wet deposition.

In consideration of the high value of the contribution of organic acids to acidity in rainwater at Mount Lu, the rain

deposition flux of organic acids might greatly affect the local ecological system. In this work, it was estimated that the annual rain deposition flux was $3.51 \text{ g m}^{-2} \text{ year}^{-1}$ for total organic acids in 2011 and $3.66 \text{ g m}^{-2} \text{ year}^{-1}$ for total organic acids in 2012. Previous studies were limited on the wet deposition fluxes of low-molecular-weight organic acids. The annual rain deposition fluxes of total organic acids in Mount Lu were slightly lower than those calculated in the SET Station of the Tibetan Plateau (Liu et al. 2014) but obviously lower than those calculated in the tropical ecosystem of Agoufou, Africa (Laouali et al. 2012). The annual wet deposition fluxes of total organic acids in this study were found not to be at a high level.

Discrimination of organic acids between summer and spring

Cloud water and rainwater samples were collected in the summer of 2011 and the spring of 2012. Organic acid concentration levels and contribution to acidity in summer and spring were contrasted to estimate the discrimination of organic acids between the two seasons.

A comparison of the VWM concentration of organic acids in cloud water between summer and spring is shown in Fig. 2. The VWM of total organic acid in summer samples of cloud water was $48.81 \mu\text{eq/L}$, obviously higher than that of spring ($34.38 \mu\text{eq/L}$). Formic acid, acetic acid and oxalic acid predominated in summer samples of cloud water, with

concentrations of 14.84, 13.40, and $13.99 \mu\text{eq/L}$, respectively, higher than those of spring samples (8.14, 8.07, and $9.04 \mu\text{eq/L}$, respectively). The results were due to an increase in biogenic emissions from vegetation (Wang et al. 2011) and photochemical activity because of intense solar radiation and abundant atmospheric oxidants (Kuhn et al. 2002) in summer. Different meteorological conditions such as the low frequency of fog in summer were expected to have non-negligible effects on such variations of organic acids, too.

A contrast of the VWM concentrations of organic acids in rainwater for summer and spring is presented in Fig. 2. The VWM of total organic acid in summer samples of rainwater was $34.77 \mu\text{eq/L}$, close to the value of that in spring samples ($33.04 \mu\text{eq/L}$). However, concentrations of formic acid, acetic acid, and oxalic acid revealed a different seasonal discrimination regularity. The concentration of formic acid in summer was $12.63 \mu\text{eq/L}$, higher than that in spring ($9.61 \mu\text{eq/L}$), whereas the concentrations of acetic acid ($10.43 \mu\text{eq/L}$) and oxalic acid ($4.47 \mu\text{eq/L}$) were lower in summer than in spring (11.40 and $5.22 \mu\text{eq/L}$ for acetic acid and oxalic acid, respectively).

In addition to the prosomatic cloud of rainwater, the scavenging of rainfall in aerosols was another important source of organic acid in rainwater (Sun et al. 2010). For the sake of exploring the contribution of organic acid in aerosols to the concentration of organic acids in rainwater, the concentration of organic acids in TSP of summer and spring was investigated, as shown in Fig. 2. The average concentration of organic acids in TSP samples of spring was 1698.69 ng/m^3 , higher than the value of 929.68 ng/m^3 in summer. The first two abundant organic acids were acetic acid and oxalic acid in the two seasons. In spring, the most abundant organic acid was acetic acid, with a concentration of 1222.55 ng/m^3 , followed by oxalic acid, with a concentration of 232.88 ng/m^3 . However, concentrations of these two acids in summer were obviously lower (550.60 and 163.97 ng/m^3 for acetic acid and oxalic acid, respectively). Formic acid occupied a significant percentage both in rainwater and cloud water, whereas the percentage of formic acid in TSP was not high. However, the concentration of formic acid in TSP in spring was 93.15 ng/m^3 , higher than that in summer (54.49 ng/m^3).

In addition to prosomatic cloud water, aerosols were another main source of acetic acid and oxalic acid in rainwater. Higher concentrations of acetic acid and oxalic acid in TSP increased the concentrations of acetic acid and oxalic acid in rainwater in spring. Therefore, rainwater and cloud water presented different seasonal discrimination regularity.

The contribution of organic acids to acidity in both cloud water and rainwater in summer and spring was shown in Fig. 3. The contribution ratios during the summer season were lower than those during the spring period in both rainwater (12.24 % in summer vs 19.89 % in spring) and cloud water (2.20 % in summer vs 2.83 % in spring), attributed to more

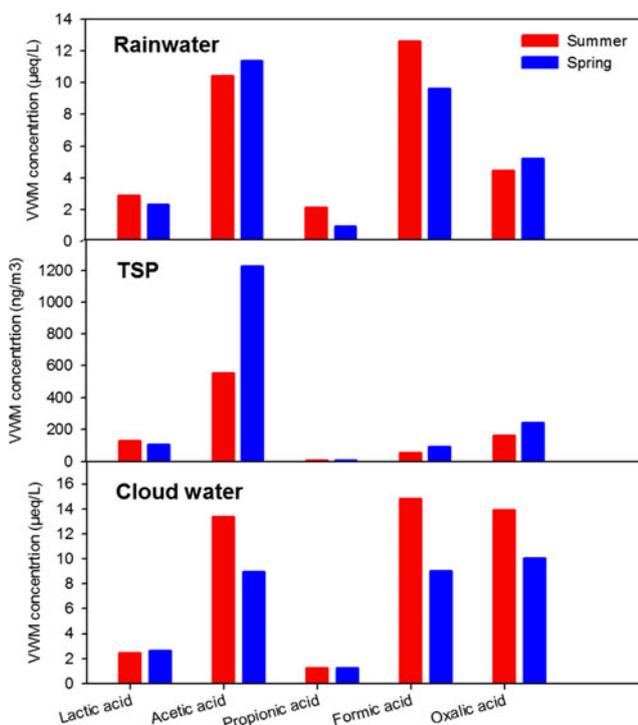


Fig. 2 Comparison of the VWM concentration of organic acids between summer and spring in cloud water, TSP, and rainwater

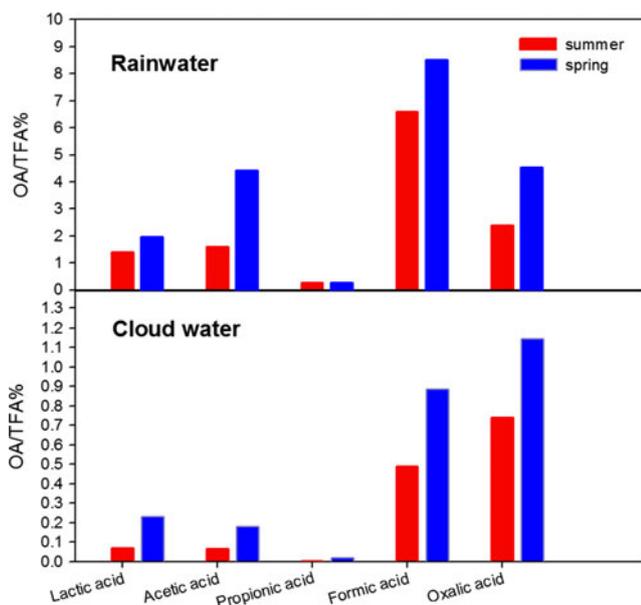


Fig. 3 Contributions of major organic acids to total free acidity in cloud water and rainwater for summer and spring

acidic cloud water and rainwater in the summer period to some extent and preventing the dissociation of weak organic acids (Wang et al. 2011). The contributions of organic acids to the total anionic content of cloud water and rainwater in summer were 6.2 and 28.09 %, respectively, lower than the values in spring (7.4 and 42.95 %, respectively) (Sun et al. 2015).

Determining primary or secondary sources by formic-to-acetic acid ratio

For further analysis of the sources of organic acid in cloud water and rainwater at Mount Lu, *F/A* is applied in this section. Sources of organic acids in the atmosphere were divided into primary sources, such as vegetation, biomass burning, ocean, soil, and automotive vehicle discharge directly, and secondary sources, such as the photochemistry oxidation of unsaturated carbon hydrocarbons (Carlton et al. 2007; Chebbi and Carrier 1996; Khare et al. 1999; Tan et al. 2010). Considering that formic acid and acetic acid were emitted from similar sources or source strengths, the ratio of *F/A* could be applied to analyze the sources of organic acids in the atmosphere (Khare et al. 1997b; Kieber et al. 2002). In this study, correlation coefficients between formic acid and acetic acid were calculated to be 0.74 and 0.79 in cloud water and rainwater, respectively, close to the values of New Zealand rainwater (0.7) (Kieber et al. 2002) and North Central India rainwater (0.78) (Khare et al. 1997b), respectively. Consequently, formic acid and acetic acid presented similar sources or source strengths in cloud water and rainwater in our study. In the gas phase, primary sources were in a dominant position when *F/A* < 1, whereas if *F/A* > 1, secondary formation gained

ascendancy (Andreae et al. 1990; Kumar et al. 1996). The differences between the liquid phase and the gas phase were that *F/A* in the liquid phase was associated with Henry’s constant, the dissociation constant, and pH. The computational method is mentioned in Johnson and Dawson (1993) and Winiwarter et al. (2010).

Supposing that organic acid was in a balanced state of the gaseous phase and the liquid phase, the following equation was used to identify whether the [*F/A*] of samples was above 1 or lower than 1, established according to Henry’s law and dissociation equilibria:

$$[F/A]_M = \frac{K_{H1}([H^+] + K_a)}{K_{H2}([H^+] + K_b)} [F/A] \tag{6}$$

where [*F/A*]_M = Measured [*F*] / Measured [*A*], *K*_{H1} = 5.6 × 10³ mol L⁻¹ atm⁻¹, *K*_{H2} = 8.8 × 10³ mol L⁻¹ atm⁻¹, *K*_a = 1.77 × 10⁻⁴ mol L⁻¹ and *K*_b = 1.76 × 10⁻⁵ mol L⁻¹ (*T* = 298.15 K) for formic and acetic acids, respectively (Sakugawa et al. 1993; Seinfeld and Pandis 1998).

In Fig. 4, black line was the value of [*F/A*]_M in Eq. (6) when [*F/A*] = 1, and scatters were the values of [*F/A*]_M in cloud water samples. It meant *F/A* < 1 when data points of [*F/A*]_M were below the curve and indicated that organic acids primarily derived from primary sources. Organic acids could be considered to be primarily emitted from secondary formations when data points of [*F/A*]_M were above the curve which meant *F/A* > 1. As illustrated in Fig. 4, the values of *F/A* were lower than 1 in 71.31 % of the cloud water samples, with summer and spring samples covering 25.22 and 46.09 % of total, respectively. The values of *F/A* were higher than 1 in 28.69 % of the cloud water samples, with 19.13 % of the samples collected in summer and 9.56 % of the samples collected in the spring. Therefore, the sources of organic acids in most cloud water samples were primary sources, and the sources of organic acid in the rest of the samples were secondary

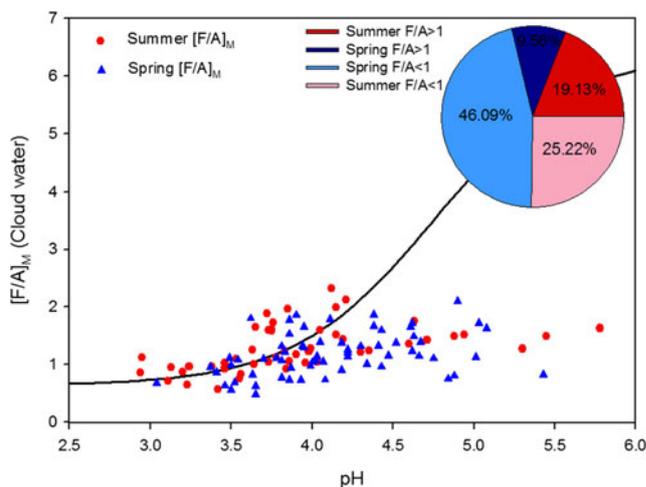


Fig. 4 The [*F/A*]_M judgment equation curve and [*F/A*]_M of cloud water samples for summer and spring seasons

formations. High solar radiation, high temperature, and high concentrations of oxide impelled the photochemistry oxidation of unsaturated carbon hydrocarbons in summer. As a result, there were more samples in summer than in spring whose major emission sources were secondary photochemical transformations.

In rainwater, prosomatic cloud water and the scavenging of rainfall in aerosols were the significant sources of organic acids. Moreover, the longer atmospheric residence time in cloud water than rainwater, propitious to the secondary formations of organic acids, caused the values of F/A in rainwater and cloud water to present diverse features.

In Fig. 5, the black line was the value of $[F/A]_M$ in Eq. (6) when $[F/A]=1$, and scatters were the values of $[F/A]_M$ in rain samples. The $[F/A]_M$ point of each rainwater sample is located under the curve ($F/A < 1$), illustrating that organic acids in all rainwater samples originated from primary sources. Moreover, the $[F/A]_M$ points of the summer samples were closer to the curve than those of the spring samples, suggesting a stronger secondary generation of organic acids in rainwater samples in summer.

Emission sources identified by PMF

PMF is adopted to quantitatively analyze the emission sources of organic acids in this section. Only cloud water samples were analyzed in this study due to the limited number of samples of rainwater. To obviously apportion the possible emission sources of organic acids in cloud water via the statistical software package EPA PMF 3.0, other non-sea salt (nss) inorganic ions detected previously in the same samples were cited in the study of Sun et al. (2015). Generally speaking, Na^+ and Cl^- were considered tracers of marine emissions. Nss components were computed by methods based on the concentrations of Na^+ , Cl^- and other inorganic ions (Zhang

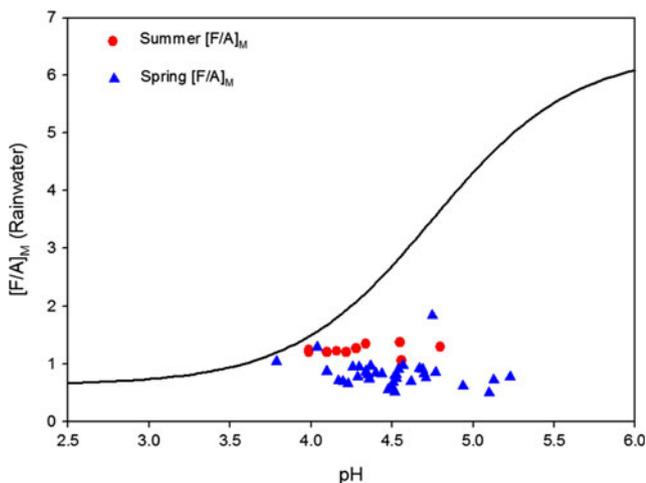


Fig. 5 The $[F/A]_M$ judgment equation curve and $[F/A]_M$ of rainwater samples for summer and spring seasons

et al. 2012). In this study, the concentrations and corresponding uncertainty values of 106 cloud water samples with ten species were considered as the input, and PMF was run multiple times while varying the number of factors. Finally, optimal computational results were obtained. With a resultant f_{peak} of 0.1 and Q_{robust} (975.9) and Q_{true} (971.6) values close to Q_{theory} ($106 \times 10 = 1060$), four factors were physically reasonable and could be explained by the potential sources at this site. Correlations between the measured and predicted concentrations of species by the model were used to authenticate the model, and the correlation coefficients of 10 species were all greater than 0.68 ($R^2 > 0.68$), indicating that the four sources analyzed by the PMF mode could accurately estimate changes in mass concentrations of 10 species in cloud water. The four sources obtained by PMF analysis in this study were biogenic emissions, anthropogenic emissions, marine emissions, and soil emissions. The source profiles of the factors and explained species variations are shown in Fig. 6.

Biogenic emissions were characterized by a very low loading of nss ions and a high loading of three major organic acids (acetic acid, formic acid, and oxalic acid). Biogenic emissions explained 65.3 % of acetic acid, 73.0 % of formic acid and 52.8 % of oxalic acid; hence, biogenic emissions were the major source of organic acids at Mount Lu. Biogenic organic

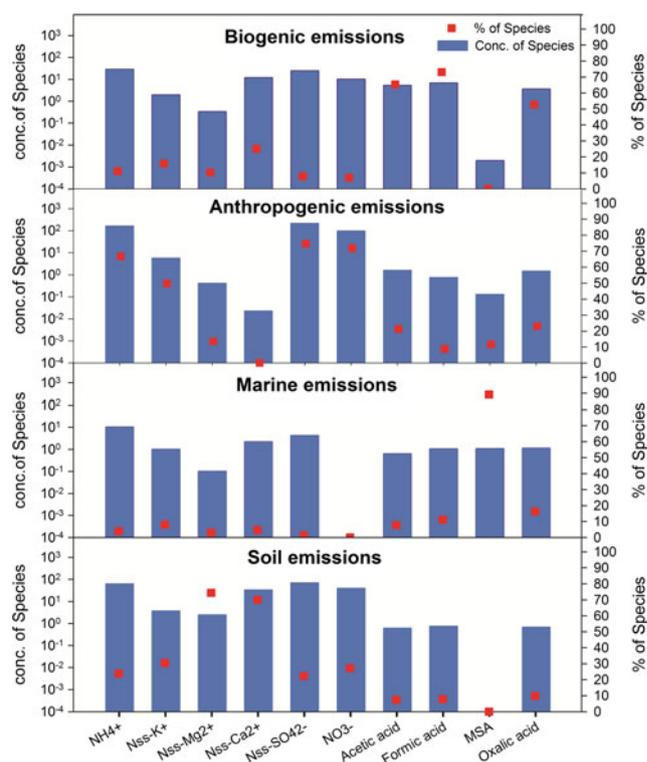


Fig. 6 Factor profile for the site. Concentrations and percentages of species in the four factors identified via PMF are illustrated. Four factors at the site were identified: biogenic emission, anthropogenic emissions, marine emissions, and soil emissions

gas, such as isoprene, delivered from vegetation was identified as an important potential source of organic acids in the subtropical forests of Taiwan (Ying and Kuo 2013) and on mountains of China (Heinrich 2007).

Because of the high loading of sulfate, nitrate, and ammonium, anthropogenic emissions were confirmed to be sources of organic acids at Mount Lu, explaining 19.6 % of acetic acid, 8.0 % of formic acid, 21.1 % of oxalic acid and 11.8 % of MSA. Khare et al. discussed organic acids emitted from automobiles at peak traffic hours at a suburban site in India (Khare et al. 1997a). Anthropogenic sources can also be attributed to air masses polluted due to the combustion of fossil fuel, wood, and agricultural waste, among others (Kawamura et al. 2000).

Marine emissions were determined because of the high loading of MSA. It is widely known that dimethylsulfide (DMS), the precursor of MSA, primarily originated from phytoplankton in the sea (Bates et al. 1992). Thus, MSA was considered a typical marker of marine emissions. Marine emissions explained 89.2 % of MSA, 7.7 % of acetic acid, 11.2 % of formic acid and 16.3 % of oxalic acid. Fu et al. noted that organic acids such as oxalic may come from marine phytoplankton by oxidizing biogenic precursors such as unsaturated fatty acids in the sea (Fu et al. 2013).

Due to the high loading of elements Ca^+ and Mg^+ , soil emissions were determined. Soil emissions contributed less to organic acids and explained 7.4 % of acetic acid, 7.9 % of formic acid and 9.8 % of oxalic acid. Moreover, biogenic metabolites and microbes that could produce organic acids enabled soil particles to be a potential source of organic acid in the atmosphere (Sanhueza and Andreae 1991).

Consequently, 61.8, 15.28, 15.07, and 7.85 % of the organic acid in cloud water at Mount Lu came from biogenic emissions, anthropogenic emissions, marine emissions, and soil emissions, respectively.

Conclusions

The chemical characteristics and sources of organic acids in cloud water and rainwater were investigated at a mountain site in an acid precipitation region, southern China. The VWM concentrations of total organic acids were 38.42 $\mu\text{eq/L}$ in cloud water and 33.39 $\mu\text{eq/L}$ in rainwater, and formic acid, acetic acid, and oxalic acid were found to be the predominant components. The concentrations of organic acids in cloud water and rainwater at Mount Lu were comparable to those at forest ecosystem and mountain sites but higher than those at urban and marine sites. The contribution of organic acids to the acidity of rainwater was significant, up to 17.66 %. However, it was estimated that the annual wet deposition fluxes of total organic acids were not high in 2011 and 2012. Organic acids in cloud water in summer exhibited obviously

higher concentrations than in spring, whereas organic acids in rainwater presented few differences in spring and summer. The discrepant seasonal discrimination of organic acid concentrations between summer and spring resulted from different sources of organic acid in cloud water and rainwater. Organic acids in cloud water primarily originated from plant emissions and photochemical oxidation. In addition to the prosomatic cloud of rainwater, the scavenging of rainfall on TSP contributed considerably to organic acid in rainwater. The low F/A values indicated that the main sources of organic acid in cloud water and rainwater were primary emissions, whereas more secondary formations of organic acid were found in cloud water than in rainwater. The discriminations of F/A in cloud water samples confirmed that secondary formations played a more important role in sources of organic acids in summer than in spring. PMF confirmed that biogenic emissions were the most significant sources of organic acids, whereas anthropogenic emissions and marine emissions contributed less but accounted for a certain proportion. We expect that the contribution of organic acids to wet deposition was nonignorable, but organic acids do not present significant ecological risks in acid precipitation regions in China.

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