Characteristics of formate and acetate concentrations in precipitation at Jeju Island, Korea

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ABSTRACT

$HCOO^-$ and CH_3COO^- concentrations were analyzed in precipitation samples collected at two sites on Jeju Island during 1997–2003: one at Mt. Halla and the other within Jeju City. The volume-weighted mean concentrations of $HCOO^-$ and CH_3COO^- were 1.28 and 0.89 µmol/L at Mt. Halla, and 2.06 and 1.15 µmol/L in Jeju City, respectively. Those ionic components showed low concentrations in summer compared to other seasons. In order to investigate major factors to affect the concentration variations of the organic acids in precipitation, the concentrations of the organic acids between growing and non-growing seasons of plants, the regression analyses and the ratios of $HCOO-/CH3COO^-$ were examined. As a result, it is considered that the concentrations of $HCOO^-$ and CH_3COO^- in precipitation might be influenced mainly by photochemical conversion of precursors emitted from terrestrial vegetation during active plant growing seasons, but by direct emission from the anthropogenic sources such as vehicles during non-growing seasons. The high concentrations of $HCOO^-$ and CH_3COO^- were mostly associated with northwesterly winds from the continental area, on the other hand, the low concentrations with the winds coming from the North Pacific. The contributions to precipitation acidity by HCOOH and CH_3COOH tended to increase during the plant growing seasons, remaining at a low 10% throughout most of the events, while increasing to 30–40% during occasional precipitation events.

1. Introduction

Generally the rain acidity tends to be influenced by sulfur oxides (SO_x) and nitrogen oxides (NO_x) emitted from industrial activities and vehicles. These oxides are then converted to acidic compounds via photochemical reactions with hydroxyl radical (HO·), hydrogen peroxide, and peroxy radicals (HOO, ROO) in the atmosphere. In addition, several organic acids and methanesulfonic acid (MSA) also partially contribute to the precipitation acidity. Although their extents are generally less than those by inorganic acids such as H_2SO_4 and HNO_3, their relative contributions tend to be increased in remote areas such as tropical forests (Galloway et al., 1982).

Formic acid (HCOOH) and acetic acid (CH_3COOH) were present in the atmosphere over 90% in mass in the gaseous form and less than 10% in the particulate phase and, particularly, about 80% of carboxylic acids in the particulate phase are in fine particles with diameters of less than 1.0 µm in a semiurban site in northeastern USA (Khwaja, 1995). In the eastern USA and Amazon Bay, only 10–20% of pyruvic acid ($CH_3COCOOH$) and 1–2% of formic acid occurred in the particle phases (Andreae et al., 1987). It was also reported that formic acid and acetic acid occurred principally in the gas phase ($\geq$98%) at a site in eastern Virginia (Talbot and Beecher, 1988). In Southern California, 94% of the formic acid and 88% of the acetic acid in the atmosphere were present as gaseous species (Grosjean, 1989).

Organic acids in the atmosphere originate mainly from biogenic and anthropogenic sources. The direct emissions from vegetation growing processes are among typical biogenic
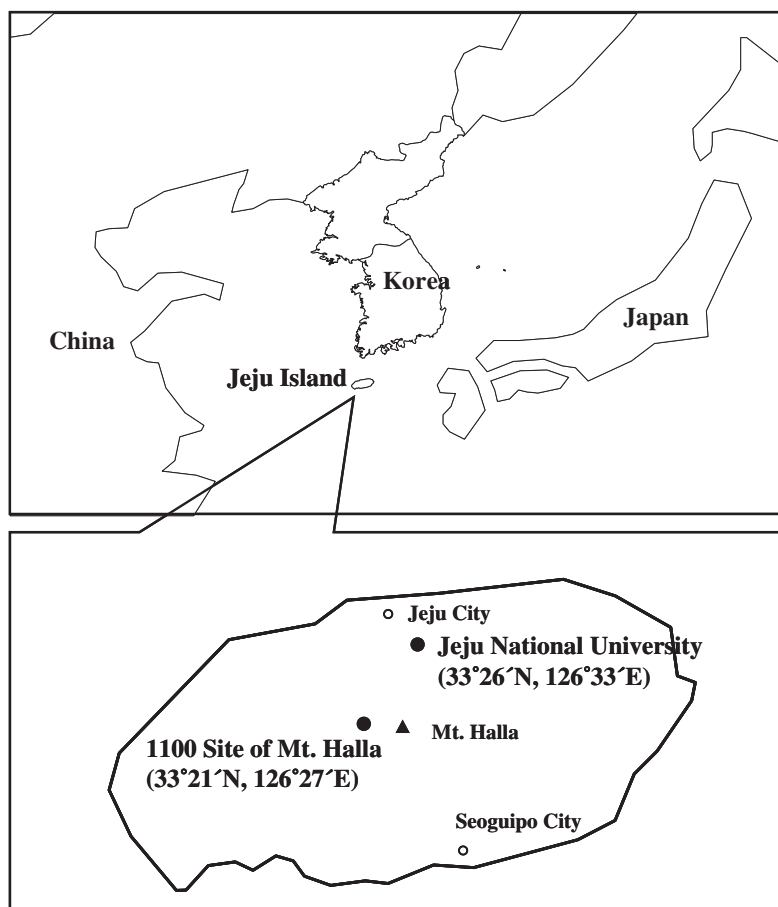
Fig. 1. Location of two sampling sites.

sources, whereas anthropogenic sources include vehicle emissions as well as the combustion of wood and agricultural debris (Chebbi and Carlier, 1996; Khare et al., 1997). In addition, organic acids can be formed indirectly via photo-oxidation reactions of precursors such as isoprene (C_5H_8), ethene (C_2H_4), and propene (C_3H_6), commonly emitted from woods, biological activities within the ocean, and combustion of fossil fuels (Likens et al., 1987; Keene and Galloway, 1988; Galloway and Keene, 1989).

The $CH_3COOH(g)$ and $HCOOH(g)$ concentrations and their ratios in the atmosphere vary according to the emission sources as well as their production paths. Commonly the

concentrations of organic acids emitted directly from vegetation and formed secondarily in the atmosphere increase during the spring and summer plant growing seasons, as do those from marine sources (Keene and Galloway, 1988; Galloway and Keene, 1989; Pena et al., 2002; Avery et al., 2001, 2006). The concentration ratios of $CH_3COOH(g)/HCOOH(g)$ were about 2–10 from biomass burning (Talbot and Beecher, 1988). The ratio lies in the range of 1.8–2.4 for the vehicle emissions that are typical of most anthropogenic sources, and more or less in the range 2.1–2.5 when organic acids are emitted directly from plants. However, when isoprene is actively emitted and/or photo-oxidation occurs, the concentration ratio can decrease down below unity (Sanhueza et al., 1992; Chebbi and Carlier, 1996; Legrand and Angelis, 1996; Granby et al., 1997; Kesselmeier et al., 1998).

Prior to this study, little research had been undertaken examining organic acids in precipitation in Korea and their acidification contribution. In this study, trace amounts of $HCOO^-$ and CH_3COO^- as well as major ionic components have been analyzed in precipitation at Jeju Island, which is a clean air area in Korea, between 1997 and 2003. This investigation reveals not only the concentration characteristics of the $HCOO^-$ and CH_3COO^- but also their emission sources and contribution to precipitation acidity in Jeju area.

Table 1

Instrumental detection limit (IDL) and coefficient of variation (CV) for ion chromatography analysis.

Species	F^-	$HCOO^-$	CH_3COO^-	$CH_3SO_3^-$	NH_4^+	Na^+
IDL(μg/L)	1.4	0.7	0.9	1.7	11.9	6.2
CV(%)	0.9	0.4	0.6	1.1	6.1	3.1

Species	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-
IDL(μg/L)	14.1	5.3	10.3	8.1	9.8	4.4
CV(%)	5.1	6.5	3.6	2.2	2.7	2.0

Table 2
Yearly volume-weighted mean concentrations (μmol/L) of HCOO⁻ and CH₃COO⁻ in precipitation.

Site	Species	1997	1998	1999	2000	2001	2002	2003	Mean
Mt. Halla	HCOO⁻	0.38	1.83	1.59	–	2.00	1.34	0.80	1.28
	CH₃COO⁻	0.15	1.30	1.15	–	1.42	0.91	0.53	0.89
Jeju City	HCOO⁻	1.05	2.73	1.91	1.35	3.14	0.69	3.17	2.06
	CH₃COO⁻	0.88	1.82	1.00	1.30	1.77	0.40	1.18	1.15

2. Experimental

2.1. Precipitation sampling

Jeju Island is located at about 100 km south of the Korean Peninsula, about 500 km west of China (Jiangsu province), and about 200 km east of the Japanese Islands (Kyushu), as shown in Fig. 1. Jeju Island is one of the clean areas in Korea, with low emissions of air pollutants. Thus it is an excellent location to study the transport and transformation of ambient trace species in northeast Asia and to study the impact of continental outflow (Park et al., 2004).

A total of 232 precipitation samples were collected at a frequency of one per 5–7 days at 1100 m site of Mt. Halla (33°21′N, 126°27′E), and 369 samples during rainy days were collected at the Jeju National University (33°26′N, 126°33′E) in Jeju City, during 1997–2003. Mt. Halla site is located at the western part of Mt. Halla (1950 m above sea level), with 1100 m altitude surrounded by forest, and about 15 km south from the downtown of Jeju City. It has been known that this site is less influenced by the local emissions of Jeju Island. Jeju National University is located on the outskirt (about 7 km south from the downtown) of Jeju City, which is an urban city with about 270,000 inhabitants and lies in the northern coastal part of Jeju Island.

Automatic rain samplers (Shinil, SL-4-001, Korea) with a rainwater sensor and sampling inlet with inner diameter of 253 mm were used. Each sampler was set at the roof of a trailer installed at Mt. Halla site and at the roof of a building in Jeju National University campus. The sampling inlets were placed 1 m above the roof of each site. The sampling inlet and HDPE bottles were cleaned frequently with distilled water. The samples at Mt. Halla site were stored for one or two days before transport to the lab, but it occasionally took a few more days due to the difficult accessibility in winter season due to heavy snowfall. However, the samples at Jeju City site were carried immediately to the lab just after the rain stopped. And then the pH and electric conductivity were measured immediately in the laboratory. The remaining samples were divided into two fraction parts. One aliquot was stored in a deep freezer at − 20 °C without pre-treatment to be analyzed for eight major ions, and the other aliquot was stored at the same temperature, after adding a drop of chloroform for the analysis of organic acids. The precipitation analysis was then performed within a month (Galloway and Likens, 1976, 1978; Kang et al., 1999, 2003). We had corrected the lab blanks through the IC analysis of ultrapure water after storing it with the precipitation samples.

2.2. Precipitation analysis

The concentrations of HCOO⁻ and CH₃COO⁻ in each precipitation sample were analyzed by ion chromatography (Dionex, DX-500) with gradient elution system, using an IonPac AG11 and IonPac AS11 column with a SRS 100 mA suppressor and a conductivity detector with a 1 μS range. The flow rate of eluent was 2.5 mL/min, and the loop volume was 25 ~ 50 μL. For gradient elution analysis, the mobile phase was
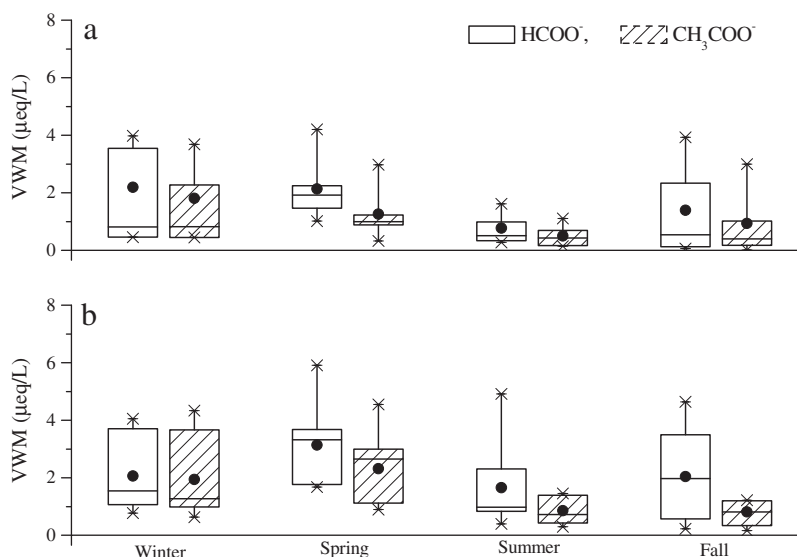

Fig. 2. Seasonal variations of volume-weighted mean concentrations (μeq/L) of HCOO⁻ and CH₃COO⁻. a: Mt. Halla, b: Jeju City.

Table 3
Volume-weighted mean concentrations of $HCOO^-$ and CH_3COO^- in rainwater around the world.

Location	Concentration (μmol/L)		Reference
	$HCOO^-$	CH_3COO^-	
Marine site			
Bermuda (Atlantic ocean)	2.0	0.8	Galloway and Keene (1989)
Amsterdam island (Indian ocean)	3.2	0.5	Galloway et al. (1982)
Remote site			
Amazonia (Brazil)[a]	5.1	3.0	Andreae et al. (1990)
Amazonia (Brazil)[b]	17.9	11.4	Andreae et al. (1988)
IVIC (Venezuela)	8.8	7.9	Sanhueza et al. (1992)
Rural site			
Basque (Spain)	6.1	4.2	Durana et al. (1992)
Gopalpura (India)	5.4	4.8	Khare et al. (1997)
Mae Moh valley (Thailand)	0.1	0.7	Thepanondh et al. (2005)
Suburban site			
Wilmington (USA)	9.9	7.3	Avery et al. (2001)
Galicia (Spain)	7.0	8.3	Pena et al. (2002)
Urban site			
Los Angeles (USA)	12.4	4.1	Sakugawa et al. (1993)
Mt. Halla	1.3	0.9	This study
Jeju City	2.1	1.2	This study

[a] Dry season.
[b] Wet season.

eluted with 0.25 mM NaOH for the initial 5 min, 5 mM for 4 min, and finally, 0.25 mM for 7 min. The standard concentrations for recording the calibration curves were 10, 50, 100, 200 μg/L, prepared from sodium salts of formic and acetic acids (Andreae et al., 1987). Meanwhile, the other inorganic ions of precipitation were analyzed mostly by Metrohm ion chromatography (Metrohm, Modula IC) and partially by Dionex ion chromatography (Dionex, DX-500). For analysis of NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}, a Metrohm Metrosep Cation 1-2-6 column was employed with a flow rate of 1.0 mL/min, injection volume of 20 μL, and eluent of 4.0 mM tartaric acid/1.0 mM pyridine-2,6-dicarboxylic acid. The analyses of SO_4^{2-}, NO_3^- and Cl^- were undertaken using a Metrohm Metrosep A-SUPP-4 IC with a flow rate of 1.0 mL/min, injection volume of 100 μL, eluent of 1.8 mM $NaHCO_3$/1.7 mM Na_2CO_3, and suppressor solution of 0.1% H_2SO_4 (Kang et al., 2003; 2006).

The instrumental detection limits (IDL) and coefficients of variation (CV) for the analyses of major inorganic ions and trace organic ions in this study are presented in Table 1. To get 98% confidence level, IDL was obtained by measuring 10 μg/L standard solutions 7 times repeatedly and multiplying 3.14 to their standard deviations. And CV was less than 1% for $HCOO^-$ and CH_3COO^-, and less than 6.5% for the inorganic ions as shown in Table 1.

The Kendall–Theil regression method, which is resistant to the effects of outliers and nonnormality in residuals, has been used in order to investigate linearity between $HCOO^-$ and CH_3COO^- in precipitation (Granato, 2006; Helsel and Hirsch, 2002).

2.3. Air mass backward trajectory

The backward trajectories of air masses moved into Jeju Island during the sampling period were ascertained using the HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model from National Oceanic and Atmospheric Administration (NOAA). This model is a complete system for computing both simple air parcel trajectories and complex dispersion and deposition simulations. The model calculation method is a hybrid between the Lagrangian approach, which uses a moving frame of reference as the air parcels move from their initial location, and the Eulerian approach, which uses a fixed three-dimensional grid as a frame of reference. In the model, advection and diffusion calculations are made in a Lagrangian framework following the transport of the air parcel, while pollutant concentrations are calculated on a fixed grid (NOAA, 2009).

The information about wind direction and speed for the northern hemisphere was provided by FNL (FiNaL run at NCEP). Accordingly, the grid size was 190.5×190.5 km, and it was composed of 14 vertical layers from the surface to 850 hPa. The starting height of the trajectories was 1500 m and the total run time was 120 h.

3. Results and discussion

3.1. Data quality

The imbalance (%) between the sums of cationic and anionic equivalent concentrations ($\sum c_{Cation}$ and $\sum c_{Anion}$) has been investigated according to the equation of ($\sum c_{Cation} - \sum c_{Anion}$)/$\sum c_{Cation}$ in order to examine the variance of the analyzed data. The results showed that 11 (4.7%) out of the total 232 samples at Mt. Halla and 9 (2.4%) out of the total 369 samples at Jeju City had over 50% imbalances. The imbalance tended to decrease at high ionic concentrations and increase at low concentrations as previously reported (Miles and Yost, 1982; Shim et al., 1994). Since the data should be excluded in case of breakdown of equipment and inclusion of impurities as well as over 50% imbalance for a quality assurance/quality control (QA/QC), 25
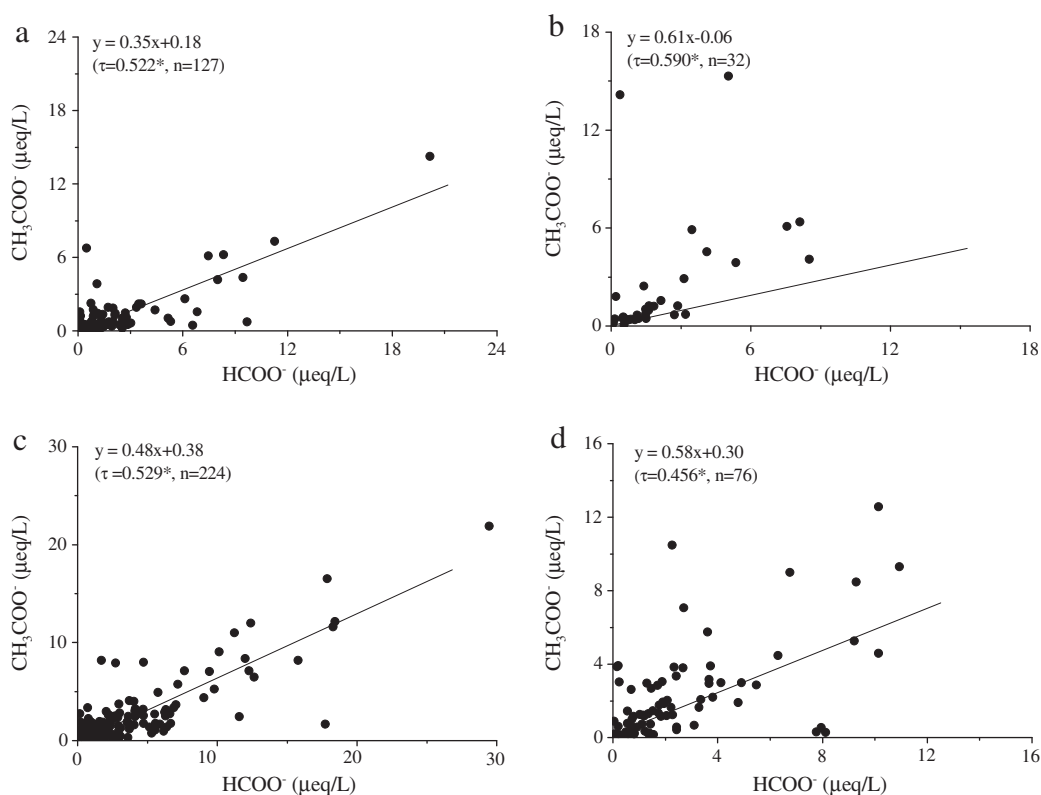
Fig. 3. Kendall–Theil robust line between $HCOO^-$ and CH_3COO^- during growing season (March~September) and non-growing season (October~February). *Correlation (τ) is significant at the 0.01 level (2-tailed), a: Mt. Halla/growing season, b: Mt. Halla/non-growing season, c: Jeju City/growing season, d: Jeju City/non-growing season.

(10.8%) and 29(7.9%) out of the total samples at Mt. Halla and Jeju City were excluded.

In addition, we have checked out the quality of analytical data through the comparison of ion balances, electrical conductivities and acid fractions using the linear regression analysis method. Based on the ion balances, the correlation coefficients (r) between the sums of cationic and anionic equivalent concentrations were 0.97 and 0.98, and their slopes were obtained as 0.91 and 0.90 at Mt. Halla and Jeju City, respectively. The comparison between measured and calculated conductivities also yielded high correlation coefficients of 0.99 at the two sites (Song and Gao, 2009; Tang et al., 2005; Glavas and Moschonas, 2002). Furthermore, the correlation coefficients between the acid fraction calculated from the ionic concentration and that from pH and conductivity were 0.96 and 0.98 at Mt. Halla and Jeju City, respectively (Kramer et al., 1996). With the high correlation coefficients by three linear regression methods mentioned above, it can be assured that the quality of precipitation analytical data is quite satisfactory.

3.2. Organic acid concentrations

The concentrations of the organic acids in the precipitation samples are summarized in Table 2. The volume-weighted mean (VWM) concentrations of $HCOO^-$ and CH_3COO^- are 1.28 and 0.89 μmol/L, respectively, at Mt. Halla, and 2.06 and 1.15 μmol/L, respectively, at Jeju City. These results indicated

that the organic acid concentrations at Jeju City were mostly higher than those at Mt. Halla, except the case for 2002. The concentrations of $HCOO^-$ and CH_3COO^- at Jeju City were higher by a factor of 1.6 (min: 0.5, max: 4.0) and 1.3 (min: 0.4, max: 5.9) respectively compared to those at Mt. Halla. The annual variations indicated a similar pattern at both measuring sites, having the interesting common concentration peaks in 1998 and 2001.

Fig. 2 shows that the VWM concentrations of $HCOO^-$ and CH_3COO^- are generally high during winter, spring and fall, but low during summer. Whereas the $HCOO^-$ concentrations were a little bit higher in winter than those in fall at Mt. Halla site, they were of comparable magnitude in both winter and fall seasons at Jeju City. As shown in Fig. 2, the seasonal variations of $HCOO^-$ and CH_3COO^- concentrations were more or less in a similar pattern at both sites. The relatively higher concentrations of $HCOO^-$ and CH_3COO^- at Mt. Halla site during winter season could be reasoned by inclusion of some exceptional high concentration data in 1999.

The seasonal frequency distribution characteristics were examined by using the high 10% and low 10% concentration ranges of $HCOO^-$ and CH_3COO^-. At Mt. Halla site, the high 10% concentrations of $HCOO^-$ and CH_3COO^- had been respectively distributed as frequently as 50% and 37% during spring season, whereas the low 10% concentrations had been respectively distributed as frequently as 40% and 47% during summer season. Meanwhile, at Jeju City site, the high 10% concentrations of $HCOO^-$ and CH_3COO^- had been respectively distributed as

frequently as 43% and 47% during spring season, whereas the low 10% concentrations had been respectively distributed as frequently as 37% and 41% during summer season.

Table 3 shows the organic acid concentrations from this study, along with the results from other sites for comparison. Previously it had been reported that the concentrations of HCOO$^-$ and CH$_3$COO$^-$ were generally higher in urban areas than those in rural areas, and also especially high in tropical forests during dry season (Chebbi and Carlier, 1996). The concentrations of HCOO$^-$ and CH$_3$COO$^-$ from our study are quite similar to those from a marine area in Bermuda. In comparison with other rural and urban areas, the organic concentrations at Jeju Island were higher than those in the Mae Moh valley of Thailand, but lower than those in the Basque Country in Spain and Gopalpura in India as well as those in urban areas of USA and Spain.

3.3. Emission sources of organic acids

Mt. Halla is a dense forest area located at the center of Jeju Island, and it represents a relatively clean and unpolluted area in Korea. Therefore, natural emissions would be expected to exercise a strong effect on the concentrations of organic acids in the atmosphere. It has been known that biogenic emissions from plants (emitting precursors of organic acids as well as organic acids directly) occur with greater intensity during the plant growing season in which temperature and solar radiation are relatively high. Keene and Galloway (1986 and 1988) had reported that the concentrations of formic and acetic acids in precipitation at continental regions, especially in tropical areas, followed a seasonal cycle owing to direct emission of these acids by vegetation: higher concentrations had been observed in precipitations during the growing season compared to the winter months. However, the contribution of this emission source at the temperate regions would not be as significant as in the tropics, especially during the non-growing season (Chebbi and Carlier, 1996).

The VWM concentrations of both HCOO$^-$ and CH$_3$COO$^-$ during the growing seasons of March–September were compared with those during the non-growing seasons of October–February. The VWM concentrations of HCOO$^-$ and CH$_3$COO$^-$ during the growing seasons are 1.23 and 0.77 μmol/L, respectively, at Mt. Halla, and 1.97 and 1.12 μmol/L, respectively, at Jeju City. During the non-growing seasons, the VWM concentrations of HCOO$^-$ and CH$_3$COO$^-$ are 2.15 and 2.22 μmol/L, respectively, at Mt. Halla, and 2.20 and 1.95 μmol/L, respectively, at Jeju City. Intriguingly, contrary to previous reports, it was found that their concentrations were a little bit higher during the non-growing season. Consequently, it could be suspected that other factors rather than vegetation emissions might affect the concentrations of the organic acids in precipitation at Jeju area.

As indicated in Fig. 3, the regression analyses of the HCOO$^-$ and CH$_3$COO$^-$ concentrations show high correlations at both sampling sites (Helsel and Hirsch, 2002). The significant correlation between formic acid and acetic acid suggests that they both come clearly from the same source or processes (Keene and Galloway, 1986). The Kendall–Theil regression analysis results indicated that the slopes between the two sites seemed to be different during growing seasons (Fig. 3a and c) but similar during non-growing seasons (Fig. 3b and d).
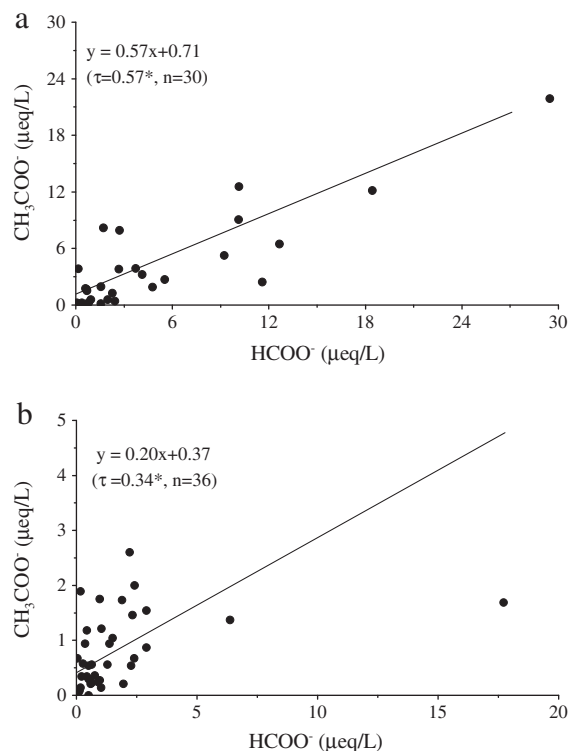

Fig. 4. Kendall–Theil robust line between HCOO$^-$ and CH$_3$COO$^-$ corresponding to a) high 10% and b) low 10% concentrations of nss-SO$_4^{2-}$ in precipitation events at Jeju City. *Correlation (τ) is significant at the 0.01 level (2-tailed).
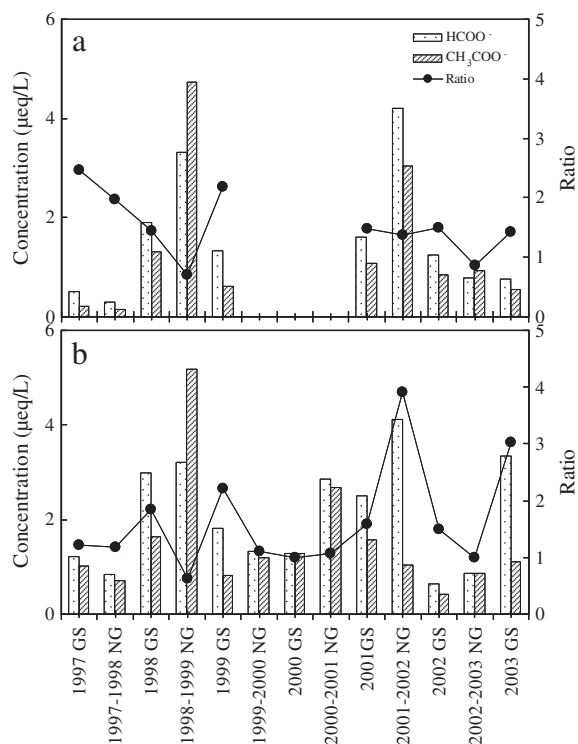

Fig. 5. Variations of HCOO$^-$, CH$_3$COO$^-$, and HCOO$^-$/CH$_3$COO$^-$ according to the growing seasons (GS) and non-growing seasons (NGS) between 1997 and 2004. a: Mt. Halla, b: Jeju City.

However, definitely, the slopes of regression lines indicated that the concentrations of CH_3COO^- increased relatively during the non-growing seasons rather than the growing seasons and the production paths of formic acid and acetic acid were clearly different between the two seasons.

Fig. 4 shows the Kendall–Theil robust lines between $HCOO^-$ and CH_3COO^- corresponding to high 10% and low 10% non-sea salt (nss) sulfate concentrations at Jeju City. The concentration of nss-SO_4^- is obtained by the equation of $[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.251[Na^+]$. Interestingly, the high correlation (Kendall's rank correlation coefficient = 0.57) was found when the sulfate concentrations were relatively high (over 10%), whereas the correlation was low (Kendall's rank correlation coefficient = 0.34) in the range of low 10% nss-SO_4^{2-} concentration. Moreover, the slopes of regression lines increased relatively in the high 10% concentrations of nss-SO_4^{2-}. The VWM concentrations of $HCOO^-$ and CH_3COO^- were 2.13 and 1.95 μeq/L at high 10%, and 1.46 and 0.63 μeq/L at low 10% of nss-SO_4^{2-}, respectively. That is, the concentrations of $HCOO^-$ and CH_3COO^- are greater by a factor of 1.5 and 3.1 respectively in the high 10% of nss-SO_4^{2-}. As a result, the concentrations of $HCOO^-$ and CH_3COO^- in the precipitation samples are likely to increase almost at the same time and, especially, the concentration of CH_3COO^- clearly increases to a high 10% of nss-SO_4^{2-}.

Figs. 5 and 6 illustrate the volume-weighted mean concentrations of formic and acetic acids, and their ratios.

The results showed that the concentrations of HCOO− and CH_3COO- were a little bit higher during the non-growing season at both sampling sites. The average concentration ratios of $HCOO^-/CH_3COO^-$ were 1.75 and 1.25 at Mt. Halla, and 1.75 and 1.47 at Jeju City, during growing and non-growing seasons respectively. This clearly indicates that the concentration ratios of $HCOO^-/CH_3COO^-$ increase during the growing seasons. It may reflect an increased impact of vegetation and/or photochemical production of formic acid during growing season (Granby et al., 1997). It has been previously reported that formic acid is produced in situ as a secondary product of anthropogenic and biogenic emissions, and the direct emission from vegetation favors acetic acid relative to formic acid (Chebbi and Carlier, 1996). Therefore, the concentration ratio of formic to acetic acids can be expected to be higher during growing season through photochemical conversions of precursors when solar radiation is more intense and the duration is longer.

As noted, the calculated concentration ratio of $HCOO^-/CH_3COO^-$ at Jeju City was generally lower during the non-growing seasons. This suggests that anthropogenic inputs appear to be the principal source of acetic acids to the atmosphere during the non-growing season. Talbot and Beecher (1988) hypothesized that the seasonal variability of the concentration ratios of formic to acetic acids in ambient air is due to a shift in the relative dominance of biogenic versus anthropogenic sources. Especially, in urban areas,
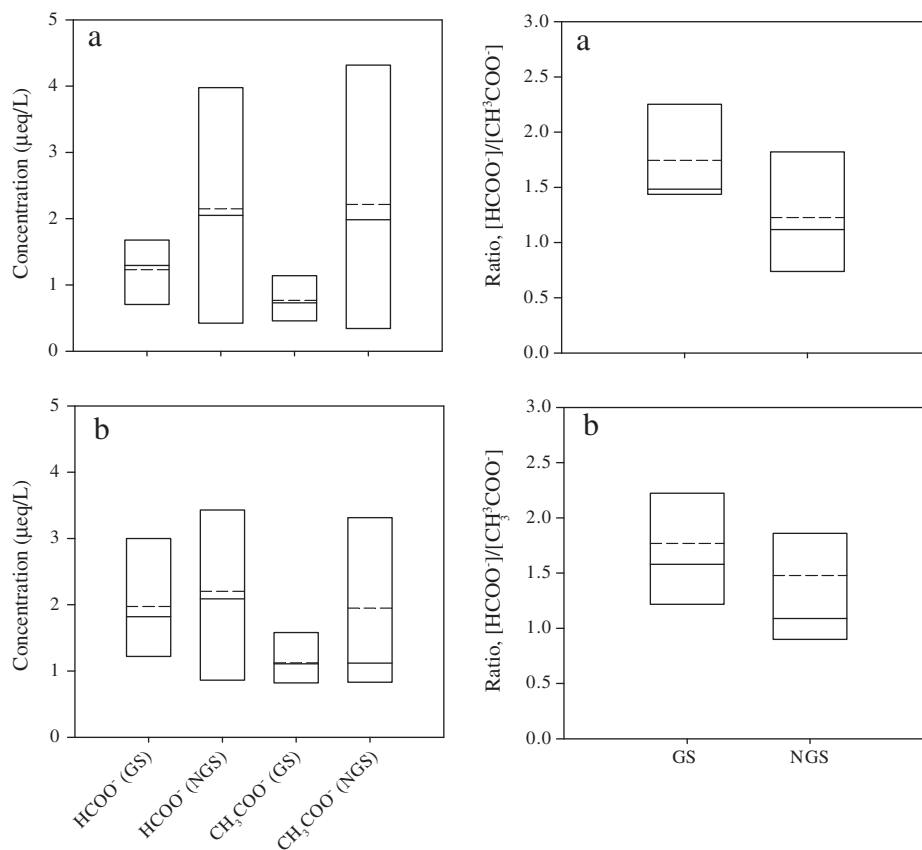

Fig. 6. Box plots of $HCOO^-$, CH_3COO^-, and $HCOO^-/CH_3COO^-$ during growing seasons (GS) and non-growing seasons (NGS). Solid line: 5th, 50th, 95th percentile, Dotted line: mean value, a: Mt. Halla, b: Jeju City.

although photo-oxidation process from atmospheric precursors can mainly affect organic acid levels during the growing seasons, anthropogenic sources such as automobiles that directly emit more $CH_3COOH(g)$ than $HCOOH(g)$ can have a significant impact on their levels during the non-growing seasons (Chebbi and Carlier, 1996). By comparison, the concentration ratios of $HCOO-/CH_3COO-$ at Mt. Halla were also slightly greater than unity but were clearly lower during the non-growing seasons rather than the growing seasons. These also indicate that direct emissions from anthropogenic sources have greater impact during the non-growing seasons at Mt. Halla.

Backward trajectory analysis allows the determination of reasonable relationships between inflow pathways of air parcels passing over Jeju Island and the concentrations of organic acids in atmospheric precipitation. Specifically, backward trajectories of air parcels involved in upper-air movements can be traced over constant intervals to establish the advection paths for these air parcels. The high 10% and low 10% out of whole measured data of $HCOO^-$ and CH_3COO^- concentrations in the rainfall had been selected, and then the backward trajectory analysis was performed using HYSPLIT4 (NOAA, 2009). Figs. 7 and 8 show that the high 10% of $HCOO^-$ and CH_3COO^- concentrations are clearly associated with the trajectories of air parcels arriving from the continental areas, whereas the low 10% concentrations are correlated with the

trajectories of air parcels originating from the North Pacific and with a few from the continental area. In brief, the concentrations of both organic species have increased when the wind moved from the west and north-west, especially, during spring season, but decreased when the wind blew from the south during summer season. These results are also consistent with the seasonal variations of organic anions in precipitation described in Section 3.2.

3.4. Acidity contribution by organic acids

The acidity contribution by organic acids (ACO,%), that is the fraction of the organic anions to the total anions and indicates the contribution to precipitation acidity, is given by

$$ACO(\%) = \frac{[HCOO^-] + [CH_3COO^-]}{[nss-SO_4^{2-}] + [NO_3^-] + [HCOO^-] + [CH_3COO^-]} \times 100$$

where the unit of concentration is the equivalent concentration. Therefore, the ACO(%) above is mainly related with compositions of acidic ionic species of precipitation samples. Fig. 9 shows that the ACO(%) generally increases during the growing seasons and Fig. 10 shows that the seasonal ACO(%) increments during spring and summer.
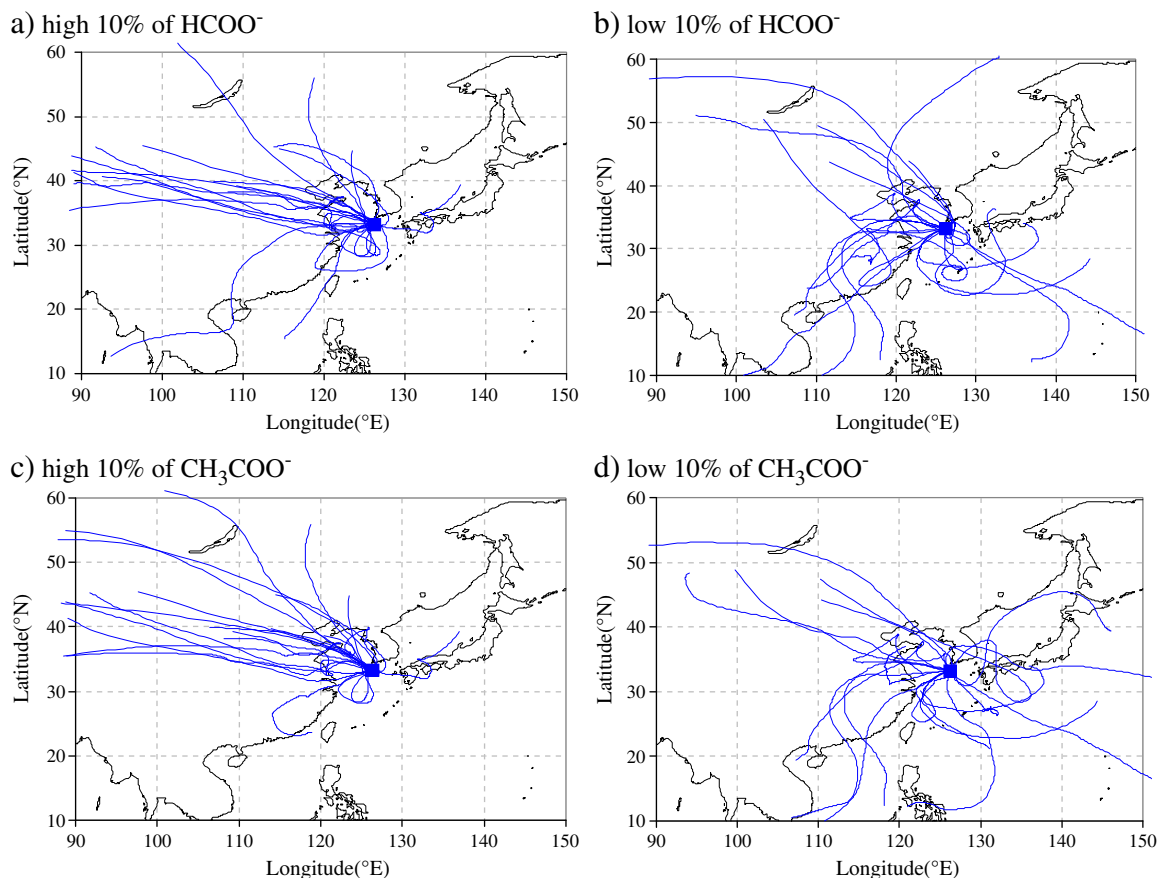

a) high 10% of HCOO⁻   b) low 10% of HCOO⁻

c) high 10% of CH₃COO⁻   d) low 10% of CH₃COO⁻

Fig. 7. Backward trajectories corresponding to high and low 10% concentrations of $HCOO^-$ and CH_3COO^- in precipitation events at Mt. Halla.

a) high 10% of HCOO⁻

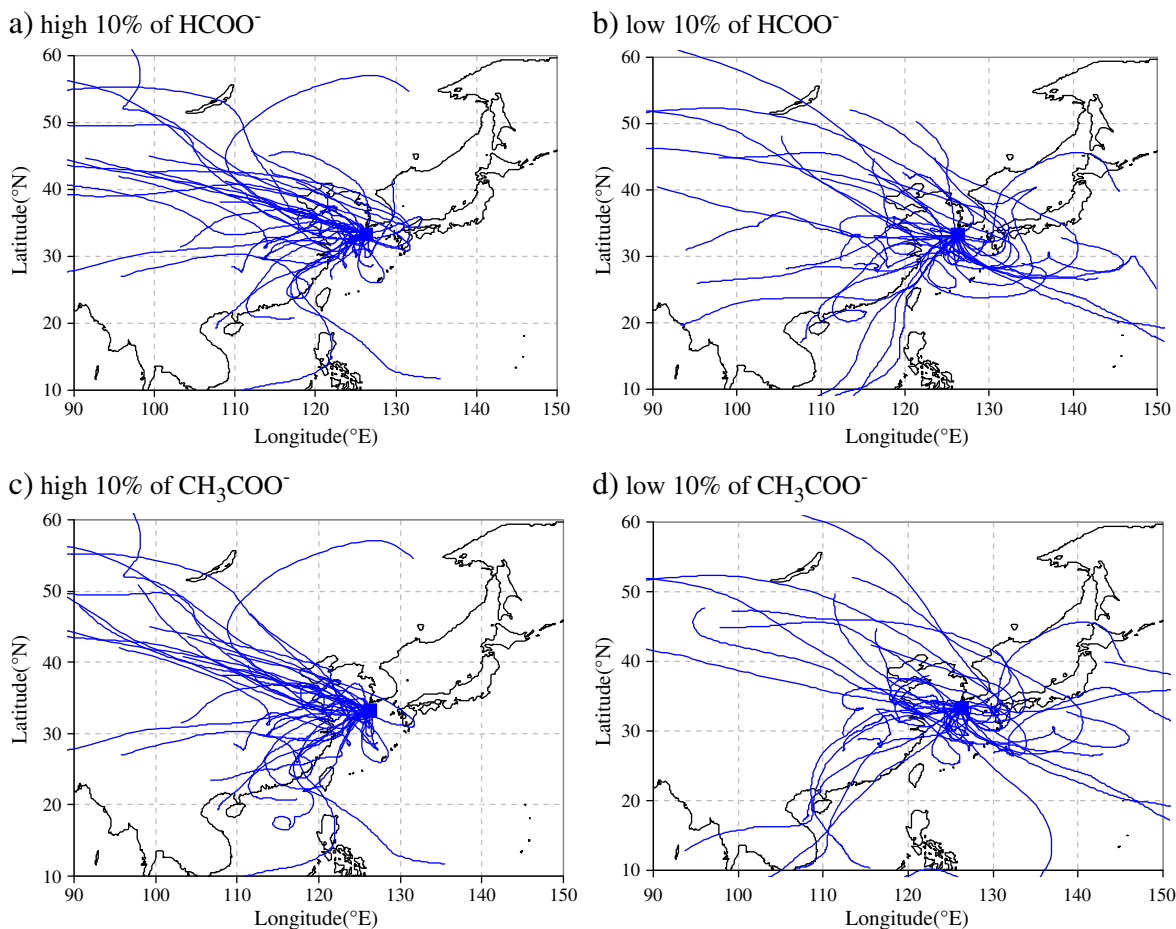b) low 10% of HCOO⁻

c) high 10% of CH₃COO⁻

d) low 10% of CH₃COO⁻

Fig. 8. Backward trajectories corresponding to high and low 10% concentrations of HCOO⁻ and CH₃COO⁻ in precipitation events at Jeju City.

The distributions of the HCOO⁻ and CH₃COO⁻ concentrations indicated that they were a little bit higher during the non-growing seasons as described in Section 3.3. Therefore, it is interesting to note the increase of ACO(%) during the growing seasons contrary to concentration distributions of the HCOO⁻ and CH₃COO⁻. Previous study indicated that, from the seasonal comparison, the variations of precipitation components showed that the concentrations of H^+, NO_3^-, and nss-SO_4^{2-} were higher in winter and spring at both sites (Kang et al., 2003). As a result, the decrease of ACO(%) during the non-growing seasons implies a definite increase of inorganic acidic anions rather than increments of the HCOO⁻ and CH₃COO⁻ concentrations. However, in case of growing season, especially in spring, the ACO(%) increased altogether even though the concentrations of inorganic acidic anions increased. This could be explained by the fact that the organic anions might affect the acidity more relatively compared to the inorganic anions.

The acidity contributions of nss-SO_4^{2-} and NO_3^- were 85–94% at Mt. Halla and 88–96% at Jeju City, respectively. In contrast, the acidity contributions of HCOO⁻ and CH₃COO⁻ were only 5.0–8.0% at Mt. Halla and 3–10% at Jeju City, respectively. Thus the acidity contribution by organic acids is low and insignificant compared to that by sulfuric and nitric acids in Jeju area. Galloway et al. (1982)

reported that the acidity contributions by organic acids were 66%, 41%, and 13% at San Carlos, Katherine, and Amsterdam, respectively. And in the case of Poker Flat and Bermuda, the contributions were not significant. Keene and Galloway (1984) also reported that it was 16% at Virginia in USA and 18–35% based on National Atmospheric Deposition Program (NADP) data. Pena et al. (2002) reported that their contribution to the total free acidity (TFA) in the rainwater samples was 27.5% (formic acid 9.4%, acetic acid 5.2%, oxalic acid 7.1%, lactic acid 4.6%, and citric acid 1.2%) at the area surrounding Galicia located in Northwest Spain. Our results of organic acidity contributions in Jeju area were quite low compared to those in the remote sites referred above. However, the contribution by organic acids would increase up to 30–40% when only specific and infrequent precipitations during heavy rainy seasons had been considered.

4. Summary

The traceable HCOO⁻ and CH₃COO⁻ as well as major ionic species were analyzed from the precipitation samples collected at Mt. Halla and Jeju City of Jeju Island between 1997 and 2003.
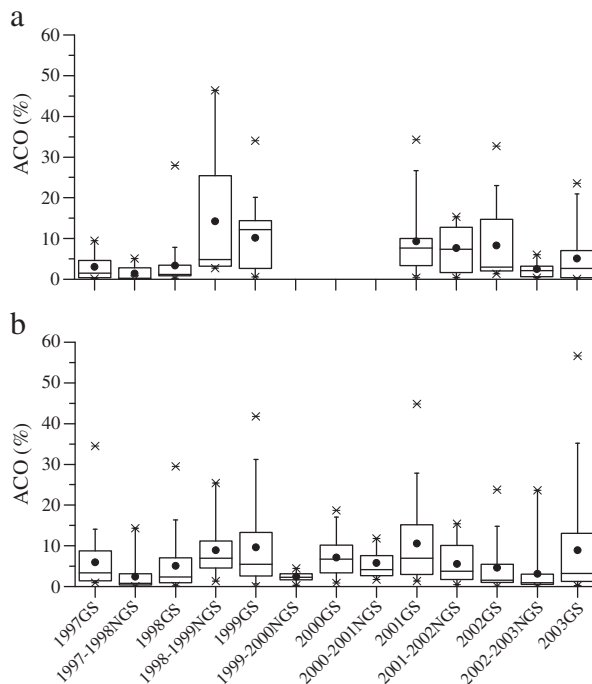
Fig. 9. Variations of the acidity contribution by organic acids (ACO) in precipitation events according to the growing seasons (GS) and non-growing seasons (NGS). a: Mt. Halla, b: Jeju City.

From three linear regression results by the comparison of ion balances, electrical conductivities and acid fractions, the quality of precipitation analytical data was satisfactorily assured with high correlation coefficients.

The concentrations of $HCOO^-$ and CH_3COO^- at Jeju City were higher by a factor of 1.6 and 1.3 respectively compared to those at Mt. Halla, and their seasonal concentrations showed generally high in spring but low in summer. The $HCOO^-$ and CH_3COO^- concentrations were little bit higher during non-growing season (October~February) compared to those in growing season (March~September), and it could be suspected that other factors rather than vegetation emissions might affect the concentrations of the organic acids in precipitation at Jeju area. Furthermore, these concentrations are likely to increase almost at the same time as the $nss\text{-}SO_4^{2-}$ concentration increase, and the concentration of CH_3COO^- especially increases clearly when the $nss\text{-}SO_4^{2-}$ concentration shows high. Meanwhile the concentration ratios of formic to acetic acids can be expected higher during growing season due to the photochemical conversions of precursors as solar radiation is more intense and the duration is longer.

From the backward trajectory analysis, the $HCOO^-$ and CH_3COO^- concentrations were found to increase when the wind was directed from the west and north-west during spring season, but they decreased when the wind blew from the south during summer season.

The acidity contributions of $nss\text{-}SO_4^{2-}$ and NO_3^- were 85–94% at Mt. Halla and 88–96% at Jeju City, respectively. In contrast, the acidity contributions of $HCOO^-$ and CH_3COO^- were only 5.0–8.0% at Mt. Halla and 3–10% at Jeju City, respectively. Therefore the acidity contribution by the organic acids can be assured to be low and insignificant compared to that by sulfuric and nitric acids in Jeju area.
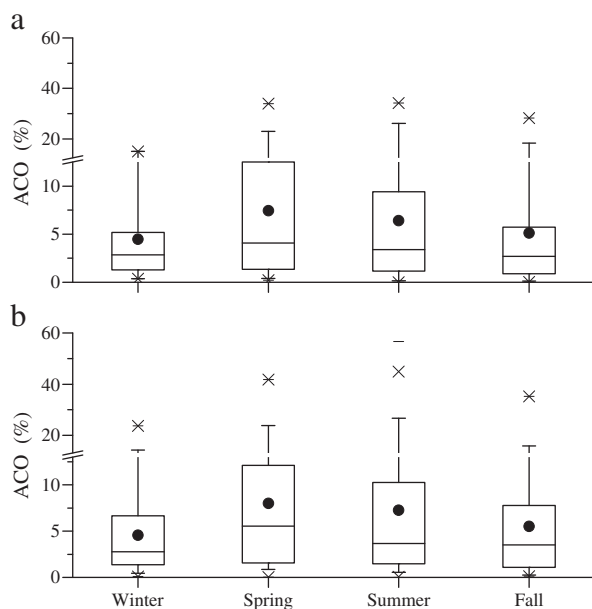
Acknowledgement

Fig. 10. Seasonal variations of the acidity contribution by organic acids (ACO) in precipitation events. a: Mt. Halla, b: Jeju City.

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