Distributions and sources of gaseous and particulate low molecular weight monocarboxylic acids in a deciduous broadleaf forest from northern Japan

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Abstract. To better understand the distributions of low molecular weight (LMW) monocarboxylic acids (monoacids) and their sources in the forest, we conducted simultaneous collection of gaseous and particulate samples at a deciduous broadleaf forest site in northern Japan. LMW normal (C_1–C_{10}), branched chain (iC_4–iC_6), hydroxyl (lactic and glycolic) and aromatic (benzoic) monoacids were detected in gas and particle phases. The dominant LMW monoacids in gas phase were formic (mean: 953 ng m^{-3}) and acetic (528 ng m^{-3}) acids. In particle phase, we found that isopentanoic (159 ng m^{-3}) and acetic (104 ng m^{-3}) acids are dominant species together with lactic acid. Concentrations of LMW monoacids did not correlate with nss-SO_4^{2-} and NO_3^- that are used as anthropogenic tracers, indicating that LMW monoacids are derived from the local sources within the forest ecosystem. Concentrations of C_1–C_6 monoacids in gas phase showed positive correlations (r^2 = 0.21–0.91) with isobutyric acid (iC_4), which is produced by soil. Forest soil may be a source of gaseous C_1–C_6 monoacids in the forest atmosphere. Acetic acid in particle phase positively correlated with nonanoic acid (C_9) (r^2 = 0.63), suggesting that formation of acetic and nonanoic acids are associated with the oxidation of unsaturated fatty acids. The particle-phase fractions (F_p) of formic and acetic acids showed good correlations with ambient temperature (C_1: r^2 = 0.49, C_2: r^2 = 0.60) and relative humidity (C_1: r^2 = 0.30, C_2: r^2 = 0.55) in daytime, suggesting that these parameters are important for the gas to particle conversion in the forest atmosphere. Our results suggest that forest ecosystem is an important source of organic gases and aerosols in the atmosphere.

1 Introduction

Homologous series (C_1–C_{10}) of low molecular weight (LMW) monocarboxylic acids (monoacids) are known to exist in the atmosphere as gas and particle phases (e.g., Kawamura et al., 1985; 2000; Liu et al., 2012). They have been reported from urban (Kawamura et al., 2000), forest (Andreae et al., 1988), marine (Miyazaki et al., 2014; Boreddy et al., 2017), and Antarctica samples (Legrand et al., 2004). Short chain monoacids such as formic and acetic acids are dominant chemical species in the atmosphere. LMW monoacids and their salts in aerosols are water-soluble and thus can act as cloud condensation nuclei (CCN), contributing to the radiative forcing directly or indirectly (Kanakidou et al., 2005) and affecting the radiation budget of the earth's atmosphere. On the other hand, high abundances of LMW monoacids in the troposphere can adversely affect air quality and human health and also increase the acidity of rainwater (Keene et al., 1983; Kawamura et al., 1996).

LMW monoacids are directly emitted from fossil fuel combustion and biomass- and biofuel-burning (Kawamura et al., 1985; Paulot et al., 2011) and terrestrial vegetation (Kesselmeier et al., 1997; Jardine et al., 2011). In addition, secondary production from photochemical oxidations of biogenic volatile organic compounds (VOCs) such as isoprene and anthropogenic VOCs such as acetylene and ethane are important sources of LMW monoacids (Paulot et al., 2011). Recently,

Stavrakou et al. (2012) conducted satellite measurement of formic acid on a global scale. They suggest that boreal and tropical forests are important sources of formic acid in the troposphere. In model experiment, Paulot et al. (2011) estimated that global source of formic and acetic acids are ~1200 Gmol $year^{-1}$ and ~1400 Gmol $year^{-1}$, respectively, however, these values are highly uncertain.

In our previous study on organic acids, normal (C_1-C_{10}), branched chain (iC_4-iC_6), and hydroxy (lactic and glycolic) monoacids were detected in gas, aerosol and snow pit samples (Kawamura et al., 2000; Mochizuki et al., 2016; 2017). In particular, branched chain (iC_5) and hydroxy (lactic) monoacids were abundantly detected in aerosol samples from North East China (Mochizuki et al., 2017). Detected branched chain (iC_4 and iC_5) and hydroxy (lactic) monoacids are derived from microorganisms and plants (Uta et al., 2012; Curl, 1982). However, these monoacids have not been reported in the previous studies from the forest atmosphere, in which ion chromatograph was mainly used and the species detected are generally limited to formic and acetic acids. Because branched chain and hydroxy monoacids are highly water-soluble, they have a potential to change the hygroscopic properties of atmospheric particles. In addition, there is no study on gas/particle partitioning of normal (C_1–C_{10}), branched chain (iC_4–iC_6), and hydroxy (lactic and glycolic) monoacids in the forest atmosphere. Therefore, the study of LMW monoacids in forest is important.

In this study, we collected gas and particle samples in a deciduous broadleaf forest in northern Japan in summer. To better understand the distributions and sources of LMW monoacids, samples were analyzed for normal (C_1–C_{10}), branched (iC_4–iC_6), hydroxyl (lactic and glycolic), and aromatic (benzoic) monoacids in both gas and particle phases, along with inorganic ions in particle phase. We discuss the importance of monoacid-enriched aerosols and their possible sources in the forest atmosphere.

2 Experimental

The Sapporo forest meteorology research site (SAP) (42º59' N, 141º23' E, 182 m a.s.l.) is located in Sapporo, Hokkaido, Japan (147 ha) on a hilly area neighbouring urban district of Sapporo city (Figure 1). Residential area is located north, east and west of the site. The forest type is mature secondary deciduous broadleaf forest. The major tree is Japanese white birch (*Betula platyphylla* var. *japonica*) and a Japanese oak (*Quercus mongolica* var. *grosse serrata*). The major understory is a dwarf bamboo (*Sasa kurilensis* and *Sasa senanensis*). Ambient temperature, relative humidity (RH), UV-A, wind speed, wind direction, and precipitation were measured on a meteorological tower (Figure 2). Details of the micrometeorological measurements and site information have been described in Yamanoi et al. (2015) and Miyazaki et al. (2012a; 2012b). During the campaign period (June to July, 2010), ambient air temperature ranged from 18 °C to 26 °C (average: 21±2.3 °C), whereas RH ranged from 69% to 96% (average: 87±7.9%). UV-A was high during the first half of the measurement period (except for 7 July) and low during the second half of the measurement period. The dominant wind direction throughout the sampling period was from east and south. Wind speed ranged from 0.2 to 0.6 m s^{-1} (average: 0.4 m s^{-1}). Precipitation occurred in the morning of 1 July (11 mm), in the evening of 4 July (1.2 mm), and in the morning of 8 July (6.6 mm).

Samplings were conducted from 28 June to 8 July 2010. The samples were collected for 15 hours (5:00–20:00 LT) in daytime (n = 11) and 9 hours (20:00–5:00 LT) in nighttime (n = 11). Total suspended particle (TSP) and gaseous organic acids were collected using a low-volume air sampler equipped with the two-stage filter packs (URG-2000-30FG) at a flow rate of 15 L min^{-1} (Kawamura et al., 1985). The particles were collected onto precombusted (450°C, 6 hours) quartz-fiber filters (47 mm diameter) (first stage), whereas gaseous organic acids were collected on the quartz-fiber filter impregnated with potassium hydroxide (KOH) (second stage). The KOH impregnated filters were prepared by rinsing the precombusted quartz filter in a 0.2 M KOH solution and then dried in an oven at 80 °C. Each filter was placed in a clean glass bottle with a Teflon-lined screw cap. After the sampling, the filter samples were stored in a freezer room at -20 °C prior to analysis. Semi-volatile organic acids collected on the first filter may evaporate, causing negative artifacts. On the other hand, second filter

may absorb organic vapors evaporated from the first filter, causing positive artifacts. Although such artifacts are possible for any filter-based measurements for ambient conditions, these effects are limited (Kawamura et al., 1985).

LMW monoacids were determined as p-bromophenacyl esters using a capillary gas chromatograph equipped with a flame ionization detector (GC-FID) and GC-mass spectrometer (GC-MS) (Kawamura and Kaplan, 1984; Mochizuki et al., 2017). Briefly, an aliquot of filter (4.3 cm^2) was extracted for water-soluble organic compounds with organic-free ultrapure water (resistivity of > 18.2 MΩ cm) under ultrasonication. To remove particles, the water extracts were filtered through quartz wool packed in a Pasteur pipette. The pH of filtrates was adjusted to 8.5–9.0 with 0.05 M KOH solution. The samples were concentrated down to 0.5 mL using a rotary evaporator under vacuum at 50 °C. The concentrations were passed through a cation exchange resin (DOWEX 50W-X4, 100-200 mesh, K^+ form) packed in a Pasteur pipette. Free monocarboxylic acids were converted to organic acid salts ($RCOO^-K^+$). After confirming the pH of 8.5–9.0, the samples were dried using a rotary evaporator under vacuum at 50 °C, followed by blowdown with pure nitrogen gas. Organic acids were derivatized to p-bromophenacyl esters in acetonitrile (4 ml) with α,p-dibromoacetophenone (0.1 M, 50 µl) as a derivatization reagent and dicyclohexyl-18-crown-6 (0.01 M, 50 µl) as a catalyst at 80°C for 2 hours (Kawamura and Kaplan, 1984). In addition, OH functional groups in p-bromophenacyl esters of hydroxymonoacids were reacted with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 µl of pyridine at 70°C for 3 hours to derive trimethylsilyl (TMS) ethers of p-bromophenacyl esters (Kawamura et al., 2012).

p-Bromophenacyl esters and their TMS ethers were identified and quantified using a capillary gas chromatograph (HP GC6890, Hewlett-Packard, USA) equipped with a flame ionization detector and GC-mass spectrometer (Agilent GC7890A and 5975C MSD, Agilent, USA). Details of the methods have been described in Kawamura and Kaplan (1984) and Kawamura et al. (2012). Recoveries of authentic monoacids (C_1–C_{10}, iC_4–iC_6, lactic, glycolic, and benzoic acids) spiked to a quartz filter were better than 80%. Analytical errors using authentic monoacids were within 12%.

To measure inorganic ions, a portion of quartz-fiber filter (first filter) was extracted with ultrapure water under ultrasonication. The extracts were passed through a membrane disk filter (0.22 µm, Millipore Millex-GV, Merck, USA). The filtrates were injected into an ion chromatograph (Model 761 compact IC, Metrohm, Switzerland) (Boreddy and Kawamura, 2015). We measured cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (F^-, MSA^-, Cl^-, NO_2^-, NO_3^-, PO_4^-, and SO_4^{2-}) in aerosol samples. Inorganic ions were not detected in the field blanks. Concentrations of non-sea-salt SO_4^{2-} [nss-SO_4^{2-}] is calculated by the following equation:

$$[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.25 \times [Na^+],$$

where $[SO_4^{2-}]$ and $[Na^+]$ are concentrations of total SO_4^{2-} and Na^+, respectively (Duce et al., 1983, Berg and Winchester, 1978).

We calculated seven-day air mass back trajectories at a height of 300 m above sea level using the Meteorological Data Explorer (METEX) provided by the National Institute for Environmental Studies (http://db.cger.nies.go.jp/metex/index.html).

3 Results

Low molecular weight normal (C_1–C_{10}), branched chain (iC_4–iC_6), hydroxyl (lactic and glycolic), and aromatic (benzoic) monoacids were detected in gas and aerosol samples from a deciduous broadleaf forest in northern Japan (Table 1). Figure 3 shows mean concentrations of monoacids in gas and particle phases. In gas phase, formic acid was the dominant species (188–2260 ng m^{-3}, mean: 953 ng m^{-3}), followed by acetic acid (277–1590 ng m^{-3}, mean: 528 ng m^{-3}). In particulate phase, isopentanoic acid was found as the dominant species (36–1478 ng m^{-3}, mean: 159 ng m^{-3}), followed by acetic acid (22–263 ng m^{-3}, mean: 104 ng m^{-3}) and formic acid (2.2–216 ng m^{-3}, mean: 71 ng m^{-3}). Lactic acid, which is a hydroxyl monoacid, was generally the fourth most abundant LMW monoacid in particle samples (8.4–522 ng m^{-3}, mean: 65 ng m^{-3}).

Figure 4 shows day-night variations of selected monoacids in gas and particle phases. Gaseous formic acid did not show any day/night trend, whereas particulate formic acid showed a diurnal distribution with higher concentrations in nighttime than daytime. Abundances of gaseous acetic acid were higher in daytime than in nighttime, whereas opposite trend was found for particle phase acetic acid, that is, particulate acetic acid was more abundant in nighttime than in daytime. Day-to-day variations in other monoacids did not show a clear diurnal trend.

The highest concentrations of isopentanoic and lactic acids in particle phase were observed at night on 30 August. Temporal variation of isopentanoic acid in particle phase was similar to that of lactic acid. Gaseous and particulate concentrations of isopentanoic and lactic acids did not show any clear diurnal variation.

The particle-phase fractions (F_p) of individual monoacids were calculated as F_p = P/(G+P), where P is particle phase concentration and G is gas phase concentration. Table 1 summarizes mean F_p of individual monoacids in daytime and nighttime in the deciduous broadleaf forest. F_p of individual monoacids ranged from 0.04 (C_3) to 0.63 (iC_5) in daytime and 0.05 (C_3) to 0.69 (iC_5) in nighttime. Formic (C_1) and acetic (C_2) acids are largely present in gas phase. Nonanoic (C_9) and decanoic (C_{10}) acids are present not only in gas phase but also in particle phase. Lactic acid is largely present in aerosol phase in the forest atmosphere.

We detected cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (NO_3^-, SO_4^{2-}, MSA^-, Cl^-, NO_2^-, and F^-) in particle samples from a deciduous broadleaf forest. Nss-SO_4^{2-} (mean: 2240 ng m^{-3}) is major anion and NH_4^+ (mean: 972 ng m^{-3}) is major cation. Concentrations of major inorganic ions did not show clear diurnal and temporal variations. pH of the water extracts from particle samples ranged from 3.5 to 6.3 (mean: 5.0). The particle samples were always acidic.

This forest site is located a few kilometers south of Sapporo city. The dominant wind direction was from east and south throughout the sampling period. We compared the concentrations of individual monoacids together with nss-SO_4^{2-} and NO_3^-: anthropogenic aerosol tracers to evaluate the influence of anthropogenic air mass transport from urban area. We confirmed that individual monoacids in both gas and particle phases did not show correlation with nss-SO_4^{2-} ($r^2 < 0.14$) and NO_3^- ($r^2 < 0.11$). The majority of sampling air was not affected by urban area. In addition, Figure 5 shows seven-day air mass back trajectories (300 m a.s.l.) for the study period from 28 June to 8 July at the sampling site. Most of the air masses passed through the Pacific Ocean during the measurement period, except for 28 June. This result may suggest that the air masses arriving at the forest site are not affected by the outflows from East Asia and far East of Russia.

4. Discussion

4.1 Possible sources of LMW monoacids

LMW monoacids are directly emitted from fossil fuel combustion (Kawamura et al., 1985) and plant leaves (Kesselmeier and Staudt, 1999) and also produced in the atmosphere by photo-oxidation of anthropogenic and biogenic VOCs (Paulot et al., 2011). LMW monoacids have a variety of anthropogenic and biogenic sources. Concentrations of formic and acetic acids in gas phase were higher than those of C_3-C_{10} monoacids. The rate constants of gaseous formic, acetic, propionic, butyric, and isobutyric acids with OH radicals are 0.45, 0.67, 1.20, 1.79, and 2.06×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively (provided by NIST Chemical Kinetics Database). The rate constants of LMW monoacids with oxidant (OH radicals and ozone) may increase with an increase in carbon numbers of monoacids. Formic and acetic acids are stable, leading to higher concentrations of formic and acetic acids in the atmosphere. In addition, we measured LMW monoacids in soil sample (surface ~3 cm) collected at a broad-leaf forest from Chubu University campus in Central Japan on October 31, 2018. LMW normal (C_1–C_4, C_7–C_{10}), branched chain (iC_4), and hydroxyl (lactic and glycolic) monoacids were detected. Concentrations of formic (7400 ng $g_{wet\ soil}^{-1}$) and acetic (4260 ng $g_{wet\ soil}^{-1}$) acids were significantly higher than that of other detected monoacids (~ 1800 ng $g_{wet\ soil}^{-1}$) (Kunwar et al., unpublished data, 2018). Major portion of monoacids in the forest atmosphere is similar to that in forest soil sample, suggesting forest soil is a source of LMW monoacids as well.

In gas phase, isobutyric acid (iC_4) showed positive correlations with C_1 (day: $r^2 = 0.36$, night: no correlation), C_2 (0.53, 0.43), C_3 (0.76, 0.64), C_4 (0.82, 0.80), C_5 (0.91, 0.81) and C_6 (0.72, 0.74) monoacids (Figure 6). Branched chain monoacids including isobutylic acid are known as common metabolites of bacteria (e.g., *Bacteroides distasonis*) and fungi in soils (Uta et al., 2012 and references therein). LMW monoacids such as acetic and propionic acids can be produced by microbiological processes (Uta et al., 2012). In addition, exudation of organic acids is known to occur in vascular plants, mainly from roots (Curl, 1982). Shen et al. (1996) reported that formic, acetic, and propionic acids are contained in forest soil and rhizosphere soil and. Although we detected formic, acetic, propionic, and isobutylic acids in forest soil (unpublished data), a quantitative contribution from the forest floor cannot be evaluated in the present study. On the other hand, photo-oxidation of BVOCs such as isoprene and monoterpenes are major sources of formic and acetic acids in the atmosphere (Paulot et al., 2011). Our results suggest that forest floor may be a source of gaseous C_1–C_6 monoacids to the atmosphere.

Gaseous lactic acid in daytime did not show positive correlations with C_1–C_6 monoacids ($r^2 < 0.004$), whereas lactic acid in nighttime show positive correlations with C_3–C_6 ($r^2 = 0.45$–0.65) although they were rather scattered. Particulate lactic acid also did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Formation processes of C_1-C_6 acids may be different from hydroxy monoacids.

In particle phase, a positive correlation was observed between acetic acid and nonanoic acid (day: $r^2 = 0.63$, night: $r^2 = 0.63$) (Figure 7). Unsaturated fatty acids (UFAs) such as oleic ($FA_{18:1}$) and linoleic ($FA_{18:2}$) acids are generally present in terrestrial higher plants and soil fungi (Yokouchi and Ambe, 1986; Kaur et al., 2005). Nonanoic (C_9) and hexanoic (C_6) acids are produced by the heterogenous oxidation of $FA_{18:1}$ and $FA_{18:2}$ in aerosols, respectively, via the cleavage of a double bond at C_9-position (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987). Longer-chain monoacids may produce acetic acid via photochemical breakdown with OH radicals. UFAs may also contribute to the formation of acetic acid in aerosol in a deciduous broadleaf forest.

In this study, relatively high concentrations of particulate lactic and isopentanoic acids were observed. Lactic acid is primary produced by Bacteria (*lactobacillus*) (Cabredo et al., 2009) and from the plant tissues (Raja et al., 2008). Lactic acid can also be produced by the oxidation of isoprene with ozone in (Nguyen et al., 2010). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Uta et al., 2012 and references therein). A positive correlation was observed between lactic acid and isopentanoic acids in particle phase ($r^2 = 0.98$). We confirmed that lactic acid is abundantly present in forest soil (1860 ng $g_{wet\ soil}^{-1}$) but isopentanoic acid is not (unpublished data). Lactic and isopentanoic acids may be linked to the biosynthetic processes in the forest soil system as well.

4.2 Gas/particle partitioning of LMW monoacids

Generally, F_p increases with an increase in carbon numbers of monoacids (Yatavelli et al., 2014) due to lower vapor pressures of higher MW organic acids. The smaller F_p of formic (daytime: 0.08) and acetic (daytime: 0.14) acids can be explained by higher vapor pressure (C_1: 5.6×10^{-2} atm, C_2: 2.1×10^{-2} atm) among LMW monoacids determined. The values of F_p for formic and acetic acids measured in a deciduous broadleaf forest in daytime are comparable to those reported from the Pacific Ocean (C_1: $F_p = 0.04$, C_2: $F_p = 0.06$) (Miyazaki et al., 2014) and urban Los Angeles (C_1: $F_p = 0.16$, C_2: $F_p = 0.06$) (Kawamura et al., 2000), in which the same sampling and analytical protocols were used.

Formic and acetic acids in particle phase show clear day-night variations and their concentrations in particle phase in nighttime were higher than those in daytime. The higher concentrations in nighttime may be associated with shallower planetary boundary layer, which can accumulate organic acids near the ground surface. Because wind speed in nighttime (average: 0.3 m s^{-1}) was comparable to that in daytime (average: 0.4 m s^{-1}) and anti-correlation was not observed between formic and acetic acids and wind speed ($r^2 < 0.01$), accumulation of formic and acetic acids in the forest canopy followed by the increased concentrations may not show any clear day-night trend. Formic and acetic acids are intermediate products in the oxidative degradation of various VOCs. They may be very stable intermediate products before the oxidation to CO_2.

We investigated the effects of ambient temperature on gas/particle partitioning of LMW monoacids. F_p of formic and acetic acids were found to decrease with increasing ambient temperature (C_1: r^2 = 0.49, C_2: r^2 = 0.60) (Figure 8), whereas other LMW monoacids did not show a correlation with ambient temperature (r^2 < 0.37), except for butyric acid (r^2 = 0.70) in daytime. Although F_p of LMW monoacids did not show a correlation with ambient temperature in nighttime (r^2 < 0.16), except for propionic acid (r^2 = 0.31), we found average F_p of LMW monoacids in nighttime were higher than those in daytime (Table 1). Khan et al. (1995) reported that ambient temperature is an important factor to determine the gas/particle partitioning of organic acids. Higher temperature promotes the transfer of aerosol phase formic and acetic acids to gas phase in daytime by evaporation, which is consistent with Henry's Law constants.

We found that F_p of formic and acetic acids increase with increasing RH (C_1: r^2 = 0.30, C_2: r^2 = 0.55) (Figure 9), whereas other LMW monoacids did not show a correlation with RH (r^2 < 0.20), except for butyric acid (r^2 = 0.55) in daytime. Although F_p of LMW monoacids did not show correlation with RH in nighttime (r^2 < 0.15), we found that average F_p of LMW monoacids in nighttime were higher than those in daytime (Table 1). Al-Hosney et al. (2005) and Prince et al. (2008) reported that the uptake of formic and acetic acids by $CaCO_3$ can be enhanced by higher RH (C_1: RH > 62%, C_2: RH > 53%). In addition, liquid water contents (LWC) of aerosols were estimated using ISORROPIA-II model (Fountoukis and Nenes, 2007) with the data of inorganic ions and meteorological parameters. The aerosol LWC ranged from 1.4 to 14.6 μg m^{-3} (av. 6.4 μg m^{-3}). Although F_p of LMW monoacids did not show strong correlations with LWC (r^2 < 0.24), strong positive correlations were found between RH and aerosol LWC in daytime (r^2 = 0.47) and in nighttime (r^2 = 0.74). Higher RH may enhance the partitioning of gaseous formic and acetic acids to aerosol phase as a result of the condensation of water vapour on aerosol particles. Our results suggest that higher temperature depresses a transfer of gaseous formic and acetic acids to aerosol phase and higher RH enhances the partitioning of gaseous formic and acetic acids to aerosol phase in the forest atmosphere.

The larger F_p of lactic acid (daytime: 0.60, nighttime: 0.69) was observed. This level is comparable to that reported for the Pacific Ocean (F_p = 0.82) (Miyazaki et al., 2014). Even though the vapor pressure of lactic acid (5.3×10^{-4} atm) is higher than those of C_5–C_{10} monoacids (vapor pressure: 1.6×10^{-4}–1.6×10^{-10} atm), the F_p of lactic acid was larger than those of C_5–C_{10} monoacids (F_p: 0.11–0.50). Although lactic acid is highly water-soluble, F_p of lactic acid did not show a clear correlation with relative humidity. High relative humidity (average: 87%) may be involved with the large F_p of lactic acid.

Gaseous organic acids react with alkaline particles such as calcium and consequently the reaction enhances the partitioning of gaseous organic acids to aerosol phase (Alexander et al., 2015). We calculated total cation equivalents (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) minus total anion equivalents (F^-, MSA^-, Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) including monoacids detected, although CO_3^-, HCO_3^-, and unidentified organic anions were not considered. Total cations were higher than total anions. Excess cations exist in the aerosol. No positive correlations were observed (r^2 < 0.04) between F_p of individual LMW monoacids and excess cations. This result indicates that excess cations are not an important factor to control the gas/particle partitioning of LMW monoacids in the forest atmosphere. F_p of LMW monoacids showed positive correlations with mass concentrations of total LMW monoacids in particle phase (r^2 = 0.24–0.46), except for C_3, C_9, and C_{10}. Although we did not measure the aerosol mass, gaseous LMW monoacids in the forest atmosphere may be adsorbed on the existing particles.

4. Summary and Conclusions

We conducted simultaneous sampling of gaseous (G) and particulate (P) LMW monoacids in a deciduous broadleaf forest from northern Japan followed by p-bromophenacyl ester derivatization and gas chromatographic determination. LMW normal (C_1–C_{10}), branched chain (iC_4–iC_6), hydroxyl (lactic and glycolic), and aromatic (benzoic) monoacids were detected in both gas and aerosol samples. Formic and acetic acids were found as the dominant species in gas phase. Isopentanoic and acetic acids were detected as the dominant species in particle phase. Particle-phase fractions (F_p = P/(P+G)) of major LMW monoacids were low (F_p: 0.04-0.50), except for isopentanoic (F_p = 0.68) and lactic (F_p = 0.66) acids. Concentrations of long-

lived monoacids (formic and acetic acids) in gas phase showed positive correlation with short-lived monoacids (C_3–C_6). Concentrations of LMW monoacids in gas and particle phases did not correlate with nss-SO_4^{2-} and NO_3^- (anthropogenic tracers). These results suggest that anthropogenic contribution is not important, but local contribution is more important as a source of LMW monoacids. Concentrations of C_1–C_6 monoacids in gas phase showed positive correlations with isobutyric acid (iC_4) (r^2 = 0.21–0.91). Branched chain monoacids can be used as an indicator of soil microorganism processes (Uta et al., 2012 and references therein). Many kinds of LMW monoacids are exuded by plant roots (Curl, 1982) and derived from soil microorganism (Uta et al., 2012). We suggest that forest floor is another important source of gaseous LMW monoacids. Acetic acid in particle phase showed a positive correlation with nonanoic acid (C_9), which is produced by the oxidation of unsaturated fatty acids such as oleic acid. F_p of formic and acetic acids showed good correlations with ambient temperature (C_1: r^2 = 0.49, C_2: r^2 = 0.60) and RH (C_1: r^2 = 0.30, C_2: r^2 = 0.55) in daytime, suggesting that these parameters are important for the gas to particle conversion in the forest atmosphere. The present study demonstrates that deciduous broadleaf forest is an important source of LMW monoacids in gas and particle phases in the atmosphere of northern Japan.

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Figure captions

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Figure 3. Average concentrations of LMW monocarboxylic acids in gas and particle phases.

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Figure 5. Seven-day air mass back trajectories at a height of 300 m a.s.l. during the sampling period.

Figure 6. Concentrations of C_1–C_6 monoacids against isobutyric acid (iC_4) in gas phase. The coefficient of determination shows that regression line is statistically significant ($p < 0.05$).

Figure 7. Concentrations of formic and acetic acids in gas phase as a function of nonanoic acid. The coefficient of determination shows that regression line is statistically significant ($p < 0.05$).

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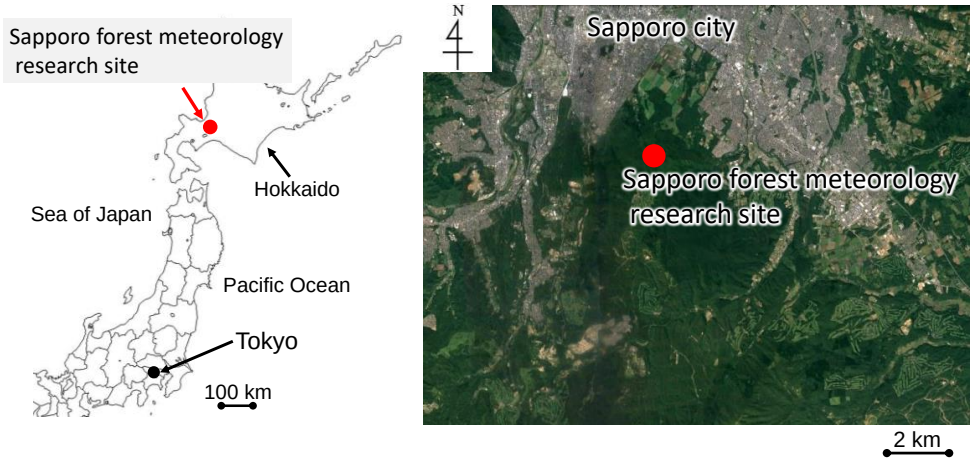
Figure 9. Particle-phase fractions (F_p) of formic and acetic acids against relative humidity. The coefficient of determination shows that regression line is statistically significant ($p < 0.1$).



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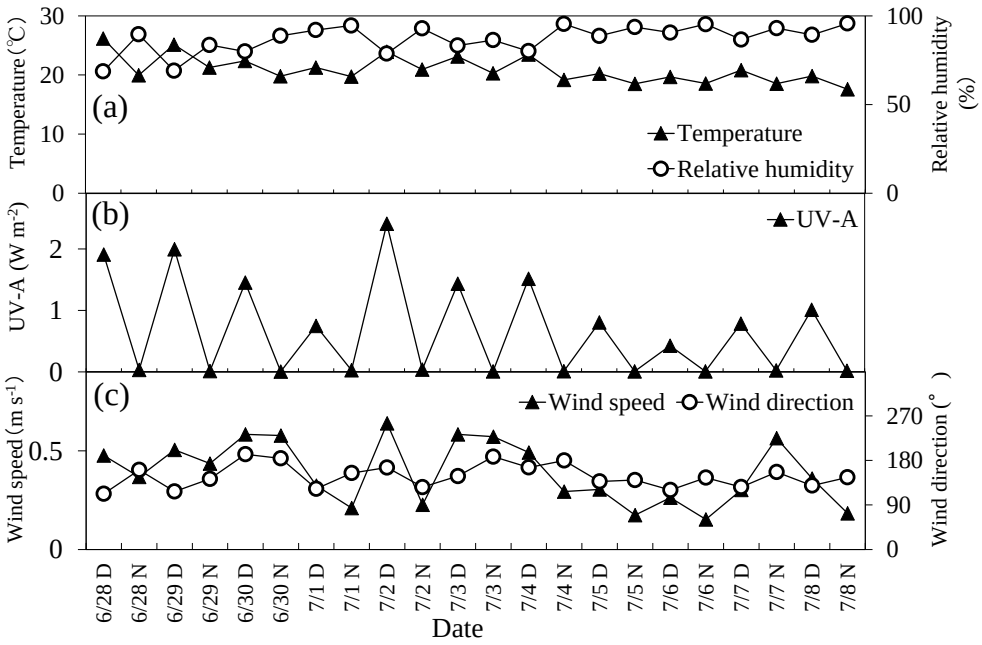

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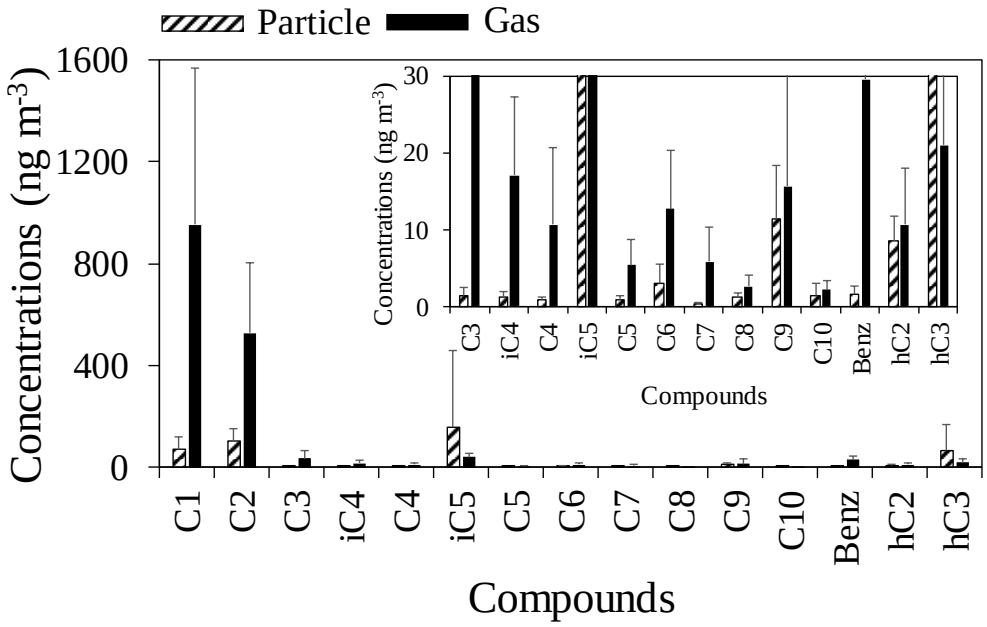

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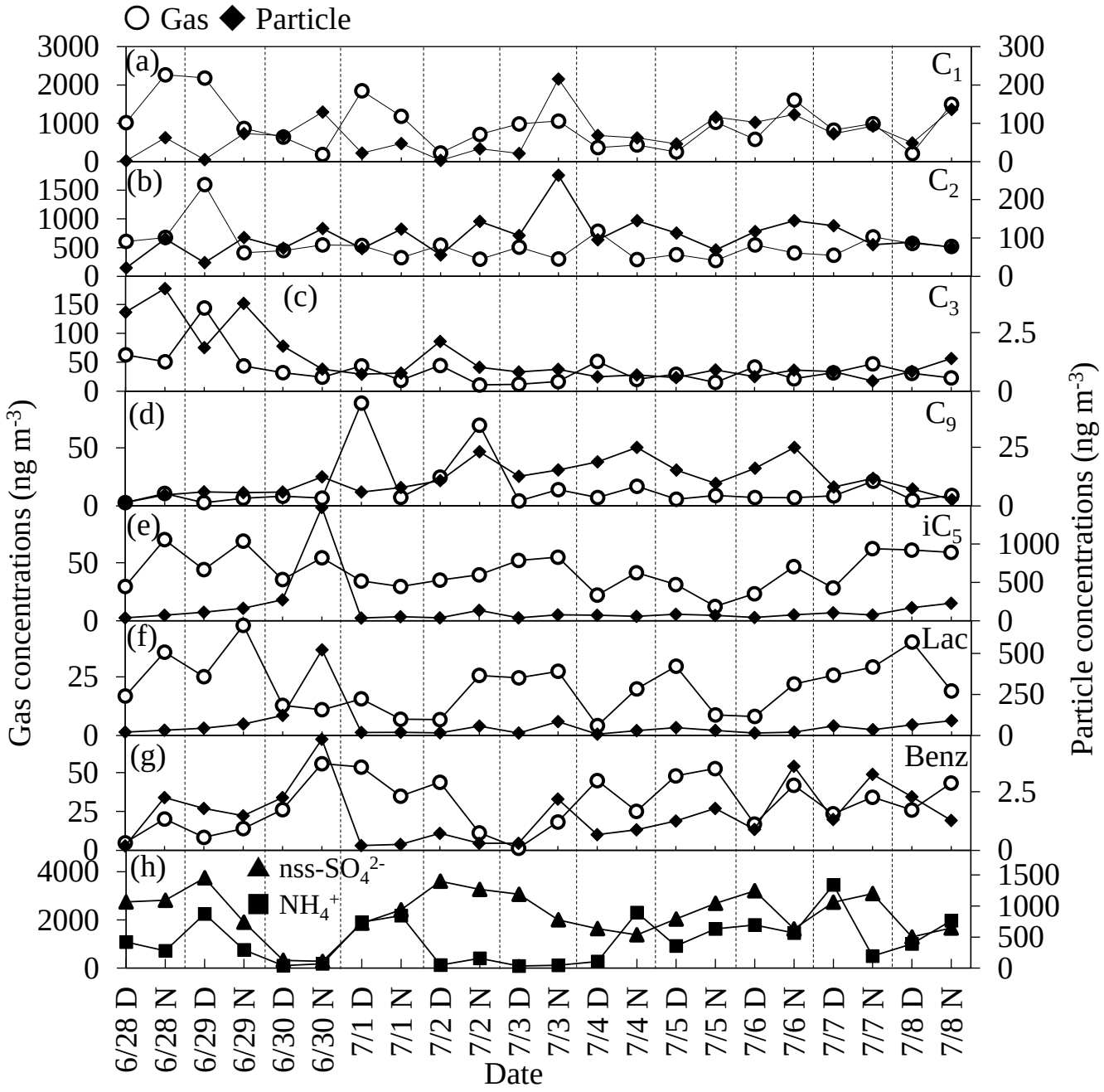

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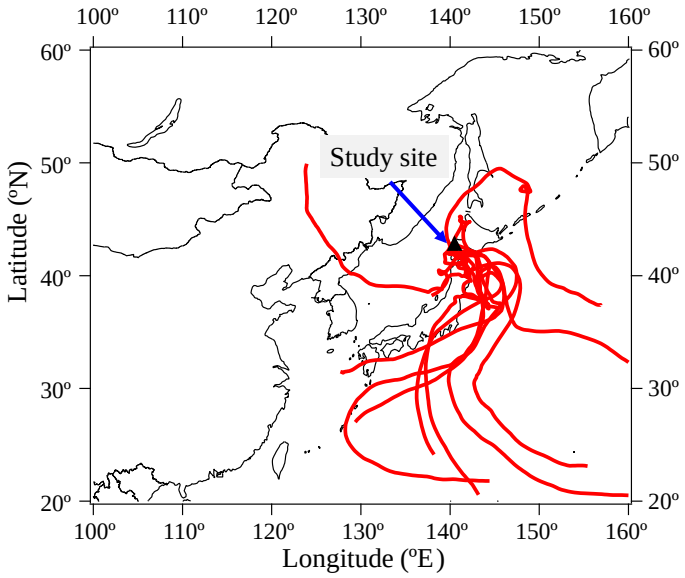

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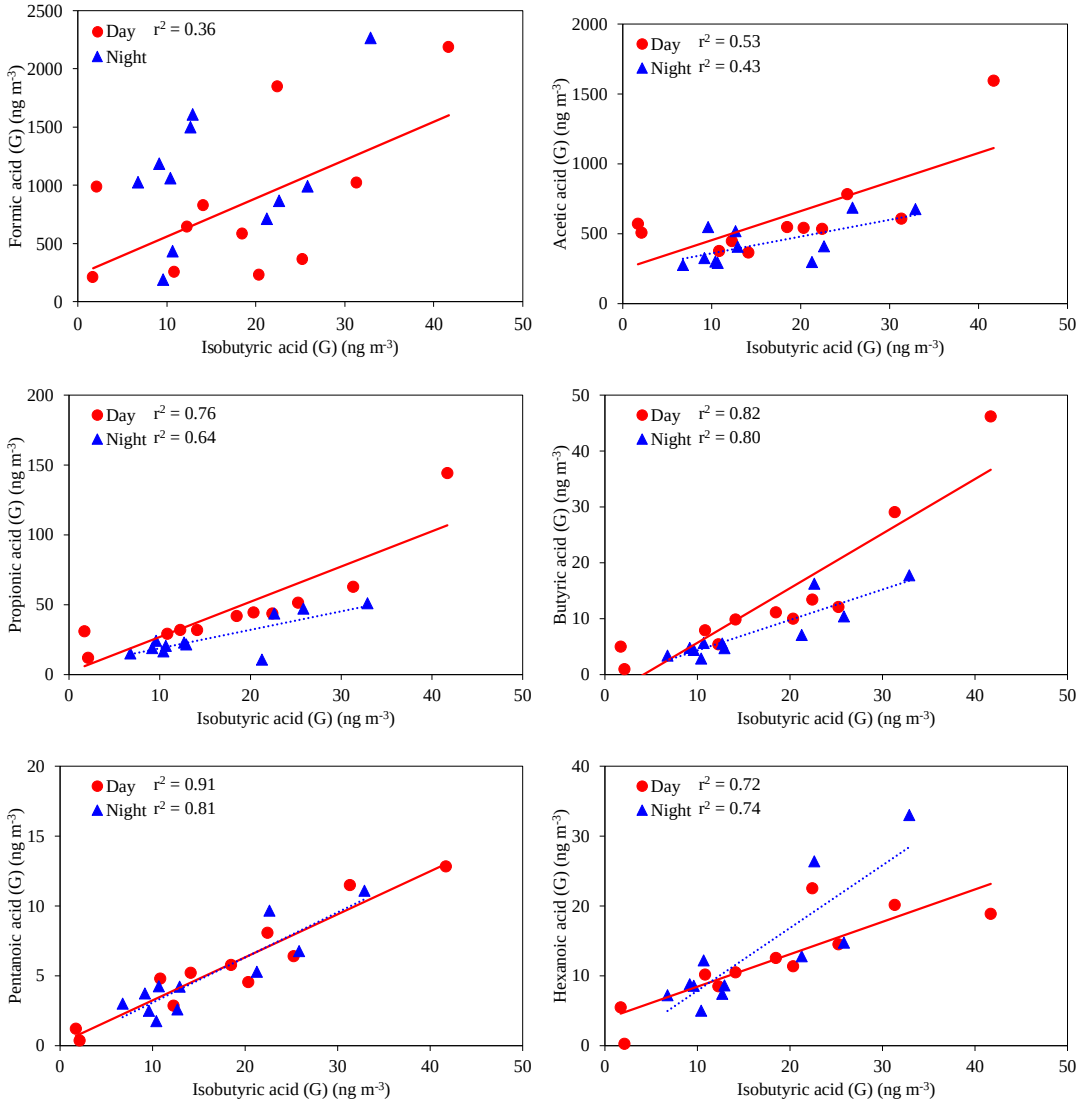

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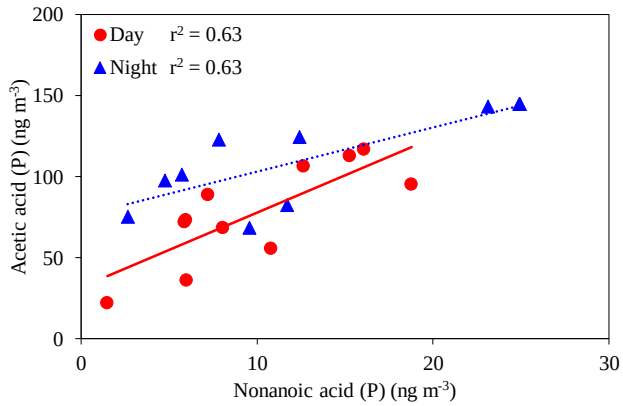

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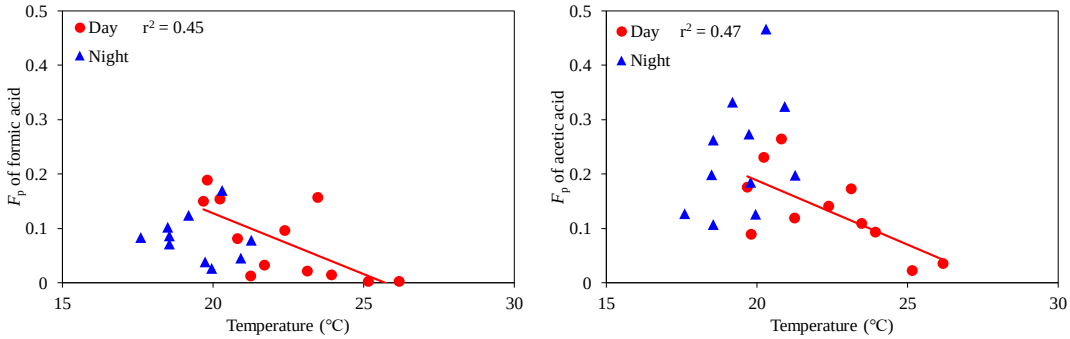

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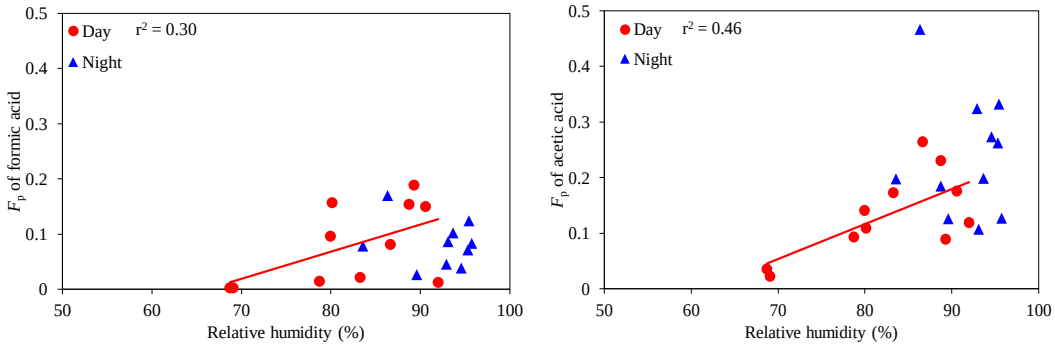

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Table 1. Average concentrations (ng m^{-3}) with standard deviation (S.D.) of LMW monocarboxylic acids in gas and particle phases and particle-phase fraction (F_p) in a deciduous broadleaf forest from northern Japan.

	Particle phase				Gas phase				F_p			
	Day		Night		Day		Night		Day		Night	
Organic acids	Ave.	STD	Ave.	STD	Ave.	STD	Ave.	STD	Ave.	STD	Ave.	STD
Aliphatic acids												
Formic, C_1	41	32	99	52	832	627	1075	572	0.08	0.07	0.11	0.11
Acetic, C_2	81	34	124	54	603	334	431	154	0.14	0.07	0.24	0.11
Propionic, C_3	1.5	1.1	1.5	1.3	46	33	27	14	0.04	0.03	0.05	0.02
Isobutyric, iC_4	1.1	0.8	1.3	0.7	18	11	16	8.4	0.07	0.05	0.08	0.04
Butyric, C_4	0.8	0.4	0.9	0.4	13	12	7.5	5.1	0.07	0.04	0.13	0.09
Isopentanoic, iC_5	86	72	226	419	41	20	49	17	0.63	0.19	0.69	0.14
Pentanoic, C_5	0.7	0.3	1.2	0.3	5.6	3.7	5.0	3.0	0.14	0.11	0.23	0.10
Hexanoic, C_6	1.6	1.0	4.6	2.7	12	6.3	13	8.8	0.13	0.08	0.28	0.10
Heptanoic, C_7	0.2	0.2	0.3	0.2	4.5	3.0	7.0	5.4	0.11	0.06	0.13	0.13
Octanoic, C_8	0.8	0.4	1.5	0.6	2.2	1.2	3.1	1.4	0.30	0.12	0.34	0.11
Nonanoic, C_9	9.2	5.5	13	8.1	14	24	16	18	0.50	0.22	0.47	0.17
Decanoic, C_{10}	1.6	1.2	1.3	1.9	1.7	0.9	2.6	1.2	0.49	0.21	0.34	0.23
Sub total	225		475		1594		1652					
Hydroxyacids												
Glycolic, Glyco	8.4	3.4	8.6	3.1	11	9.4	10	4.1	0.48	0.14	0.47	0.13
Lactic, Lac	38	33	90	145	24	21	23	12	0.60	0.17	0.68	0.16
Sub total	46		99		36		33					
Aromatic acid												
Benzoic, Benz	1.0	0.8	2.0	1.4	26	18	32	15	0.06	0.06	0.06	0.04