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Secondary formation of oxalic acid and related organic species from biogenic sources in a larch forest at the northern slope of Mt. Fuji

Tomoki Mochizuki[1,4], Kimitaka Kawamura[*,1,5], Yuzo Miyazaki[1], Ryuichi Wada[2], Yoshiyuki Takahashi[3], Nobuko Saigusa[3], and Akira Tani[4]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

[2]Department of Natural and Environmental Science, Teikyo University of Science, Uenohara 409-0193, Japan

[3]National Institute for Environmental Studies, Tsukuba 305-8506, Japan

[4]Graduate Division of Nutritional and Environmental Sciences, University of Shizuoka, Shizuoka 422-8526, Japan

[5]Now at Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan

*Correspondence to: K. Kawamura (kkawamura@isc.chubu.ac.jp)

Highlights:

We analyzed water-soluble organic aerosols from a larch forest

Oxalic acid was the dominant dicarboxylic acid species

Terpenes and unsaturated fatty acids are important precursors of dicarboxylic acids

Inflow of O_3 and other oxidants enhanced the formation of dicarboxylic acids

Keywords: Water-soluble organic aerosol, Oxalic acid, Unsaturated fatty acids, *Larix kaempferi* forest, Terpenes, Ozone

Abstract

To better understand the formation of water-soluble organic aerosols in the forest atmosphere, we measured low molecular weight (LMW) dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, unsaturated fatty acids (UFAs), and water-soluble organic carbon (WSOC) in aerosols from a *Larix kaempferi* forest located at the northern slope of Mt. Fuji, Japan, in summer 2012. Concentrations of dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and WSOC showed maxima in daytime. Relative abundance of oxalic acid in LMW dicarboxylic acids was on average 52% and its average concentration was 214 ng m^{-3}. We found that diurnal and temporal variations of oxalic acid are different from those of isoprene and α-pinene, whereas biogenic secondary organic aerosols (BSOAs) derived from isoprene and α-pinene showed similar variations with oxalic acid. The mass concentration ratios of oxalic acid/BSOAs were relatively constant, although a large variation in the concentrations of toluene that is an anthropogenic volatile organic compound was observed. These results suggest that formation of oxalic acid is associated with the oxidation of isoprene and α-pinene with O_3 and other oxidants in the forest atmosphere. In addition, concentrations of UFAs were observed, for the first time, to decrease dramatically during daytime in the forest. Mass concentration ratios of azelaic acid to UFAs showed a positive correlation with O_3, suggesting that UFAs are oxidized to yield azelaic acid, which may be further decomposed to oxalic acid in the forest atmosphere. We found that contributions of oxalic acid to WSOC are significantly high ranging from 3.7 to 9.7% (average 6.0%). This study demonstrates that forest ecosystem is an important source of oxalic acid and other dicarboxylic acids in the atmosphere.

1. Introduction

Low molecular weight (LMW) dicarboxylic acids (diacids) have been detected in atmospheric particles from urban, marine, forest, and polar regions (e.g., Li and Winchester, 1989; Kawamura and Bikkina, 2016; Kourtchev et al., 2009). Oxalic acid is the most abundant species of organic aerosols and major portion of oxalic acid (90%) is present in particle phase (Lim et al., 2005). LMW diacids are directly emitted from motor exhausts (Kawamura and Kaplan, 1987), biomass burning (Kawamura et al., 2013), domestic cooking (Schauer et al., 2002) and marine sources (Rinaldi et al., 2011). Furthermore, photochemical oxidations of natural organic precursors (hydrocarbons) are important sources of LMW diacids (e.g., Huang et al., 2011). Diacids are highly water-soluble (Giebl et al., 2002), and thus they can act as cloud condensation nuclei (CCN) to result in the formation of clouds having an influence on the radiative forcing and climate changes (Kanakidou et al., 2005).

Biogenic volatile organic compounds (BVOCs), such as isoprene and monoterpenes, are emitted from vegetation. In particular, plant leaves, leaf litter, and roots are important sources of BVOCs (Lin et al., 2007; Tani and Kawawata, 2008; Mochizuki et al., 2011). The annual global emissions of BVOCs were estimated to be 1000 Tg $year^{-1}$ (Guenther et al., 2012), which is several times higher than that of anthropogenic VOCs (AVOCs) including toluene (Boucher et al., 2013). Because BVOCs are highly reactive with OH radicals and O_3 (Atkinson and Arey, 2003), they are closely involved with the formation of secondary organic aerosols (SOAs). In model experiment, the amount of biogenic SOAs (BSOAs), including 2-methyltetrols as isoprene SOA tracers and pinonic acid as α-pinene SOA tracer, is several times higher than that of anthropogenic SOA on a global scale (Hallquist et al., 2009). However, BSOAs loadings from BVOC oxidation are highly uncertain (Hallquist et al., 2009).

In our previous study, we conducted simultaneous measurements of BVOCs such as isoprene and α-pinene and their oxidation products such as isoprene- and α-pinene-SOA

tracers as well as oxidants (O_3) in a *Larix kaempferi* forest (Mochizuki et al., 2015). We reported that isoprene and α-pinene emitted from the forest ecosystem are important precursors of BSOAs and that O_3 and other oxidants promote the formation of BSOAs from BVOCs just below the forest canopy. Based on laboratory experiments, BVOCs are known to contribute to the formation of LMW dicarboxylic acids (Huang et al., 2011; Kawamura et al., 2014). However, there is no study on the simultaneous measurements of BVOCs and dicarboxylic acids such as oxalic acid, other organic acids and intermediate compounds that may be dominant SOA components in the forest atmosphere.

Unsaturated fatty acids (UFAs) are emitted from terrestrial higher plants and marine algae (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987). UFAs such as oleic and linoleic acids are important sources for the formation of azelaic acid (C_9 diacid) (Yokouchi and Ambe, 1986), although simultaneous observations have never been conducted for the source and product. Longer-chain diacids can produce shorter-chain diacids via photochemical breakdown of UFAs with OH radicals (Kawamura et al., 1996; Pavuluri et al., 2015; Enami et al., 2015). However, there is no study on time-resolved diurnal variations of UFAs and their oxidation products (mid- and short-chain diacids) and their controlling factors in the forest atmosphere.

In the present study, to better understand the formation of oxalic acid and controlling factors that control the formation of oxalic acid in the forest atmosphere, we conducted simultaneous measurements of LMW diacids, oxocarboxylic acids (oxoacids), α-dicarbonyls, UFAs, and water soluble organic carbon (WSOC) in aerosols collected at the site of a *L. kaempferi* forest on the northern foothill of Mt. Fuji. The results of BVOCs, AVOCs, biogenic SOA tracers, and O_3 concentrations at the same time were reported previously (Mochizuki et al., 2015). Here, we report diurnal and temporal variations of diacids and related compounds and compositions of diacids. We discuss sources of oxalic acid and major contributors to the formation of oxalic acid over a Japanese larch forest.

2. Experimental

The Fuji-Hokuroku Flux Research site (35º26' N, 138º45' E) is located in Fujiyoshida city, Yamanashi, Japan on the northern foothill of Mt. Fuji (Fig. A1). *L. kaempferi* was planted in the area of over 150 ha. Almost all trees were 55 years old. The ree canopy height was approximately 20–25 m. The major understory is *Dryopteris crassirhizoma* (fern species) in June to August. Continuous measurements of ambient temperature, solar radiation, wind direction, and wind speed were conducted simultaneously on a meteorological tower (32 m). Details of the site information have been described in Urakawa et al. (2015).

Total suspended particulate matter (TSP) was collected using a high-volume air sampler (AS-810B, Kimoto Electric, Japan) and precombusted (450 °C, 6 h) quartz-fiber filters (8 inch × 10 inch) (Tissuquartz 2500QAT-UP, Pallflex, USA) at a flow rate of 1200 L min^{-1} on the steel scaffold for tree survey at a height level of 16 m within the Japanese larch canopy. The samples were collected every 3 hours (06:00–09:00, 09:00–12:00, 12:00–15:00 and 15:00–18:00 LT) in daytime (n = 20) and 12 hours (18:00–06:00 LT) in nighttime (n = 4). Before and after the sampling, each filter was placed in a clean glass bottle with a Teflon-lined screw cap. After the sampling, filters were stored in a freezer at -20°C prior to analysis. Samplings were carried out on 5, 10, and 15–17 July 2012. We focused on 5 days to investigate the formation of oxalic acid and their controlling factors. Large variations of concentration of BVOCs, AVOCs, and O_3 and ambient temperature, solar radiation, wind speed, and wind direction were observed in the specific 5 days (Fig. A2) (Mochizuki et al., 2015).

Details of the analytical procedure of diacids, oxoacids, α-dicarbonyls and unsaturated fatty acids were described in Kawamura et al. (1996) and Mochida et al. (2003a). Briefly, water-soluble organic compounds were extracted from the filter portion (12.6 cm^2) with ultrapure water (resistivity of > 18.2 MΩ cm). To remove particles, the extracts were passed

through quartz wool packed in a Pasteur pipette. After adjustment of pH to 8.5–9.0 with 0.05 M KOH solution, the filtrates were dried using a rotary evaporator under vacuum at 50 °C. Organic acids and α-dicarbonyls were derivatized to dibutyl esters and dibutoxy acetals with 14% BF_3/n-butanol at 100 °C for 1 h. The derivatives were identified and quantified using a capillary gas chromatograph (Agilent GC7890A, Agilent, USA) and GC-mass spectrometer (Agilent GC7890A and 5975C MSD, Agilent, USA). Recoveries of authentic dicarboxylic acids (C_2–C_6) spiked to a quartz filter were 78–91%. Analytical errors were within 9% based on replicate analyses using same sample filter (different parts). We confirmed that levels of field blanks were less than ~5% (diacids), ~7% (oxoacids), and ~9% (α-dicarbonyls) of those of ambient aerosols.

For the measurements of water-soluble organic carbon (WSOC), a portion of filter was extracted with ultrapure water under ultrasonication. The water extracts were filtered through a membrane disk filter (0.22 μm, Millipore Millex-GV, Merck, USA) and then analysed using a total organic carbon analyser (Model TOC-Vcsh, Shimadzu) (Miyazaki et al., 2011).

Concentrations of isoprene and α-pinene and their oxidation products (isoprene-SOA tracers: 2-methylglyceric acid and 2-methyltetrols, α-pinene-SOA tracers: pinonic acid and 3-methyl-1,2,3-butanetricarboxylic acid) and inorganic ions (SO_4^{2-}) and pH values of the water extracted samples were reported in Mochizuki et al. (2015) (Fig. A2).

3. Results and discussion

3.1 Diurnal and temporal variations of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls

We identified straight chain saturated (C_2–C_{10}) diacids, oxoacids (ωC_2–ωC_9 and pyruvic: Pyr), and α-dicarbonyls (glyoxal: Gly and methylglyoxal: MeGly) in the ambient aerosols collected from the *L. kaempferi* forest (Table 1). Total concentrations of diacids, oxoacids and α-dicarbonyls started to increase in the morning with a maximum around at noontime or in the

afternoon (Fig. 1). Average concentration of total diacids in daytime was 424 ng m^{-3}, which is several times or one order of magnitude higher than those of total oxoacids (72 ng m^{-3}) and α-dicarbonyls (13 ng m^{-3}). Oxalic acid accounts for 52% of total straight chain diacids (C_2-C_{10}), followed by malonic acid (23%).

Diurnal and temporal variations of oxalic acid in *L. kaempferi* forest aerosols are provided in Fig. 2. Oxalic acid concentrations started to increase in the morning with a maximum around at noontime or in the afternoon, and then decreased to minimize in nighttime. Concentration of oxalic acid peaked ca. 3 hours behind the peaks of isoprene and α-pinene (Fig. 1 and Fig. A2). Concentrations of oxalic acid (76 – 458 ng m^{-3}) as well as other diacids (61 – 482 ng m^{-3}), oxoacids (19 – 180 ng m^{-3}), and α-dicarbonyls (5 – 33 ng m^{-3}) on 10 and 17 July were higher than those (oxalic acid: 35 – 202 ng m^{-3}, other diacids: 18 – 247 ng m^{-3}, oxoacids: 8 – 55 ng m^{-3}, and α-dicarbonyls: 2 – 15 ng m^{-3}) on 15 and 16 July (Fig. 2 and Fig. A3). Such diurnal and temporal trends of oxalic acid are similar to those of O_3, toluene, and BSOAs (Fig. 2 and Fig. A2).

This site is located approximately 8 km northwest of the urban area of Fuji-Yoshida city. Particles containing oxalic acid of anthropogenic origin are likely transported from the urban area. To differentiate the local formation of oxalic acid in this site and the atmospheric transport from the surrounding urban areas, we show diurnal and temporal variations in the mass concentration ratios of oxalic acid to BSOAs (C_2/BSOAs) in Fig. 2. In our previous study, production rate of BSOA tracers from isoprene and α-pinene is around 3 hours in this forest. This time scale is comparable to the production rate of oxalic acid from isoprene via O_3 and OH radical oxidation in laboratory experiment (Huang et al., 2011; Kawamura et al., 2014). The wind direction in daytime on 10 July was mainly northeast, indicating an inflow of urban air from the surrounding urban area (Fig. A2e). Conversely, the wind direction in daytime on 17 July was mainly northwest, indicating an inflow of air mass from the surrounding forest area. However, the ratio of C_2/BSOAs did not differ between these days (3

on 10 July, 2 on 17 July) (Fig. 2). These results suggest that transport of oxalic acid from the surrounding urban area is rather minor in this forest. On the other hand, high ratio of C_2/BSOAs (average: 11) was observed on 15 July. Because wind speed on 15 July (average 4.2 m s^{-1}) was higher than that on 5, 10, 16 and 17 July (average: 1.9 m s^{-1}), oxalic acid may have been transported from the outside of this forest on 15 July. In order to evaluate the factors controlling the production of oxalic acid in a *L. kaempferi* forest, the data on 15 July were excluded from analysis. The factors controlling the production of oxalic acid from isoprene and α-pinene via photochemical reactions with O_3 and other oxidants will be discussed in section 3.2, except for the date of 15 July.

3.2 Production of oxalic acid from isoprene and α-pinene

In our present study, a positive correlation was observed between methylglyoxal and oxalic acid (r^2 = 0.66) and glyoxal and oxalic acid (r^2 = 0.80) in a *L. kaempferi* forest (Fig. 3). Oxalic acid is a product of the chain reactions of α-dicarbonyls as suggested by a strong relation between oxalic acid and α-dicarbonyls. During the same sampling time, isoprene and α-pinene accounted for 23% and 44% of total terpenoids, respectively (Mochizuki et al., 2015); the former is mainly emitted from fern species (*D. crassirhizoma*) whereas the latter is from *L. kaempferi* (Mochizuki et al., 2014). Laboratory experiments demonstrated that aqueous or gas phase oxidation of isoprene (Paulot et al., 2009; Carlton et al., 2009; Huang et al., 2011; Kawamura et al., 2014) and α-pinene (Fick et al., 2003; Kawamura et al., unpublished data, 2016) with OH radical and/or O_3 produce methylglyoxal and glyoxal. OH radical reactions of methylglyoxal and glyoxal lead to the production of oxalic acid (Carlton et al., 2007, Tan et al., 2009; Tan et al., 2010).

In addition, oxalic acid showed a significant correlation with O_3 (r^2 = 0.65) (Fig. 4a). In order to examine the effect of gaseous oxidants on the formation of oxalic acid from isoprene and α-pinene, we plotted the mass concentration ratios of oxalic acid to isoprene plus

206 α-pinene (oxalic acid/(isoprene+α-pinene)) against O_3 concentrations (Fig. 4b). Because
207 oxidants such as OH radicals were not measured in this study, O_3 is used here as an indicator
208 of the oxidant concentrations. A strong positive correlation was found between the mass
209 concentration ratios of oxalic acid to isoprene plus α-pinene (oxalic acid/(isoprene+α-pinene))
210 and O_3 concentrations (r^2 = 0.69) (Fig. 4b). These results suggest that O_3 and other oxidants
211 promote the formation of oxalic acid from isoprene and α-pinene in the forest of *L. kaempferi*.
212 Aerosol acidity contributes to the formation of SOA from aldehydes such as glyoxal and
213 isoprene through acid-catalyzed heterogeneous reactions (e.g., Jang et al., 2002). Sorooshian
214 et al. (2006) and Ervens et al. (2008) reported that aerosol aqueous phase is important for the
215 formation of oxalic acid from isoprene. In this study, we found that oxalic acid negatively
216 correlated with pH (range: 4.2 – 6.4) of the water extracts from aerosol samples (r^2 = 0.75),
217 but positively correlated with SO_4^{2-} (r^2 = 0.38). Further, key intermediates such as
218 methylglyoxal plus glyoxal weakly correlated with SO_4^{2-} (r^2 = 0.14). Based on the field
219 measurement, Yu et al. (2005) reported that oxalic acid in urban aerosols correlate with sulfate.
220 Conversely, Tan et al. (2009, 2010) reported that acidity is not needed for oxalic acid
221 formation from glyoxal and related compounds in aqueous phase. Production of oxalic acid
222 and sulfate may simultaneously occur in the aqueous phase. In addition, oxalic acid did not
223 show a correlation with relative humidity (RH). Zhang et al. (2011) reported that RH does not
224 affect SOA yields via the oxidation of isoprene. In contrast, Tillmann et al. (2010) reported
225 that high humidity enhances the SOA yields from α-pinene via ozonolysis. Higher RH may
226 promote the partitioning of gaseous precursors of oxalic acid to aerosol phase and may
227 enhance the acid-catalyzed heterogeneous reactions. Our results suggest that aerosol acidity in
228 aqueous phase may play an important role in the formation of oxalic acid from isoprene and
229 α-pinene in the forest atmosphere.
230 Malonic/succinic acid (C_3/C_4) ratio has been often used as an indicator of photochemical
231 processing (aging) of organic aerosols, during which the C_3/C_4 ratio increases (e.g.,

Kawamura and Ikushima, 1993). The C_3/C_4 ratios ranged from 1.2 to 1.8 (average: 1.4) in this study. However, we did not find any diurnal and temporal trends of C_3/C_4 ratio during the measurement period, suggesting that photochemical aging of organic aerosols is not significant during an early stage of photochemical processing of aerosols although the formation of oxalic acid is important in the forest atmosphere. In addition, concentrations of oxalic acid did not show any correlations with ambient temperature (r^2 = 0.0013) and solar radiation (r^2 = 0.0001), suggesting that these parameters are not important for the formation of oxalic acid in the forest atmosphere. Our results suggest that O_3 is one of major contributors to the formation of oxalic acid from isoprene and α-pinene.

3.3 Possible formation of oxalic acid from unsaturated fatty acids

We identified unsaturated fatty acids (myristoleic: $FA_{14:1}$, palmitoleic: $FA_{16:1}$, oleic: $FA_{18:1}$, and linoleic: $FA_{18:2}$) in the ambient aerosols collected under the canopy of the *L. kaempferi* forest (Table 1). UFAs are dominant lipid class compounds that are generally present in terrestrial higher plants and algae. UFAs in TSP samples showed higher concentrations in nighttime with a drastic decline in daytime (Fig. 5). Because of a double bond, UFAs can be easily oxidized by O_3 and OH radicals in the atmosphere in daytime (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987).

Azelaic acid (C_9) in the *L. kaempferi* forest is a dominant species in the range of C_6-C_{10} diacids (Table 1). UFAs such as $FA_{18:1}$ and $FA_{18:2}$ have a double bond at C9-position. Azelaic and 9-oxononanoic acids are produced by the oxidation of oleic and linoleic acids via the cleavage of a double bond at C9-position. ω-Oxidation of 9-oxononanoic acid results in azelaic acid. Concentration of azelaic acid had the highest value around noon (Fig. 5). Fig. 5 shows diurnal and temporal variations of the mass concentration ratios of azelaic acid to oleic plus linoleic acids ($C_9/(FA_{18:1}+FA_{18:2})$). The ratios started to increase in the morning with a maximum around noontime or in the afternoon. The ratios of $C_9/(FA_{18:1}+FA_{18:2})$ showed a

variation pattern similar to that of O_3 concentrations with a good correlation (r^2 = 0.56) (Fig. 6). Azelaic acid can be derived from oleic and linoleic acids via oxidation with oxidants (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987; Noureddini and Kanabur, 1999). We suggest that C_9 is mainly produced by the oxidation of oleic and linoleic acids emitted from the forest ecosystem via the oxidation with O_3 and other oxidants. Because longer-chain diacids (C_3–C_9) can produce oxalic acid via photochemical breakdown with OH radicals (Kawamura et al., 1996; Pavuluri et al., 2015; Enami et al., 2015), UFAs also contribute to the formation of oxalic acid in the *L. kaempferi* forest.

3.4 Comparison with previous studies

Average contributions of oxalic acid (C_2) to total straight chain saturated diacids (C_2-C_{10}) in daytime was 50% (range: 41–65%). Contributions of C_2 to C_2-C_{10} is lower than those of the aged organic aerosols from Chichi-jima Island (81%) in the remote western North Pacific (Mochida et al., 2003b) and Okinawa Island (74%) in the western North Pacific Rim (Kunwar and Kawamura, 2014a). On the other hand, this level is comparable to those reported from the western North Pacific during the period of high biological activity in summer (Bikkina et al., 2014) and from Tokyo in summer (55%) via photo-oxidation of anthropogenic VOCs (Kawamura and Yasui, 2005). Our result suggests that oxalic acid in this site is less aged and mainly produced via the oxidation of local BVOCs and UFAs.

Average concentration of oxalic acid in daytime was 214 ng m^{-3}. The mean concentration level of oxalic acid in TSP in the *L. kaempferi* forest is comparable to or higher than those reported from mixed coniferous/deciduous forest in Hungary (196 ng m^{-3} in $PM_{2.5}$) (Kourtchev et al., 2009) and broad-leaved forest in Taiwan (161 ng m^{-3} in $PM_{2.5}$) (Tsai and Kuo, 2013). On the other hand, this level is one order of magnitude higher than those from the remote site in high Arctic Alert, Canada (17 ng m^{-3} in TSP) (Kawamura et al., 2010), but lower than those from the urban areas in 14 cities of China (513 ng m^{-3} in PM2.5) (Ho et al.,

2007) and from Tokyo (270 ng m^{-3} in TSP) (Kawamura and Ikushima, 1993). These comparisons demonstrate that larch forest is an important source of oxalic acid in the atmosphere.

Monocarboxylic acids such as acetic and formic acids are produced in the atmosphere by photo-oxidation of BVOCs such as isoprene, in which acetic acid is key intermediate in the oxidation of isoprene (Ervens et al., 2008). These organic acids exist in the atmosphere as both gases (Kawamura et al., 2000; Khwaja et al., 1995; Liu et al., 2012; Yuan et al., 2015) and aerosols (Khwaja et al., 1995; Kawamura et al., 2000; Li and Winchester, 1989; Liu et al., 2012; Mochizuki et al., 2016). Although we did not measure acetic and formic acids in this study, we presume that acetic and formic acids are abundantly present in the forest atmosphere in both gas and particle phases.

Fig. 7 shows diurnal and temporal variations of concentrations of WSOC and mass concentration ratio of oxalic acid to WSOC (C_2/WSOC) for the aerosol samples collected at the *L. kaempferi* forest. WSOC concentrations started to increase in the morning with a maximum around at noontime or in the afternoon. Higher concentrations of WSOC were observed on 10 and 17 July. The variation pattern of WSOC concentrations was similar to that of oxalic acid (r^2 = 0.64). Overall, the peak ratios of C_2/WSOC were observed in daytime, which is consistent with O_3 concentration. Although a weak correlation was observed between the concentrations of WSOC and O_3 (r^2 = 0.15) (Fig. 8a), we found a good positive correlation between the ratios of C_2/WSOC and O_3 (r^2 = 0.41) (Fig. 8b). We suggest that secondary formation of oxalic acid from BVOCs and UFAs emitted from the forest ecosystem enhances its contribution to WSOC in the forest aerosols. The mean ratio of C_2/WSOC was 6% (range: 3.7 – 9.7%). This level is higher than that reported in aerosol samples from the western North Pacific (4.4% in TSP) (Bikkina et al., 2015), but lower than those from Okinawa Island (14% in TSP) (Kunwar and Kawamura, 2014a; Kunwar et al., 2014b) and 14 cities of China (7% in PM2.5) (Ho et al., 2007).

4. Conclusions

Dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and UFAs were detected in organic aerosols in a larch (*L. kaempferi*) forest. Oxalic acid was dominant organic acid followed by malonic acid. Higher concentrations of oxalic acid and key intermediate compounds were observed in daytime. The peak concentration of oxalic acid appeared after the peaks of isoprene and α-pinene, whereas BSOAs such as isoprene and α-pinene oxidation products and O_3 showed strong positive correlations with oxalic acid. Although oxalic acid is not only derived from biogenic VOCs but also from anthropogenic VOCs, isoprene and α-pinene were dominant sources of oxalic acid in the forest aerosols. O_3 and other oxidants enhanced the formation of oxalic acid in a *L. kaempferi* forest. In addition, oxalic acid is negatively correlated with pH of the water extracts from aerosol samples, and is positively correlated with SO_4^{2-}. Oxalic acid did not show any correlations with temperature, solar radiation, and relative humidity. Our results suggest that aerosol acidity of aqueous phase particle plays an important role in the formation of oxalic acid from isoprene and α-pinene in the forest atmosphere. In addition, lower concentration of UFAs was observed in daytime, whereas concentrations of azelaic acid that is a specific oxidation product of oleic and linoleic acids were higher in daytime. The mass concentration ratio of azelaic acid to UFAs showed a positive correlation with O_3, suggesting that azelaic acid is derived from UFAs. Oxalic acid is a product of the chain reactions of azelaic acid. Oxalic acid accounted for 6% of WSOC in a *L. kaempferi* forest. Our results suggest that forest ecosystem is an important source of oxalic acid and other dicarboxylic acids in the atmosphere.

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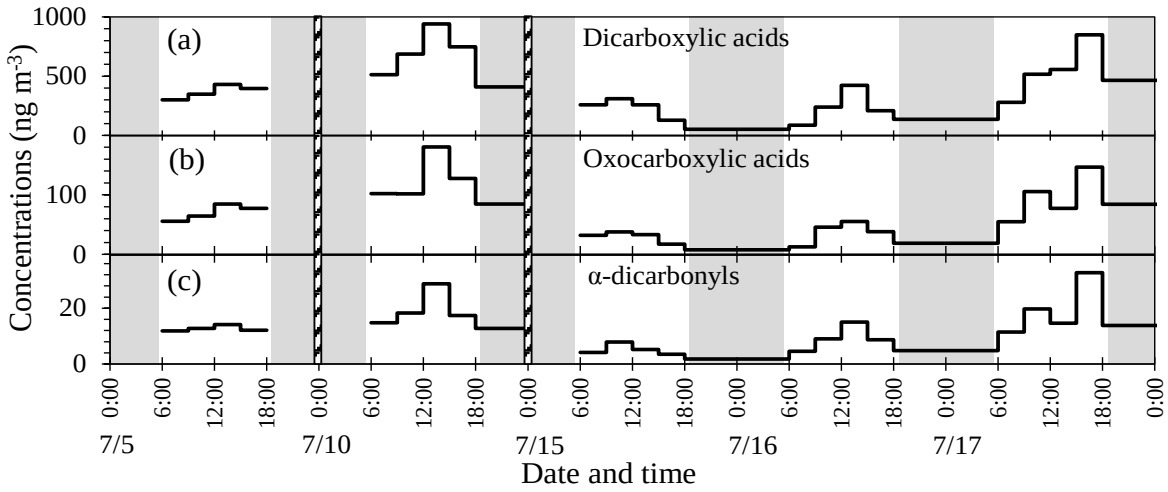
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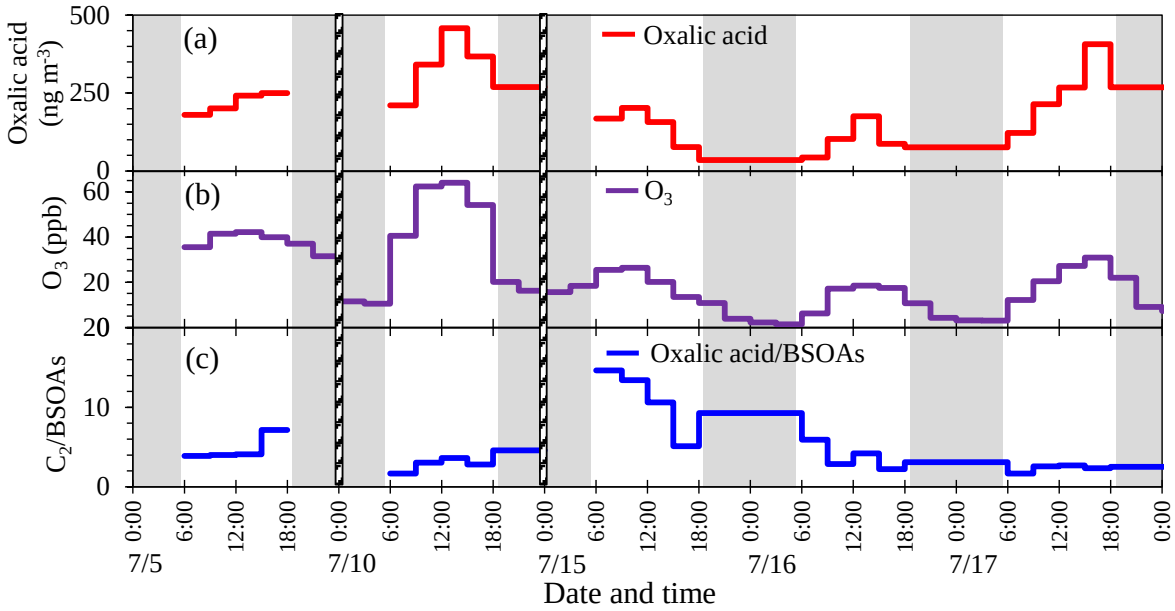
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525 Fig. 1. Diurnal and temporal variations in the concentrations of (a) total dicarboxylic acids,
526 (b) oxocarboxylic acids, and (c) α-dicarbonyls in a *L. kaempferi* forest. Shaded areas indicate
527 nighttime.

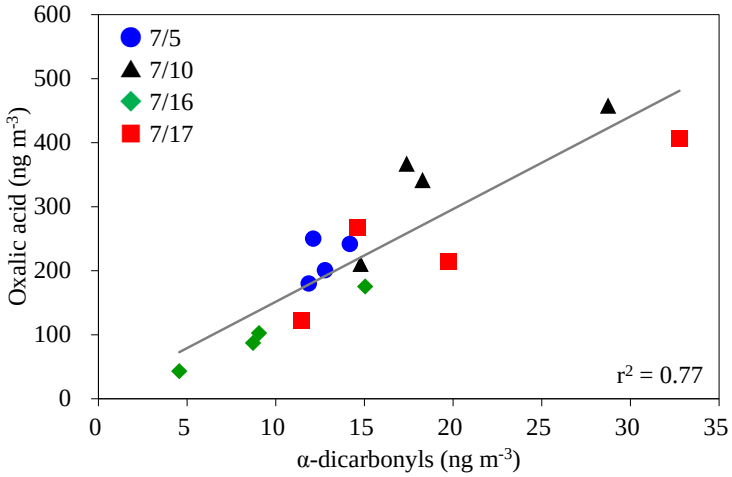
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529

530 Fig. 2. Diurnal and temporal variations in the concentrations of (a) oxalic acid and (b) O_3, and
531 (c) mass concentration ratios of oxalic acid/BSOAs in a *L. kaempferi* forest. Shaded areas
532 indicate nighttime.

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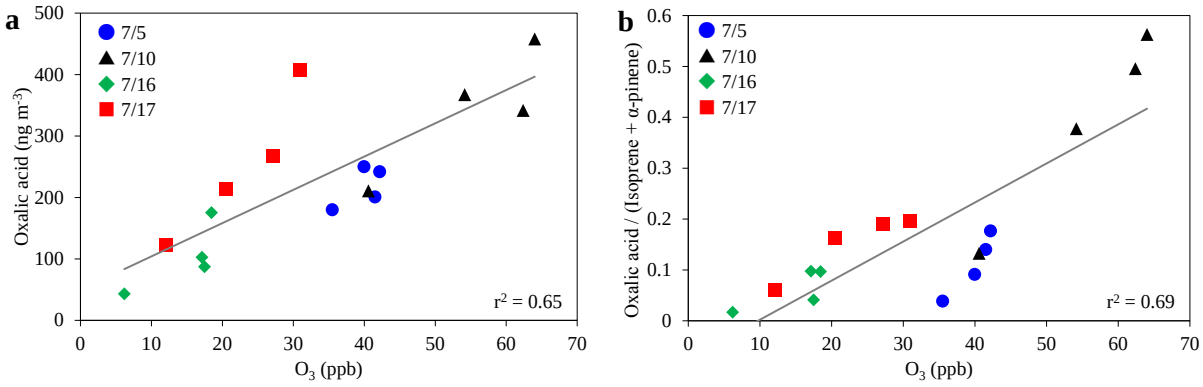


534

535 Fig. 3. Correlation plot of oxalic acid and α-dicarbonyls.

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538

539 Fig. 4. Correlation plots of (a) oxalic acid with O_3 and (b) mass concentration ratio of oxalic

540 acid to isoprene plus α-pinene (oxalic acid/(isoprene+α-pinene)) with O_3.

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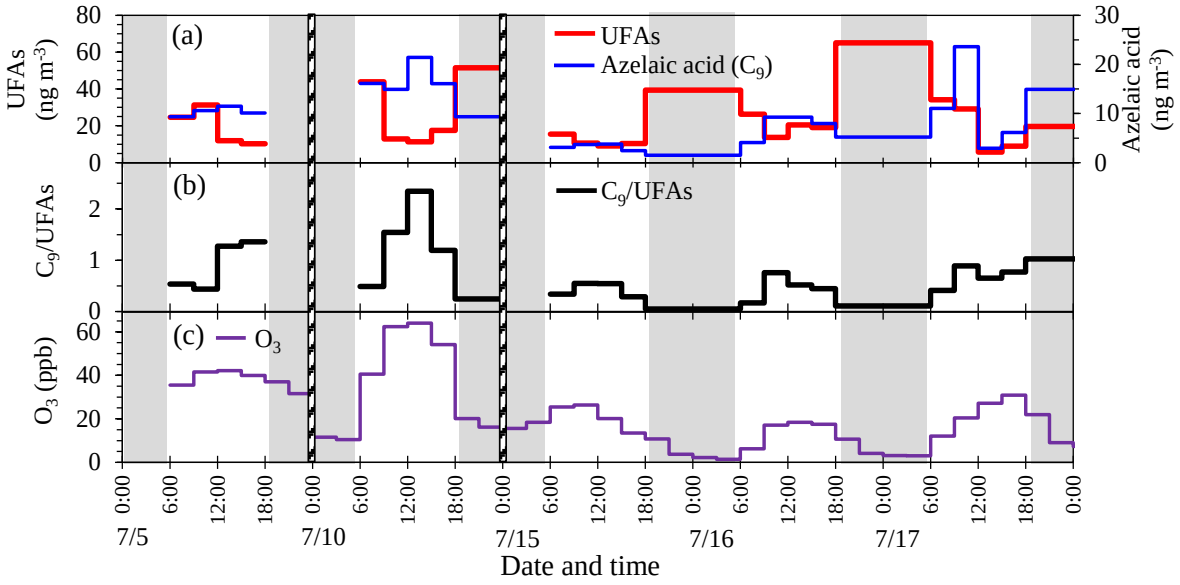


Fig. 5. Diurnal and temporal variations in (a) concentrations of unsaturated fatty acids (UFAs: oleic plus linoleic acids) and azelaic acid (C_9), (b) mass concentration ratios of azelaic acid/UFAs (C_9/UFAs), and O_3 concentrations in a *L. kaempferi* forest. Shaded areas indicate nighttime.

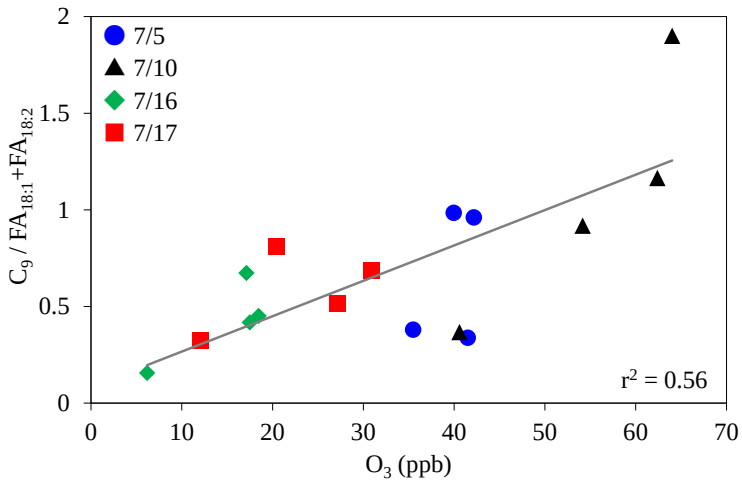
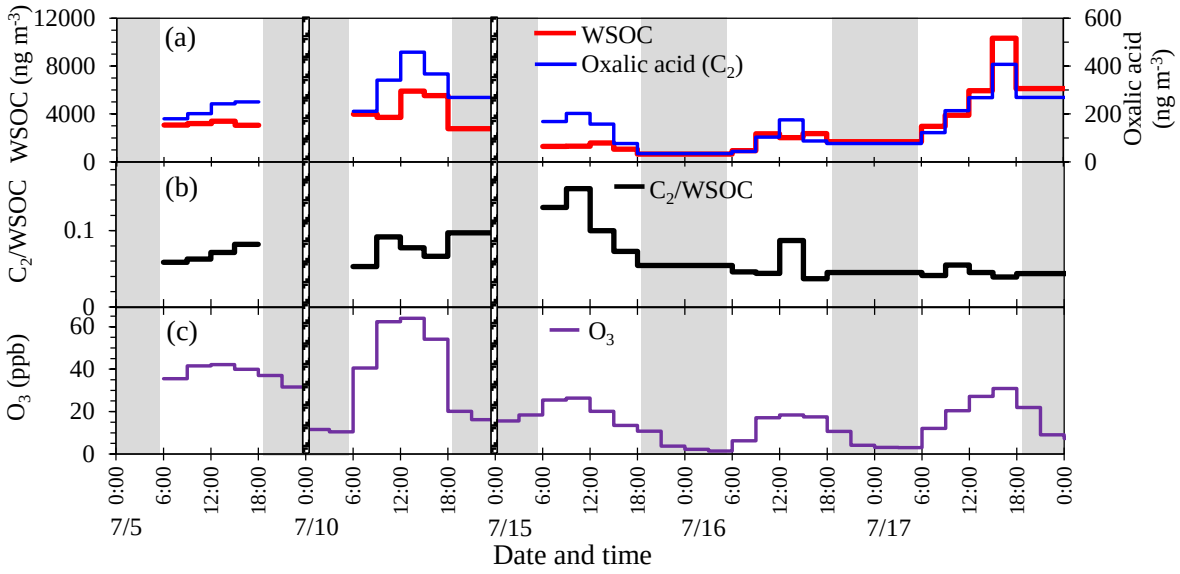


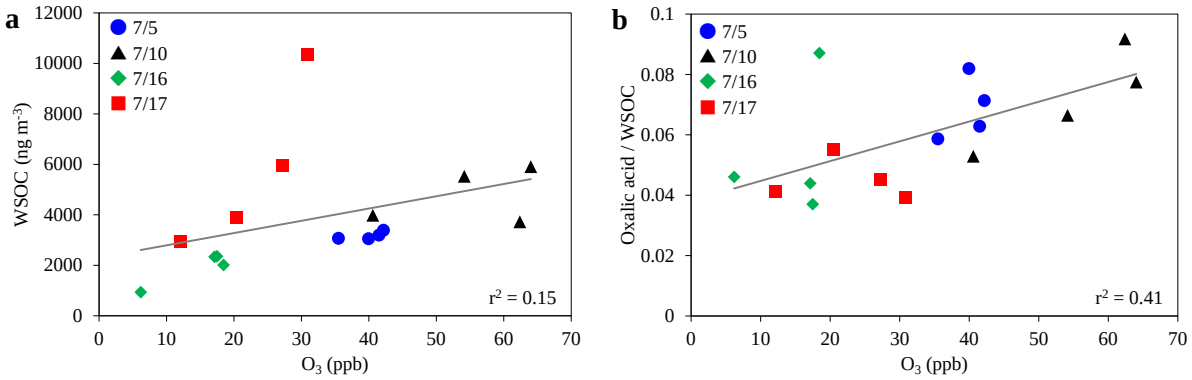
Fig. 6. Correlation plots of concentration ratios of azelaic acid (C_9) to oleic plus linoleic acids ($C_9/(FA_{18:1}+FA_{18:2})$) as a function of O_3.



552

553 Fig. 7. Diurnal and temporal variations in (a) concentrations of water-soluble organic carbon
554 (WSOC) and oxalic acid, (b) mass concentration ratios of oxalic acid to WSOC (C_2/WSOC)
555 and (c) O_3 concentrations in a *L. kaempferi* forest. Shaded areas indicate nighttime.

556



557

558 Fig. 8. Correlation plots of (a) water soluble organic carbon (WSOC) and (b) mass
559 concentration ratios of oxalic acid to WSOC (C_2/WSOC) as a function of O_3.

560

561

562 Table 1. Average concentrations (ng m^{-3}) and standard deviation (S.D.) of low molecular
563 weight dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and unsaturated fatty acids in a
564 *L. kaempferi* forest.

Compounds	Daytime		Nighttime	
	Average	S.D.	Average	S.D.
Dicarboxylic acids				
Oxalic, C_2	214	111	162	124
Malonic, C_3	100	63.9	52.6	42.0
Succinic, C_4	75.0	44.5	32.9	24.1
Glutaric, C_5	11.4	7.9	5.2	3.8
Adipic, C_6	4.4	3.7	2.0	1.5
Pimeric, C_7	1.7	2.2	1.4	1.7
Suberic, C_8	4.4	2.9	1.5	1.2
Azelaic, C_9	9.9	6.1	7.7	5.8
Sebacic, C_{10}	3.3	5.5	0.5	0.2
Total C_2-C_{10}	424		266	
Oxocarboxylic acids				
Glyoxylic, ωC_2	18.8	11.2	12.1	10.0
3-Oxopropanoic, ωC_3	7.5	5.2	5.1	4.4
4-Oxobutanoic, ωC_4	13.0	9.1	7.5	7.4
5-Oxopentanoic, ωC_5	2.6	1.6	1.6	1.3
6-Oxohexanoic, ωC_6	2.2	1.4	2.6	2.1
7-Oxoheptanoic, ωC_7	7.7	4.3	5.5	4.7
8-Oxooctanoic, ωC_8	6.3	4.1	4.7	4.4
9-Oxononanoic, ωC_9	2.6	1.7	2.8	2.0
Pyruvic, Pyr	11.8	8.7	7.0	6.5
Total oxoacids	72		49	
α-Dicarbonyls				
Glyoxal, Gly	5.9	3.8	3.7	2.6
Methylglyoxal, MeGly	7.4	4.0	4.6	3.3
Total α-dicarbonyls	13		8	
Unsaturated fatty acids				
Myristoleic, $FA_{14:1}$	0.8	0.8	1.9	0.9
Palmitoleic, $FA_{16:1}$	5.4	4.8	8.9	5.5
Linoleic, $FA_{18:2}$	5.9	4.4	12.8	5.5
Oleic, $FA_{18:1}$	12.4	6.5	31.1	17.9
Total unsaturated fatty acids	25		55	

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