Dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in atmospheric aerosols from Mt. Fuji, Japan: Implication for primary emission versus secondary formation

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Abstract

Aerosol samples were collected at the summit of Mt. Fuji in July-August 2009 and analyzed for diacids and related compounds together with major ions to decipher the sources and formation process of organic aerosols in the free troposphere. Molecular distributions of diacids showed the predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids. The average concentration of total diacids is ten times higher in whole-day samples than night-only samples due to the uplift of planetary boundary layer in daytime, suggesting the daytime formation of diacids in the uplifted ground-level air mass along the mountain slope. A strong correlation is found between C_4 and levoglucosan in whole-day and nighttime samples. Liquid water content (LWC) shows strong correlations in nighttime with anthropogenic and biogenic secondary organic aerosol (SOA) tracers (e.g., adipic (0.90, $p<0.5$) and phthalic acids (0.93, $p<0.05$) and 3-methyl 2,3,4-trihydroxy-1-butene (0.95, $p<0.05$), suggesting that aqueous-phase chemistry is important for the formation of water-soluble organic aerosols in the free troposphere. In whole-day samples, LWC is strongly correlated with organic carbon ($r=0.97$, $p<0.05$), and isoprene-SOA tracers such as methylthreitol (0.96, $p<0.05$), methylerythritol (0.97, $p<0.05$), 2-methylglyceric acid (0.94, $p<0.05$) and glycolic acid (0.98, $p<0.05$), suggesting that daytime SOAs are mainly from the oxidation of isoprene emitted from the regional forests on the foothill of Mt. Fuji. A strong correlation between LWC and glycolic acid further suggests that isoprene is the main precursor for the production of oxalic acid via glycolic acid as intermediate. This study supports the heterogeneous formation of diacids in the free troposphere.

Highlights: Max 85 characters including space per bullet

Molecular distributions of diacids, oxoacids and α-dicarbonyls over Mt. Fuji, Japan.

This study represents lower levels of tropospheric organic aerosols in nighttime.

Heterogeneous aqueous phase formation of diacids is important in daytime.

Key words: Diacids, oxoacids, α-dicarbonyls, acid-catalyzed heterogeneous reaction, Mt. Fuji

1. Introduction

Tropospheric aerosol particles can play essential roles in regional and global climate. They are produced via both natural and anthropogenic processes. Organic constituents in aerosols are recently paid more attention because they are recognized to account a substantial fraction of atmospheric aerosols, up to 50% of particle mass (Seinfeld and Pandis, 1998). In particular, water-soluble organic species can influence the hygroscopic properties of atmospheric aerosols (Boreddy et al., 2014, Kanakidou et al., 2005). Water-soluble organic aerosols may also cause health problems to human (Poschl, 2005)

Dicarboxylic acids (diacids) and related compounds are important in the atmosphere. Total diacids account for 5 to 10% of the particulate carbon in the atmosphere (Kunwar and Kawamura, 2014a, b; Kerminen et al., 2000). Oxalic acid and other short chain diacids are produced in the cloud and aerosol by aqueous phase reaction (Warneck. 2003; Carlton et al., 2007). There are various sources of diacids in the atmosphere. Automobile emission, fossil fuel combustion, meat cooking operation, biomass burning, and atmospheric oxidation of biogenic and anthropogenic organic compounds are the main source of diacids in aerosols (Kawamura et al., 1996; Kawamura et al., 2001; Mochida et al., 2003; Legrend et al., 2007; Wang et al., 2013; Deshmukh et al., 2016; Kunwar et al., 2017). Previous studies reported that the presence of dicarboxylic acids in atmospheric particles affect both deliquescence relative humidity and hygroscopicity of the aerosol particles (Cruz and Pandis, 1998; Brooks et al., 2002)

Diacids and related compounds have been studied in the urban, marine, and remote areas (Deshmukh et al., 2015, Pokhrel et al., 2015, 2016; Ho et al., 2007; Wang et al., 2010). However, their distributions have been rarely studied in the high mountain regions of the free troposphere (Kawamura et al., 2013), in which aerosols are largely influenced by long-range atmospheric transport. High levels of both primary (POA) and secondary organic aerosols (SOA) with a dominance of diacids were observed at a summit of Mt. Tai located in the North China Plain, where crop-residue burning is very common on the ground level in early summer followed by long-range atmospheric transport (Kawamura et al., 2013).

In this study, we performed the observation study on water-soluble organic aerosols at the summit of Mt. Fuji (elevation, 3776 m) in Japan during summer. In nighttime, the summit of Mt. Fuji is present in the free troposphere whereas it is within the planetary boundary layers in daytime. Ground surface aerosols and their precursors can be uplifted along the mountain slope to the summit in daytime, and thus Mt. Fuji represents the free tropospheric air quality of East Asia. Therefore, the summit of Mt. Fuji is considered as an ideal site for

the study of organic aerosols interacted between ground level and the free troposphere (Fu et al., 2014). Based on the molecular distributions of diacids, oxoacids, α-dicarbonyls together with major ions, organic and elemental carbon, back trajectory analysis, liquid water content (LWC) and SOA tracers, we discuss the sources and formation mechanisms of diacids and related compounds over Mt. Fuji.

2. Experimental

2.1. Sampling site

Total suspended particle (TSP) samples (n=8) were collected at the summit of Mt. Fuji (35.4° N, 138.7° E) during the summer of 2009. Mt. Fuji is the highest mountain in Japan and is facing the Pacific coast of Honshu Island (Figure 1). Sampling was performed for one month from 27 July to 26 August 2009 when climbing is permitted. Samples were collected using two high-volume samplers (Kimoto AS- 810B) with a flow rate of 1.0 m^3 min^{-1} using pre-combusted (450 °C for 6 h) quartz fiber filters (20 cm × 25 cm, Pallflex 2500QAT-UP). Nighttime samples (n=4, MF07−10) were collected during 23:00−8:00 from 27 July to 12 August on a basis of 3 to 4 days. Whole-day samples (n=4, MF12−15) were collected on a basis of 2 to 4 days during 13-26 August. After the sampling, each filter was placed in a pre-combusted (450 °C for 6 hrs) glass jar with a Teflon-lined screw cap and kept in a freezer room at −20 °C before analysis. A field blank was collected by placing a clean filter on the filter cartridge for a few seconds without pumping.

2.2. Chemical analysis

Filter samples were analyzed for water-soluble diacids, oxoacids, and α-dicarbonyls by the method reported previously (Kawamura and Ikushima, 1993; Kunwar and Kawamura, 2014b). A filter aliquot with known area was extracted with organic-free pure water. Carboxylic acids and α-dicarbonyls in the extracts were derivatized with 14% BF_3/n-butanol to butyl esters and/or dibutoxy acetals. Those derivatives were determined using capillary gas chromatography (GC; HP 6890). The GC peaks were identified by comparing GC retention times with those of authentic standards, and the peak identifications were confirmed by mass spectral examination using a GC/mass spectrometry (GC/MS) system. Both laboratory and field blanks were analyzed. The concentrations of all species reported here are corrected for blanks. We also performed the recovery test by spiking authentic dicarboxylic acids to quartz filter. The recoveries of spiked diacids were 90% for oxalic acid (C_2) and more than 97% for

C_3, C_4, C_5 and C_6 diacids. The standard error of reproducibility in the measurements of major diacids (C_2, C_3, C_4, C_5, and C_6) was ca. 10%.

Levoglucosan and isoprene- and monoterpenes-SOA tracers were measured by GC/MS after derivatization of the solvent extracts (dichloromethane/methanol 2:1) with N,O-bis(trimethylsilyl)trifluoroacetamide. The methods and the data are reported in Fu et al. (2014).

Major cations and anions were measured using an ion chromatograph (761 Compact IC, Metrohm, Switzerland). A detailed method can be found in Kunwar and Kawamura (2014a).

2.2. Meteorological Parameter

No rainfall events were recorded during the campaign period. Fog and cloud events occurred in nighttime and early in the morning. Figure 2 shows the changes in meteorological parameters such as average sunshine hours, relative humidity and ambient temperature recorded during the sampling period.

3. Results and Discussion

3.1. Molecular distributions of dicarboxylic acids, oxocarboxylic acids, benzoic acid and α-dicarbonyls

Table 1 summarizes the average concentrations of diacids, oxoacids, benzoic acid and α-dicarbonyls with standard deviations in the TSP samples collected from Mt. Fuji. We detected a homologous series of α, ω–dicarboxylic acid (C_2-C_{12}), unsaturated diacids (maleic, M; fumaric, F; methylmaleic, mM: phthalic, Ph; isophthalic, iPh and terephthalic, tPh), multifunctional diacids (hydroxysuccinic acid, hC_4; ketomalonic, kC_3; and ketopimelic, kC_7), ω-oxocarboxylic acids (ωC_2-ωC_9;), pyruvic acid (Pyr), and α-dicarbonyls (glyoxal, Gly and methylglyoxal, MeGly) in nighttime and whole-day samples. Benzoic acid was also detected with higher concentrations in whole-day than nighttime samples (Table 1).

The total concentrations of diacids ranged from 10 to 84 ng m^{-3} (43±28 ng m^{-3}) in nighttime and 180-450 ng m^{-3} (308±103 ng m^{-3}) in whole-day samples. Except for one nighttime sample (MF10, August 8-12), oxalic acid (C_2) was found as the most abundant species followed by succinic (C_4) and malonic (C_3) acids. MF10 sample showed a predominance of C_4, followed by C_2 and C_3 (Fig. 3c). During nighttime, glutaric (C_5) or adipic (C_6) acid is most abundant after C_3, while in whole-day samples phthalic acid (Ph) and C_6 are most abundant after C_3 (Figure 3). The average nighttime concentration of C_2 (18.4 ng m^{-3}) is an order of magnitude lower than that of whole-day samples (160 ng m^{-3}). This result suggests that air masses are totally different between day- and nighttime samples. In daytime,

air masses are uplifted from the lowland around Mt. Fuji to the summit whereas the mountaintop is within the free troposphere without the input of local aerosols. This result also suggests more secondary production of diacids in daytime by the oxidation of various organic precursors.

During nighttime, average concentrations of C_2 and C_4 are similar (C_2=18 ng m^{-3}, C_4=15 ng m^{-3}). This characteristic is different from ambient aerosols from ground levels (Kawamura and Bikkina, 2016). However, the concentration of C_3 is 3.3 times lower than C_2. In contrast, in whole-day samples, the concentration of C_2 is 2.2 times higher than C_4 and 2.5 times higher than C_3. C_3 is partly derived from the incomplete combustion of fossil fuels and biomass burning but largely produced by photochemical oxidation of C_4 in the atmosphere (Kawamura and Ikushima, 1993). Thus, C_4 become more abundant than C_3 in ambient aerosols from biomass burning, vehicular and biogenic emissions (Fu et al., 2012; Kawamura and Kaplan, 1987; Kundu et al., 2010). In one nighttime sample (MF10), collected on August 8 to 12, we found a very high concentration of C_4 followed by C_2 and C_3 (Figure 3c). Similar molecular distribution has been reported in the aerosols collected at Syowa Station in Antarctica during summer (Kawamura et al., 1996), over the Arctic Ocean during late summer (Kawamura et al., 2012) and the central northern North Pacific near the Aleutian trench (Hoque et al., 2015), where photochemical degradation of oxalic acid may occur in aqueous phase of aerosols in the presence of Fe (Kawamura et al., 2010).

Based on the laboratory experiment, Pavuluri and Kawamura (2012) reported that oxalic acid decomposes in the presence of Fe under the irradiation of UV light, but it is stable in the absence of Fe. C_3 acid could also decompose in the presence of Fe (III). However, the decomposition rate of its Fe-complex is ca. 20 times lower than that of C_2 (Faust and Zepp, 1993). The decomposition of oxalic and malonic acid may be accelerated under foggy conditions with solar irradiation (Kawamura et al., 2012). Kawamura and Kaplan (1987) reported that degradation of malonic acid is more significant than succinic acid in vehicular emissions. C_3 is thermally less stable than C_4 due to reactive hydrogen of methylene-chain adjacent to two carboxyl groups of malonic acid during the combustion process (Kawamura and Ikushima, 1993). Therefore, C_4 can be abundant in the atmosphere. However, C_4 can serve as a precursor of C_3 via photochemical oxidation (Kawamura and Ikushima, 1993).

We also detected a series of ω-oxocarboxylic acids (C_2-C_9) and pyruvic acid. Among the oxoacids, 4-oxobutanoic acid (ωC_4) is the most abundant in nighttime samples followed by 7-oxoheptanoic acid (ωC_7), 3-oxopropanoic acid (ωC_3), and glyoxylic acid (ωC_2) (Table

1). This molecular characteristic of oxoacids is in contrast to those of previously studied aerosols from marine, mountainous, urban areas from low- and mid-latitudes, in which ωC_2 is the most abundant oxoacid (Kawamura and Yasui, 2005, Kunwar and Kawamura, 2014b; Kawamura et al., 2013; Kundu et al., 2010; Kunwar et al., 2016a; Pavuluri et al., 2010; Wang et al., 2010). A very high concentration of ωC_2 was reported over Mt. Tai (106 ng m^{-3}, Kawamura et al., 2013) and Mt. Hue (26 ng m^{-3}, Meng et al., 2014). However, ωC_2 was below the detection limit in most nighttime samples. The predominance of ωC_2 and ωC_4 were frequently reported in Arctic aerosol (Kawamura et al., 1996) and Greenland ice core samples (Kawamura et al., 2001). The higher concentration of ωC_4 in this study during nighttime is due to the biogenic emission from marine unsaturated fatty acids and/or biomass burning by long-range atmospheric transport.

In Mt. Fuji aerosols, biogenic, biomass burning and anthropogenic sources may be important. In one nighttime sample (August 8-12), concentration of C_4 is very high, suggesting strong emissions from biogenic, biomass burning and/or vehicular sources. During nighttime, we found strong correlation of both C_4 and ωC_4 with levoglucosan (r=0.98, 0.96), 2-methyl threitol (2-MT) (0.95, 0.97) and 2-methyl erythritol (2-ME) (0.95, 0.97). The strong correlations of C_4 and ωC_4 with isoprene SOA tracers (2-MT and 2-ME) and levoglucosan suggest that diacids and related compounds are derived from biomass burning and biogenic emission of isoprene. Moreover, ωC_9 also strongly correlate with isoprene-SOA tracers, suggesting the formation from biomass burning and biogenic emission (Table 2). No correlation of biogenic and biomass burning tracers with C_2 is another evident for the mixed sources in Mt. Fuji aerosols. Based on the correlation analysis, we conclude that Mt. Fuji aerosols are influenced from the mixed sources in nighttime.

In daytime, there is a large contribution from local biogenic sources in lowlands along the mountain slopes. Thus, concentrations of diacids and related compounds are very high. Back trajectory analyses showed that long-range atmospheric transport is also important. In addition, higher concentration of oxalic acid further confirms that secondary formation is also important. The strong correlations of C_4 with biomass burning tracers (i.e., levoglucosan, r=0.95 and dehydroabietic acid, 0.99) during day time suggest that biomass burning (Table 3) is important. Dehydroabietic acid is a biomarker tracer for Gymnosperm (conifer) biomass burning (Simoneit et al., 1999) In whole day samples, ωC_4 showed a strong correlation with oleic acid ($C_{18:1}$) (0.99) and levoglucosan (0.96) (Table 3). Similarly, ωC_9 shows strong correlations with isoprene-SOA tracers including 2-MT (0.97) and 2-ME (0.95) and oxidation

products of α-/β-pinene including pinic acid (0.97), and 3-hydroxyglutaric acid (3-HGA, 0.98). Based on the correlation analysis, we conclude that Mt. Fuji aerosols are largely influenced by the mixed sources, that is, biogenic SOA and biomass burning products.

Two α-dicarbonyls (Gly and MeGly) were detected in Mt. Fuji aerosols. Concentrations of glyoxal (Gly) and methylglyoxal (MeGly) are 20 times higher in whole-day than nighttime samples (Figure 3), ranging from 0.00 to 0.25 ng m^{-3} (0.10±0.09 ng m^{-3}) and 0.01 to 0.19 ng m^{-3} (0.11±0.06 ng m^{-3}) in nighttime and 2.0 to 3.5 ng m^{-3} (2.8±0.60 ng m^{-3}) and 0.81 to 4.9 ng m^{-3} (1.9±1.7 ng m^{-3}) in whole-day samples. The average concentrations of Gly and MeGly are similar among nighttime samples, while concentration of Gly is 1.4 times higher than MeGly in whole-day samples (Table 1). Being similar to diacids and oxoacids, we found a higher concentration of Gly and MeGly in whole day samples. This result may suggest that anthropogenic (e.g., benzene and toluene) emissions are also important because Gly is often more abundant than MeGly in polluted aerosols collected from China and India (Ho et al., 2007; Pavuluri et al., 2010). However, in the central northern North Pacific influenced by more biogenic source, relative abundance of MeGly is more abundant than Gly (Bikkina et al., 2014). Mochizuki et al. (2017) reported higher abundance of MeGly in both daytime and nighttime aerosol samples collected in the foothill forest of Mt. Fuji. Figure 4 represents the nighttime and whole day variations of selected diacids, oxoacids and α-dicarbonyls. We found that concentrations of C_4, M, Ph, C_9 and ωC_4 were very high in the nighttime sample (August 8-12). In whole-day sample (August 18-21), higher concentrations of C_2, C_6, M, ωC_2, ωC_9, MeGly, kC_3, Pyr were also obtained.

Relative abundance of oxalic acid (C_2%) has been proposed as a tracer to decipher the photochemical aging of organic aerosols because C_2 is produced in the atmosphere by the oxidation of longer chain diacids and other precursor compounds such as aromatic hydrocarbons, isoprene and monoterpenes (Kawamura and Ikushima., 1993; Ervens et al., 2004; Legrand et al., 2007). Laboratory experiment proved that C_2 is formed by the degradation of long-chain diacids such as C_3, C_4, C_6 and C_9 (Enami et al., 2015; Legrand et al., 2007). Figure 5 shows the relative abundances of selected diacids in ΣC_2-C_{10} diacids and oxoacids to total oxoacids. Relative abundance of C_2 is higher in whole-day (53%) than nighttime samples (48%) (Figure 5a, b). The higher relative abundances of C_2 in whole day samples suggest the more secondary production of oxalic acid during the daytime. Again, the relative abundance of C_4 in nighttime (33%) is higher than the whole day (20%) samples. C_5 and C_6, which are tracers for anthropogenic source, showed higher relative abundances (2%

and 1%, respectively) during whole-day samples. Long chain diacid such as C_7 is associated with the emission of unsaturated fatty acids from terrestrial higher plants (Kunwar and Kawamura, 2014b). It showed higher abundances in daytime. C_9 is a specific oxidation product of unsaturated fatty acids emitted from micro layers of ocean surfaces for marine emission showed higher abundance during nighttime (Figure 5a). Back trajectories analysis reveals that during nighttime there is an important input of marine air mass in the free troposphere via long-range atmospheric transport (Figure 6a-d).

When concentrations of C_2 increased, its relative abundances are generally increased. However, in one sample collected during August 8 to 12, concentrations of C_2-C_{10} increased, but the relative abundances of oxalic acid decreased. Hence, there may be a degradation of oxalic acid during August 8 to 12 (Please see Figure S1 in supporting information). Contributions of C_2 to C_2-C_{10} in Mt. Fuji aerosols (48-53%) are lower than those of the aged aerosols from Chichi-jima Island (81%) in the 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 (56%) (Bikkina et al., 2014) and from Tokyo in summer (55%) via photo-oxidation of anthropogenic VOCs (Kawamura and Yasui, 2005) and from biogenic sources in a larch forest at the northern slope of Mt. Fuji (Mochizuki et al., 2017). Strong correlations of selected diacids and oxoacids with isoprene-SOA tracers and biomass burning tracer during nighttime and daytime suggest that organic aerosols of Mt. Fuji are originated from both biogenic and anthropogenic sources with an enrichment of oxalic acid but are photochemically less aged.

Among oxoacids, the relative abundance of ωC_4 is higher than ωC_2 in nighttime (Figure 5c, d). This is in contrast to other studies where higher relative abundance of ωC_2 is reported (Kawamura and Bikkina 2016; Kawamura and Sakaguchi, 1999; Kunwar and Kawamura 2016b; Kawamura et al., 2013). In contrast to ωC_2, relative abundances of ωC_3, ωC_4, ωC_7, ωC_9 in total oxoacids are higher in nighttime. This result suggests that these ω-oxoacids are produced by the photochemical oxidation of marine-derived unsaturated fatty acids. Relative abundances of pyruvic acid (Pyr) in whole-day aerosols are 3 times higher than nighttime samples, suggesting that photochemical oxidation is important in daytime because Pyr is formed in the atmosphere by the oxidation of biogenic (e.g., isoprene) and anthropogenic aromatic hydrocarbons (Legrand et al., 2007; Kawamura et al., 1996).

3.2. Comparison of Mt. Fuji aerosols with previous studies: a global perspective

Concentration of oxalic acid (av. 18 ng m^{-3}) during nighttime over Mt. Fuji is several times lower than summertime aerosols reported from Chennai (241 ng m^{-3}, Pavuluri et al., 2010), Delhi (1906 ng m^{-3}, Miyazaki et al., 2009), Raipur, India (778 ng m^{-3}, Deshmukh et al., 2017), Tokyo, Japan (July, 157 ng m^{-3}, Kawamura and Yasui, 2005),14 Chinese cities (513 ng m^{-3}, Ho et al., 2007), Gosan, Jeju Island, Korea (564 ng m^{-3}, Kundu et al., 2010), and Okinawa Island, Japan (96 ng m^{-3}, Kunwar and Kawamura, 2014b). Similarly, concentration of oxalic acid from Mt. Fuji is several times lower than Mt. Tai (1046 ng m^{-3}, Kawamura et al., 2013) and Mt. Hui, China (522 ng m^{-3}, Meng et al., 2014). Again, concentration of oxalic acid in nighttime from Mt. Fuji is ca. 3 times lower than those from from the Pacific Ocean (40 ng m^{-3}, Kawamura and Sakaguchi, 1999) and Atlantic Ocean (45-50 ng m^{-3}, Fu et al., 2013) and 3.2 times lower than northern slope of Mt. Everest (59.8 ng m^{-3}, Cong et al., 2015).

Thus, this study from the summit of Mt. Fuji provides the lowest concentrations of short chain diacids in the atmosphere of East Asia, especially during night when the mountaintop is far above the planetary boundary layer. The low level of oxalic acid over Mt. Fuji could be explained by the removal through both dry and wet depositions, as well as photochemical degradation of oxalic acid in the presence of Fe^{2+}/Fe^{3+} ions in aerosols. Thus, we conclude that nighttime aerosols over Mt. Fuji provide background concentrations of diacids and related compounds in the free troposphere of the Northern Hemisphere.

3.3. Nighttime and daytime chemistry

During nighttime, C_2 is strongly correlated with C_3 (r=0.95). Similarly, C_4 shows good correlations with C_9 (0.96), isoprene-SOA tracers such as 2-MT (0.95), and Ph (0.97), suggesting that C_4 is originated from both biogenic and anthropogenic sources. A strong correlation (0.98) between levoglucosan and C_4 again suggest that these low molecular weight diacids over Mt. Fuji are influenced by biogenic emissions of unsaturated fatty acids, isoprene-oxidation products, plastic- and biomass-burning products during nighttime via long-range atmospheric transport.

Recently, laboratory and field studies have shown that aqueous phase photo-oxidations of isoprene and other precursors are the main formation pathway of SOA and small diacids (Carlton et al., 2006; Ervens et al., 2011; Myriokefalitakis et al., 2011). In addition, during atmospheric transport organic compounds (e.g., aromatic hydrocarbons, cyclic olefins and unsaturated fatty acids) emitted from anthropogenic and biogenic sources can degrade to result in Gly, MeGly, Pyr and ωC_2 and finally in oxalic acid via in-cloud oxidation (Carlton

et al., 2007; Charbouillot et al., 2012; Ervens et al., 2004; Legrand et al., 2007). The strong correlations of Gly with Pyr (0.99) and ωC_2 (0.95) suggest that incloud oxidation process is important. However, there is no correlation (r=0.01) between C_2 and ωC_2, suggesting a presence of various sources of oxalic acid over the mountaintop during nighttime.

Isoprene and α–/β–pinenes and aromatic hydrocarbons can produce both MeGly and Gly (Legrand et al., 2007; Meng et al., 2013). During daytime, emissions of isoprene and α/β–pinenes are significant in the forest (Fu and Kawamura, 2011). MeGly presents strong correlations with 2-ME (r=0.95), 3-hydroxy glutaric acid (3-HGA) (0.99) and pinic acid (0.96). Both pinic acid and 3-HGA are SOA tracers formed by the oxidation of α–/β–pinenes (Claeys et al., 2007; Fu et al., 2014). We found strong correlations of MeGly with Pyr (0.94, $p<0.05$), glycolic acid (0.94, $p<0.05$), and ωC_2 (0.95, $p<0.05$), suggesting a heterogenous aqueous phase oxidation of short chain diacids. Very strong negative correlation (-1.0) between Gly and ωC_2 was observed in whole-day samples, suggesting a different source or different reaction mechanisms for these species. C_9 diacid, a tracer of biogenic source showed a strong negative correlation (-0.95) with Gly, suggesting that daytime Gly is derived mainly by the oxidation of aromatic hydrocarbons emitted by anthropogenic sources.

A strong linear correlation between C_2 and SO_4^{2-} was found for nighttime samples (r=0.99), which is consistent with the measurements observed in other mountainous region (Meng et al., 2014) and Chinese cities (Wang et al., 2017), indicating that oxalic acid and sulfate are both formed via a similar formation pathway (Warneck, 2003). However, we did not find such a good correlation between C_2 and SO_4^{2-} (r=0.40) in whole-day samples over Mt. Fuji. The correlations of C_2 with MeGly, ωC_2 and Pyr are not strong; this suggest that there are various sources of C_2 for whole-day samples such as biogenic emissions of unsaturated fatty acids, isoprene, monoterpenes and aromatic hydrocarbons.

3.4. Compositional Changes of diacids and related compounds

Succinic (C_4) acid has been suggested to be a precursor of malonic (C_3) acid (Kawamura et al., 1996). The mean ratio of C_3/C_4 in this study is 1.19 in whole-day versus 0.58 in nighttime samples. The nighttime C_3/C_4 ratios are higher than that for vehicular aerosols (average 0.35, Kawamura and Kaplan, 1987), but similar to that of urban aerosols from China (0.61 in winter, Ho et al., 2007). Nighttime C_3/C_4 ratios ranged from 0.18–1.16, and decreased down to 0.18 during August 9 to 12, when Ph and M maximized (Fig. 4g, i), suggesting more influences from anthropogenic emission followed by significant oxidation

because M is formed by the oxidation of aromatic hydrocarbon. The relatively high C_3/C_4 ratio (1.1) was observed during nighttime of August 4–8 when the air masses were delivered from Philippines via the Pacific Ocean to the sampling site.

The higher C_3/C_4 ratios may be caused by photochemical production of C_3 from C_4 during a long-range atmospheric transport. However, C_3/C_4 ratios in nighttime (0.18–1.16) and whole-day samples (0.42-1.9) are similar to those (0.2–1.5) from Mt. Tai aerosols (Kawamura et al., 2013), and are much lower than those (up to 10) in remote marine aerosols from the North and Central Pacific (Kawamura and Sakaguchi, 1999), where photochemical transformation is serious. The ratio is low in the fossil fuel combustion and biomass burning aerosols due to thermally unstable nature of malonic acid (Kawamura and Kaplan, 1987; Kundu et al., 2010). Aggarwal and Kawamura. (2008) clearly observed increases in C_3/C_4 ratios from the source regions to downwind remote site due to photochemical aging. Figure 7 shows a comparison of C_3/C_4 ratios of Mt. Fuji aerosols with the different aerosols from the world. The average C_3/C_4 ratios in this study in nighttime and whole-day samples are 0.57 and 1.19, respectively.

Nighttime C_3/C_4 ratios are very similar to those reported for the biomass-burning influenced aerosols from Amazonia (nighttime=0.59, Kundu et al., 2010), New Delhi (nighttime=0.58 Miyazaki et al., 2009), north slope of Mt. Everest (0.51, Cong et al., 2015), where biomass burning is an important source of organic aerosols. The C_3/C_4 ratios reported in coastal and remote islands such as Gosan (2.7), Okinawa (2.8) and Chichijima (3.8) are much higher than those from Mt. Fuji (Figure 7). Higher ratios were observed in background site of South Africa (3-5) (Limbeck et al., 2001) and in remote marine aerosols from the equatorial central Pacific (up to 10) (Kawamura and Sakaguchi, 1999). The C_3/C_4 ratios in the whole-day samples from Mt. Fuji are very similar to those in the aerosols from summertime Southern 14 Chinese cities (1.12, Ho et al., 2007), summertime Chennai, India (1.3, Pavuluri et al., 2010) and Tanzania (dry season=1.0 and wet season=1.3 for PM_{10}, dry season=0.81 and wet season=0.72 for $PM_{2.5}$, Mkoma and Kawamura, 2013). These comparisons demonstrate that mountaintop aerosols over Mt. Fuji are experienced photochemical aging during the uplift transport of ground level aerosols. However, its levels are less serious than remote marine aerosols in the central equatorial Pacific.

Both C_9/Ph and C_9/C_6 ratios can be used to evaluate the source strength of biogenic versus anthropogenic source for dicarboxylic acids and related compounds (Kunwar et al.,

2014b). C_6 and Ph are produced by the oxidation of anthropogenic cyclohexene and aromatic hydrocarbons such as naphthalene (Hatakeyama et al., 1987; Kawamura and Ikushima, 1993). In contrast, C_9 is mainly derived by the oxidation of biogenic unsaturated fatty acids containing a double bond predominantly at C-9 position (Kawamura and Gagosian, 1987; Kunwar et al., 2017). In nighttime, one sample (MF-07) collected during July 27-30 showed very high C_9/C_6 ratios (28) when concentration of Ph is below detection limit and back trajectory analysis revealed that air masses are delivered from both marine and continental areas. Except for MF-07, average C_9/C_6 and C_9/Ph ratios in nighttime are 0.81 and 4.1, respectively, whereas those of whole-day samples are 1.21 and 0.13, respectively. Very high C_9/C_6 ratio (4.1) in whole-day samples is mainly attributed to a strong vegetational activity in the foothill forest of Mt. Fuji in daytime. The average C_9/C_6 value of 4.1 at the mountaintop is higher than those from other mountain areas in summer such as Central Himalaya (2.1) (Hedge and Kawamura, 2012), northern slope of Mt. Fuji (3.1) (Mochizuki et al., 2017) and Mt. Tai (1.4) (Kawamura et al., 2013). These comparisons emphasize that organic aerosols over Mt. Fuji are largely influenced by biogenic emissions in daytime.

Field observations and model simulation suggested that the concentration ratio of particulate Gly/MeGly is about 1:5 when biogenic sources are predominant whereas it is about 1:1 when anthropogenic sources are predominant (Meng et al., 2014; Fu et al., 2008 Volkamer et al., 2007; Zhao et al., 2006). The global production ratios of Gly and MeGly are about 1:1 for anthropogenic sources and 1:5 for biogenic sources and uptake coefficients of Gly and MeGly by particles are similar (Fu et al., 2008). In nighttime, the average Gly/MeGly ratio is 1:1, which is very similar to the anthropogenic sources. Although biogenic emission is significant in daytime, the average Gly/MeGly ratio is 1:0.67. One reason for the higher ratio is the life time of MeGly (1.6 h), which is shorter than Gly (2.9 h). Very low Gly/MeGly ratios were observed in the Mt. Tai atmosphere in daytime (1:5.1) and nighttime (1:4.8), which are associated with biogenic sources (Meng et al., 2018). This comparison again demonstrates the importance of biogenic sources on Mt. Fuji aerosols.

The contribution of oxalic acid to OC (C_2-C/OC ratio) in this study ranged from 0.43 to 5.8% (ave., 3.5±2.3%) in nighttime and 2.2 to 5.1% (3.4±1.2%) in whole-day samples. Interestingly, C_4-C/OC ratio (3.8±3.4%) in nighttime is higher than those of oxalic acid (ave., 3.5±2.3%), which suggests a large production of succinic (C_4) acid in the free troposphere. Average total diacid-C/OC is higher during nighttime (10±8%) than whole-day (8.1±3.9%) samples. The average total diacid-C/OC in this study (9.1%) is higher than those reported for

aerosols from Sapporo (4.8%) (Aggarwal and Kawamura 2008), New Delhi (1.0%) (Miyazaki et al., 2009), Chennai (5.9%) (Pavuluri et al., 2010), and summertime Okinawa (3.4%) (Kunwar and Kawamura, 2014b). However, this ratio is lower than those from the Indian Ocean (13.5%) (Fu et al., 2013), California Coast (14.5-22.9%) (Fu et al., 2013), and the Atlantic Ocean (14.5-16.5%) (Fu et al., 2013). The diacids-C/OC (av. 9.1%) from this study is higher than the mountain aerosols from Mt. Tai (diacid-C/TC, 2.4%,) (Kawamura et al., 2013) and Mt Hui (6.5%) (Meng et al., 2014).

3.5. Source apportionment of diacids and related compounds

To decipher the source region of air masses, we performed backward trajectory analysis (BTA). Figure 6 shows the results of BTA for nighttime and whole-day samples. Results of BTA predict that most of the air masses delivered during nighttime are originated from marine regions and the Asian continent, whereas during daytime most of the air masses are originated from East Asia.

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is emitted from deciduous forest in daytime. Due to the presence of a double bond, it is highly reactive to oxidants such as OH, O_3, and NO_3 and degrades to result in secondary organic aerosols (SOA) (Carlton et al., 2006, 2009; Claeys et al., 2004). Isoprene emission is dependent on light and temperature (Tambunana et al., 2006), whereas monoterpene emission is not (Fu and Kawamura, 2011 and reference therein). During daytime, the valley breeze can transport large amounts of ground surface biogenic and anthropogenic VOCs together with SO_2 and NOx.

In nighttime, mountain breeze dominates the winds over the foothill of Mt. Fuji, and thus the upward transport of aerosols from the ground surface is negligible. Thus, the tropospheric aerosols over the summit of Mt. Fuji are mainly derived by long-range atmospheric transport from different source regions in which marine and biomass burning-derived organic aerosols are present.

Both isoprene- and monoterpene-SOA tracers can be oxidized to oxalic acid (Jaoui et al., 2005; Kleindienst et al., 2007; Koch et al., 2000; Legrand et al., 2007; Meng et al., 2014; Pacifico et al., 2011). Thus, it is meaningful to calculate the ratios of C_2 to isoprene- and monoterpenes-SOA tracers. Although isoprene emission is higher in daytime, we found higher C_2/2-MT and C_2/2-ME ratios in nighttime (Figure 8). The higher nighttime ratios suggest that the formation of diacids and related compounds is significant in the free troposphere. Emission of isoprene is light dependent while that of monoterpenes is light independent (Fu and Kawamura, 2011 and references therein). However, the higher ratio in

nighttime aerosols suggest that isoprene is emitted in daytime and accumulated in the free troposphere as its oxidized forms and is finally degraded to result in C_2 in the presence of oxidants. This study suggests that large amount of SOA remains in the troposphere, which can further oxidize to small chain diacids and related compounds. Heald et al. (2005) reported that large amounts SOA are present in the free troposphere.

3.6. Sources and formation of sulphate and nitrate in mountain aerosols

Ohara et al. (2007) reported an emission inventory for Asia (Regional Emission inventory in Asia) for the period 1980–2020 with estimated emission ratios of NOx to SOx of 1:1.9 from power plants, 1:2 from industry, 1:3.7 from domestic coal burning (mean NO_x to SO_2 = 1:1.3). $[NO^-]/[SO_4^{2-}]$ ratios provide the information on relative contribution of different anthropogenic activities. The ratio of greater than 1 indicates more contribution of NO_3^- emitted from automobile sources such as vehicular emissions, whereas ratio less than 1 indicates the contribution of SO_4^{2-} emitted from stationary sources such as industrial activities (Arimoto et al., 1996). Sulphur can be emitted from both marine and non-marine sources. Keene et al. (1986) and Hawley et al. (1988) suggest that long term oceanic salinity is stable enough to estimate the sea salt sulphate (ss) and non-sea salt sulphate (nss) based on the mass concentrations of the reference species sodium in seawater. nss-SO_4^{2-} can be calculated as $[\text{nss-}SO_4^{2-}] = [SO^{2-}] - (0.25 \times [Na])$. The mean $[NO_3^-]/[\text{nss}SO_4^{2-}]$ ratios in nighttime and whole-day samples from Mt. Fuji are 0.19±0.16 and 0.13±0.16, respectively. Similar ratios during nighttime and whole-day samples suggest that stationary source emissions contribute significantly in the study site.

Due to the high abundances of SO^{2-} and NO^-, aerosols show acidic nature. SO^{2-} and NO_3^- ions are produced by the oxidation of gaseous precursors (SO_2 and NO_x) in the atmosphere and are neutralized by mineral aerosols (Ca^{2+} and Mg^{2+} and NH_4^+) (Han et al., 2007). Ca^{2+} is primarily emitted from soil and dust and largely presents in coarse mode particles. The strong correlation between SO^{2-} with Ca^{2+} (r=0.97) in nighttime suggest that aerosols are neutralized by alkaline species such as Ca^{2+}. Ca^{2+} can adsorb SO_2 in the presence of water and make a thin film of SO^{2-} around its surface. Hence, heterogeneous aqueous phase reaction is very important in nighttime samples. Both NH_4^+ and SO^{2-} exist in fine mode (Kulshrestha et al., 1995, Kunwar and Kawamura, 2014). The strong correlation (0.97) between nss-SO_4^{2-} and NH_4^+ suggests that NH_4^+ plays a major role to neutralize the acidic species during daytime or they are derived from similar sources.

The acid neutralization capacity of different cations can also be estimated by calculating neutralization factors (NF) with respect to particular cation. The calculation of NF

is based upon the facts that NO_3^- and SO_4^{2-} are the major acidifying anions and Ca^{2+}, NH_4^+, Mg^{2+} and K^+ are major acid-neutralizing cations in aerosols. The neutralization factor can be calculated as:

$$NF\ (Ca^{2+}) = [Ca^{2+}]/[SO^{2-}] + 2[NO^-] \quad \text{……..(2)}$$

$$NF\ (Mg^{2+}) = [Mg^{2+}]/[SO_4^{2-}] + 2[NO^-] \quad \text{……(3)}$$

$$NF\ (NH_4^+) = [NH_4^+]/2[SO^{2-}] + [NO_3^-] \quad \text{..……....(4)}$$

We observed that Ca^{2+}, Mg^{2+} and NH_4^+ are the major neutralizing components with average neutralization factors of 0.067 ±0.01, 0.02 ± 0.03 and 0.15 ± 0.12 in nighttime, and 0.09 ±0.09, 0.05 ± 0.09 and 0.09 ± 0.05 in whole-day samples. These results suggest that, during nighttime NH_4^+ plays the major role in neutralizing aerosols, whereas Ca^{2+} and NH_4^+ act as major neutralizing species in daytime.

3.7. Influences of liquid water content and relative humidity for the formation of diacids and related compounds

He et al. (2013) and Liu et al. (2012) reported various factors that influence SOA formation in clouds. These studies suggested that liquid water content (LWC) is an important factor that drives the incloud production of SOA. In this context, it is important to investigate whether the aerosol LWC could be a principal factor in mountaintop SOA. Here, we estimated the LWC using ISORROPIA-II model for both nighttime and whole-day aerosol samples (Nenes et al., 1998; Deshmukh et al., 2016). We also investigated the relationships between aerosol LWC and measured chemical constituents (e.g., OC, total diacids, and isoprene-SOA tracers) to evaluate the role of LWC in the formation of diacids and related compounds.

Deshmukh et al. (2017) found that LWC well correlated with oxalic acid in summer aerosols from India, indicating that aqueous phase formation of C_2 is important. During nighttime, LWC shows strong correlations with anthropogenic tracers such as C_6 and Ph, suggesting that aqueous phase chemistry is also important for the formation of C_6 and Ph. Similarly, we found a very strong correlation of LWC with 3-methyl 2, 3, 4 trihydroxy-1-butene (0.98), which is a SOA tracer produced by the oxidation of isoprene (Fu et al., 2011). The strong correlations of LWC with C_6, Ph, and 3-methyl 2,3,4-trihydroxy-1-butene, suggest that heterogeneous aqueous phase oxidation is important for the formation of anthropogenic and biogenic SOAs in nighttime because C_6 and Ph are produced by the oxidation of cyclic aliphatic and polycyclic aromatic hydrocarbons while 3-methyl 2, 3, 4 trihydroxy-1-butene is a SOA tracer of isoprene.

Kleindienst et al. (2009) reported the SOA formation during the reaction of isoprene + OH in the absence of NOx and showed the presence of the three isoprene tracer compounds, 2-methyl glyceric acid (2-MGA), 2-methylthreitol, and 2-methylerythritol. The isoprene SOA tracer compounds have previously been reported in laboratory irradiations of isoprene (Edney et al., 2005) and from field samples, particularly in areas having strong isoprene emissions (Claeys et al., 2004). While low levels of SOA were detected from isoprene/NOx irradiations, the tracers were found to increase dramatically along with an increased formation of SOA following the addition of SO_2 with the likely formation of acidic sulfate aerosol in the system (Edney et al., 2005; Surratt et al., 2007; Jaoui et al., 2008). During daytime, LWC is strongly correlated with OC (0.97), 2-MT (0.96), 2-ME (0.97), 2-methyl glyceric acid (0.94) and glycolic acid (r=0.98). The higher concentration of SO_4^{2-} in whole-day samples further supports that acid catalyzed heterogeneous aqueous phase reaction is important in daytime for the formation of diacids and related compounds from isoprene. A strong correlation between LWC and glycolic acid further suggests that isoprene is main precursor via glycolic acid for the formation of oxalic acid. However, daytime LWC shows strong negative correlation with Gly (-0.97). Thus, we hypothesize that major pathway for the production of oxalic acid in daytime is acid catalyzed heterogeneous aqueous reaction via glycolic acid.

4. Conclusions

We studied dicarboxylic acids and related compounds in the tropospheric aerosols from the top of Mt. Fuji (3776 m asl), which is faced to the Pacific coast of Honshu Island in Japan. The molecular distributions of diacids showed the predominance of oxalic acid followed by succinic and malonic acids. The relative abundance of C_2 (53%) in daytime samples is higher than that of whole-day samples (48%), whereas the relative abundance C_4 is higher in nighttime (33%) than whole-day samples (20%).

Averaged ratio of total diacids-C/OC is higher in nighttime (10.2) than whole-day samples (8.1). The higher ratios suggest that nighttime aerosols are more aged during long-range transport. The averaged total diacids-C/OC in this study (9.1%) is higher than those reported in urban aerosols. However, this value is lower than those of aerosols collected in the remote marine aerosols. Thus, Mt. Fuji aerosols are photochemical more aged than the ground-level continental aerosols but less aged than the remote marine aerosols. For whole-day samples, strong correlations of C_4 with levoglucosan, dehydroabietic acid and isoprene-SOA tracers suggest that diacids have mixed sources over Mt. Fuji. During nighttime, C_4 shows good correlations with C_9, isoprene-SOA tracers such as 2-methylthreitol (0.95) and 2-methylerythreitol (0.95) and also Ph (0.97), suggesting the C_4 is involved with both biogenic

and anthropogenic sources. Concentration ratios of diacids/isoprene-SOA tracers are higher in nighttime than whole-day samples, whereas the ratios of diacids/monoterpenes-SOA tracers showed the opposite trend.

This study from Mt. Fuji provides background concentrations of short chain diacids in the free troposphere of East Asia, especially in nighttime when the mountaintop is far above the planetary boundary layer. Strong correlations of LWC with OC (r=0.97), 2-MT (0.96), 2-ME (0.97), 2-methylglyceric acid (0.94) and glycolic acid (0.98) together with higher concentration of SO_4^{2-} in daytime support that acid catalyzed heterogeneous aqueous phase reaction is important for the formation of diacids and related compounds from isoprene. During nighttime, LWC shows strong correlations with anthropogenic (e.g., C_6 and Ph) and biogenic SOA tracers (e.g., 3-methyl 2,3,4-trihydroxy-1-butene), suggesting that aqueous phase chemistry is important for the formation of C_6 and Ph and biogenic SOA.

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Figure captions:

Figure 1. Geographical location of Mt. Fuji, Japan.

Figure 2. Meteorological parameters (a) average sunshine (hr), (b) relative humidity (%), and (c) temperature (°C) recorded during study period over Mt. Fuji.

Figure 3. Molecular distributions of straight chain diacids (C_2-C_{12}), branched chain diacids (iC_4-iC_6), unsaturated diacids (M, mM, F, Ph, iPh, and tPh), multifunctional diacids (hC_4, kC_3 and kC_7), oxoacids (ωC_2-ωC_9, and pyruvic), and α-dicarbonyls (Gly and MeGly) in aerosols collected from Mt. Fuji for (a) average nighttime, (b) average whole day and (c) August 8/8-12 samples. The error bars represent the standard deviation.

Figure 4. Nighttime and whole day variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) glutaric acid (C_5), (e) adipic acid (C_6), (f) azelaic acid (C_9), (g) malic (M), (h) fumaric (F), (i) phthalic acid (Ph) and (j) ketomalonic acid (kC_3), (k) ketopimelic acid (kC_7), (l) hydroxysuccinic acid (hC_4), (m) glyoxylic acid (ωC_2), (n) 9-nonanoic acid (ωC_9, (o) 4-oxobutanoic acid (ωC_4), (p) pyruvic acid (Pyr), (q) methylglyoxal (MeGly), and (r) glyoxal (Gly) in aerosols collected from Mt. Fuji, Japan.

Figure 5. Relative abundances (%) of individual diacid during (a) night-time and (b) whole day, and individual oxoacid during (c) night-time and, (d) whole day samples in aerosols collected from Mt. Fuji, the highest peak of Japan. Please refer to Table 1 for diacid and oxoacid identities.

Figure 6. Five-day backward trajectory analysis for (a) 7/27-7/30, (b) 7/30-8/4, (c) 8/4-8/8, (d) 8/4-8/12 (e) 8/12-8/15 (f) 8/15- 8/18 (g) 8/18- 8/21 and (h) 8/18- 8/21. Backward trajectories at 3800m above sea level were drawn with the NOAA HYSPLIT model.

Figure 7. Comparison of C_3/C_4 ratio in aerosols collected from Mt. Fuji with the different locations of the World.

Figure 8. Nighttime and whole-day variations in concentration ratios of oxalic acid to isoprene and monoterpene SOA tracers (a) C_2/2-methylthreitol, (b) C_2/2-methylerythreitol, (c) C_2/pinic acid, (d) pinonic acid, (e) C_2/3HGA and (f) $C_2/C_{18:1}$ in aerosols collected from Mt. Fuji, Japan.

875

876 Table 1. Concentrations (ng m^{-3}) of diacids, oxoacids, and α-dicarbonyls in the TSP samples collected from Mt.

877 Fuji, Japan

Species	Nighttime		Whole-day	
	Min-Max	AV±STD	Min-Max	AV±STD
		Diacids		
Oxalic, C_2	4.4-30	18±9.0	103-206	160±37
Malonic, C_3	1.4-8.0	5.5±2.5	33-63	54±12
Succinic, C_4	3.5-37	15±14	24-136	63±44
Glutaric, C_5	0.17-1.4	0.79±0.48	3.7-7.6	5.9±1.6
Adipic, C_6	0.01-0.76	0.46±0.32	2.2-4.0	2.9±0.72
Pimelic, C_7	0.00-0.12	0.06±0.05	0.51-0.76	0.65±0.10
Suberic, C_8	0.09-0.41	0.21±0.13	0.16-0.64	0.33±0.20
Azelaic,C_9	0.26-0.71	0.44±0.19	0.35-1.0	0.80±0.28
Sebacic, C_{10}	0.03-0.13	0.10±0.04	0.05-0.38	0.15±0.13
Methylmalonic, iC_4	0.10-0.22	0.16±0.05	0.98-2.4	1.6±0.51
Methylsuccinic, iC_5	0.06-0.21	0.15±0.06	1.03-2.1	1.7±0.43
Methylglutaric, iC_6	0.00-0.18	0.08±0.06	0.48-0.95	0.64±0.19
Maleic, M	0.03-1.21	0.50±0.44	1.4-3.5	2.6±0.89
Methylmaleic, mM	0.07-0.87	0.31±0.32	1.0-2.7	2.0±0.63
Fumaric, F	0.02-0.35	0.17±0.12	0.51-0.98	0.68±0.19
Phthalic, Ph	0.00-0.78	0.33±0.30	4.4-9.7	6.5±1.9
Isophthalic, iPh	0.00-0.04	0.03±0.02	1.2-1.9	1.5±0.27
Terephthalic, tPh	0.01-0.56	0.22±0.21	0.72-1.9	1.2±0.47
Hydroxysuccinic, hC_4	0.00-0.03	0.02±0.01	0.17-0.56	0.34±0.14
Ketomalonic, kC_3	0.00-0.20	0.10±0.09	0.80-2.1	1.4±0.48
Ketopimelic, kC_7	0.00-0.22	0.11±0.08	0.79-1.6	1.0±0.32
Total diacids	**10-83**	**43±28**	**179-450**	**308±102**
		Oxoacids		
Pyruvic acid	0.00-0.52	0.23± 0.19	5.3-9.3	6.7 ±1.6
Glyoxylic, ωC_2	0.00-1.0	0.26±0.45	11-17	14±2.4
3-oxopropanoic, ωC_3	0.08-0.42	0.28±0.14	0.19-2.4	1.6±0.84
4-oxobutanoic ωC_4	0.10-3.3	1.2±1.3	3.21-6.18	4.7±1.4
7-oxoheptanoic, ωC_7	0.12-0.75	0.46±0.22	0.86-4.58	3.0±1.4
8-oxooctanoic, ωC_8	0.05-0.31	0.22±0.10	1.27-2.01	1.7±0.31
9-oxononoic, ωC_9	0.02-0.22	0.09±0.08	0.36-3.0	1.2±1.0
Total oxoacids	**0.37-6.6**	**2.7 ± 2.4**	**22-44**	**33± 22**
Benzoic	0.08-2.0	0.70±0.80	1.4-4.7	3.0±1.3
		α-Dicarbonyls		
Glyoxal, Gly	0.00-0.25	0.10±0.09	2.0-3.5	2.8±0.60
Methylglyoxal, MeGly	0.01-0.19	0.11±0.06	0.81-4.9	1.9±1.7
Total α-dicarbonyls	**0.01-0.44**	**0.21±0.15**	**2.83-8.39**	**4.7±2.3**

878 Note: Ave. means average and SD means standard deviation. Limit of detection (LOD) is (.001 ng m^{-3}

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882 Table 2. Nighttime correlation analysis of the selected diacids, oxoacids, α-dicarbonyls, fatty acids, isoprene-SOA tracers, monoterpenes-SOA tracers and levoglucosan (Levo) in aerosols over
883 Mt. Fuji

Species	C_2	C_3	C_4	C_6	C_9	Ph	BzA	Pyr	ωC_2	ωC_4	ωC_9	Gly	MeGly	$C_{18:1}$	levo	DHAA	2-MT	2-ME	3-HGA	Pinic
C_2	1																			
C_3	0.95*	1																		
C_4	0.26	0.53	1																	
C_6	0.81	0.93	0.76	1																
C_9	0.42	0.64	0.96*	0.87	1															
Ph	0.46	0.70	0.97*	0.88	0.97*	1														
BzA	0.79	0.68	0.07	0.66	0.34	0.24	1													
Pyr	0.40	0.65	0.93	0.75	0.85	0.95*	0.00	1												
ωC_2	0.01	0.31	0.95*	0.54	0.84	0.88	-0.22	0.90	1											
ωC_4	0.23	0.50	0.99**	0.72	0.94*	0.96*	0.00	0.95*	0.97*	1										
ωC_9	0.20	0.49	0.97*	0.67	0.89	0.95*	-0.09	0.97*	0.98*	0.99**	1									
Gly	0.27	0.53	0.90	0.63	0.78	0.89	-0.17	0.99*	0.95*	0.93	0.97*	1								
MeGly	0.60	0.80	0.83	0.81	0.78	0.89	0.14	0.96*	0.75	0.83	0.90	0.90	1							
$C_{18:1}$	0.07	-0.08	-0.29	0.04	-0.05	-0.25	0.67	-0.55	-0.47	-0.36	-0.50	-0.70	-0.55	1						
Levo	0.12	0.39	0.98*	0.68	0.95*	0.92	0.06	0.83	0.94*	0.96*	0.90	0.80	0.68	-0.15	1					
DHAA	-0.92	-0.91	-0.27	-0.69	-0.32	-0.45	-0.48	-0.51	-0.10	-0.26	-0.30	-0.40	-0.72	0.31	-0.08	1				
2-MT	0.03	0.32	0.95*	0.54	0.83	0.88	-0.23	0.91	0.99**	0.97*	0.98*	0.90	0.77	-0.50	0.93	-0.13	1			
2-ME	0.03	0.33	0.95*	0.54	0.83	0.88	-0.23	0.92	0.99**	0.97*	0.98*	0.90	0.78	-0.51	0.93	-0.13	1.0**	1		
3-HGA	0.51	0.59	0.63	0.82	0.82	0.69	0.75	0.41	0.39	0.55	0.45	0.30	0.38	0.53	0.68	-0.20	0.38	0.37	1	
Pinic	0.57	0.30	-0.64	0.01	-0.47	-0.46	0.60	-0.49	-0.81	-0.67	-0.68	-0.60	-0.24	0.36	-0.72	-0.47	-0.80	-0.79	-0.09	1

884 Note: DHAA: 3-dihydroxy abietic acid, 2-MT: 2-methylthreitol, 2-ME: 2-methylerythritol, 3-HGA= 3-hydroxyglutaric acid

885 Table 3. Whole-day correlation analysis of the selected diacids, oxoacids, α-dicarbonyls, fatty acids, isoprene-SOA tracers, monoterpenes-SOA tracers and levoglucosan (Levo) in
886 aerosols over Mt. Fuji

Species	C_2	C_3	C_4	C_6	C_9	Ph	BzA	Pyr	ωC_2	ωC_4	ωC_9	Gly	MeGly	$C_{18:1}$	Levo	DHAA	2-MT	2-ME	3-HGA	Pinic
C_2	1																			
C_3	0.89	1																		
C_4	0.38	0.36	1																	
C_6	0.89	0.58	0.35	1																
C_9	0.34	-0.06	0.60	0.66	1															
Ph	0.89	0.64	0.03	0.95*	0.37	1														
BzA	0.07	-0.31	-0.58	0.40	0.29	0.51	1													
Pyr	0.49	0.09	-0.28	0.76	0.46	0.83	0.90	1												
ωC_2	0.58	0.19	0.58	0.84	0.96*	0.60	0.33	0.59	1											
ωC_4	0.68	0.42	0.82	0.80	0.87	0.53	-0.03	0.32	0.93	1										
ωC_9	0.73	0.34	0.05	0.94	0.62	0.92	0.70	0.95*	0.783	0.61	1									
Gly	-0.58	-0.19	-0.58	-0.85	-0.95*	-0.61	-0.32	-0.59	-1.0**	-0.92	-0.78	1								
MeGly	0.72	0.35	-0.06	0.91	0.53	0.94*	0.73	0.95*	0.70	0.52	0.99**	-0.70	1							
$C_{18:1}$	0.64	0.41	0.86	0.75	0.86	0.46	-0.11	0.24	0.90	0.99**	0.54	-0.90	0.44	1						
Levo	0.54	0.36	0.95*	0.61	0.81	0.29	-0.28	0.05	0.81	0.96*	0.36	-0.81	0.26	0.90	1					
DHAA	0.26	0.24	0.99**	0.25	0.61	-0.09	-0.59	-0.34	0.54	0.77	-0.03	-0.55	-0.13	0.82	0.92	1				
2-MT	0.72	0.32	0.24	0.95*	0.77	0.87	0.60	0.86	0.89	0.75	0.97*	-0.89	0.95*	0.70	0.54	0.17	1			
2-ME	0.74	0.35	0.33	0.96*	0.80	0.85	0.52	0.80	0.94	0.81	0.95*	-0.93	0.91	0.77	0.63	0.26	0.99**	1		
3-HGA	0.64	0.25	-0.12	0.87	0.53	0.91	0.80	0.98*	0.68	0.46	0.98*	-0.68	0.99**	0.39	0.20	-0.20	0.93	0.89	1	
Pinic	0.55	0.12	-0.04	0.85	0.67	0.83	0.81	0.96*	0.77	0.53	0.97*	-0.77	0.96*	0.47	0.29	-0.09	0.95*	0.92	0.98*	1

** Correlation is significant at the 0.01 level (2tailed)
* Correlation is significant at the 0.05 level (2tailed)

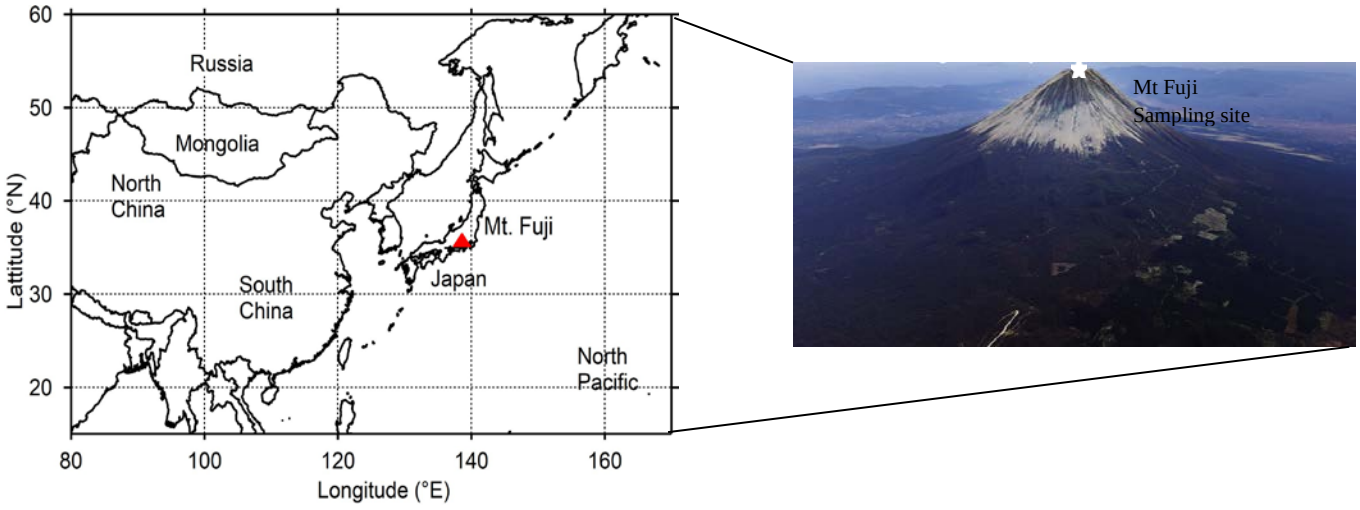


Figure 1. Geographical location of Mt. Fuji, Japan.

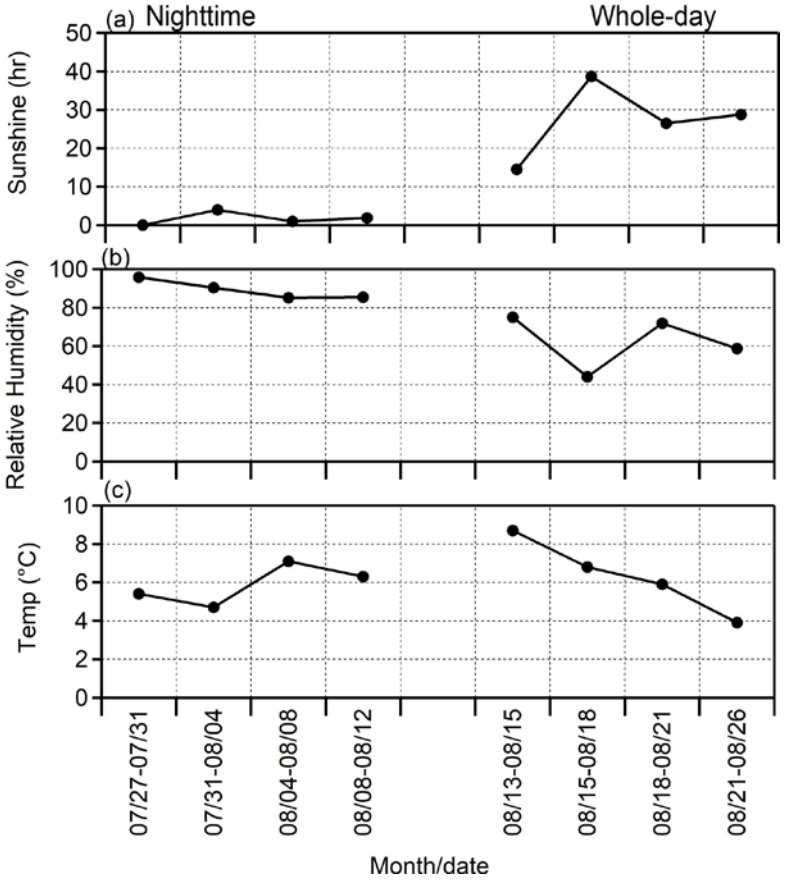


Figure 2. Meteorological parameters (a) average sunshine (hr), (b) relative humidity (%), and (c) temperature (°C) recorded during study period over Mt. Fuji.

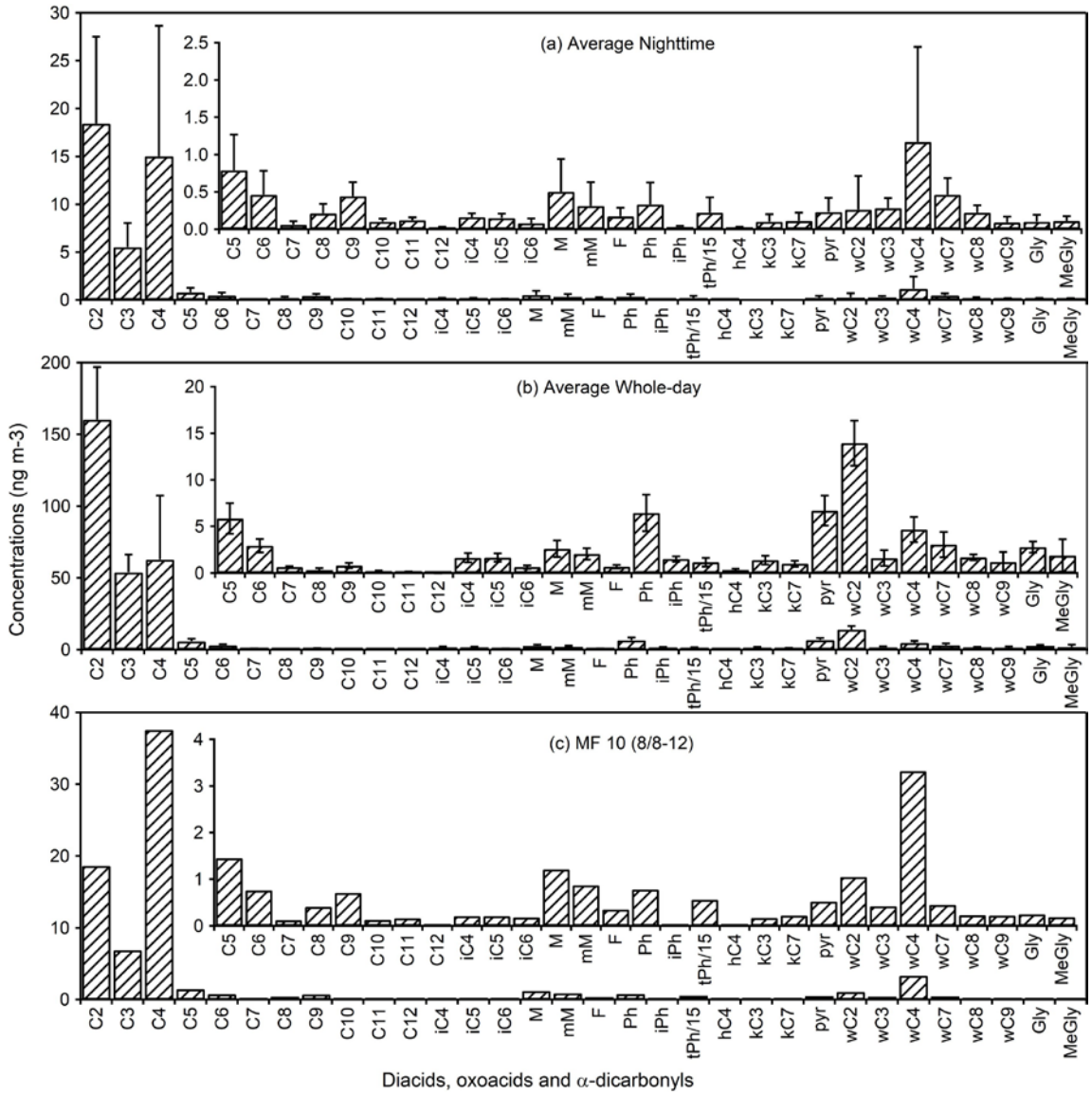


Figure 3. Average molecular distributions of straight chain diacids (C_2-C_{12}), branched chain diacids (iC_4-iC_6), unsaturated diacids (M, mM, F, Ph, iPh, and tPh), multifunctional diacids (hC_4, kC_3 and kC_7), oxoacids (ωC_2-ωC_9, and pyruvic), and α-dicarbonyls (Gly and MeGly) in aerosols collected from Mt. Fuji during (a) nighttime (27 July to 12 August), (b) whole-day (August 13-26), and (c) nighttime (August 8-12). The error bars represent the standard deviation.

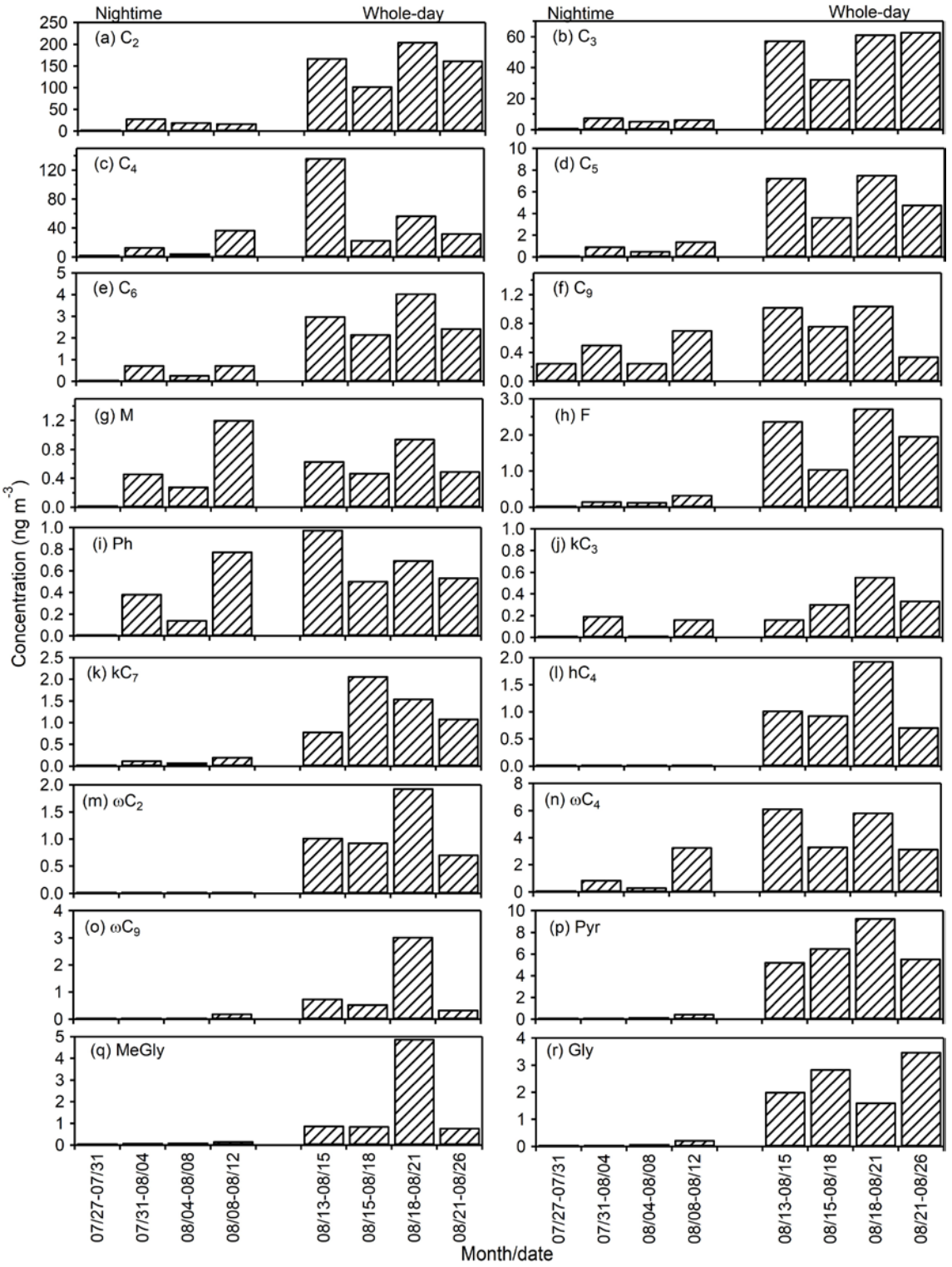
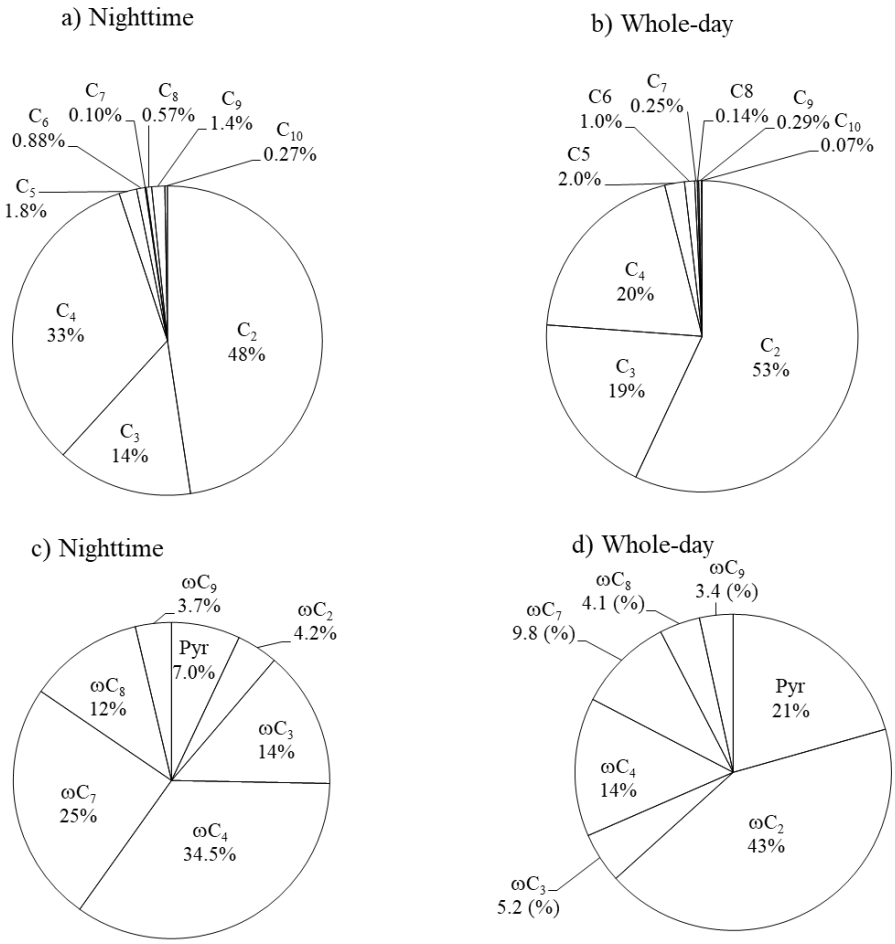


Figure 4. Nighttime and whole day variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) glutaric acid (C_5), (e) adipic acid (C_6), (f) azelaic acid (C_9), (g) malic (M), (h) fumaric (F), (i) phthalic acid (Ph) and (j) ketomalonic acid (kC_3), (k) ketopimelic acid (kC_7), (l) hydroxysuccinic acid (hC_4), (m) glyoxylic acid (ωC_2), (n) 9-nonanoic acid (ωC_9), (o) 4-oxobutanoic acid (ωC_4), (p) pyruvic acid (Pyr), (q) methylglyoxal (MeGly), and (r) glyoxal (Gly) in aerosols collected from Mt. Fuji, Japan.



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917 Figure 5. Relative abundances (%) of individual diacid during (a) night-time and (b) whole-
918 day, and individual oxoacid during (c) night-time and, (d) whole-day samples in aerosols
919 collected from Mt. Fuji, the highest peak of Japan. Please refer to Table 1 for diacid and
920 oxoacid identities.

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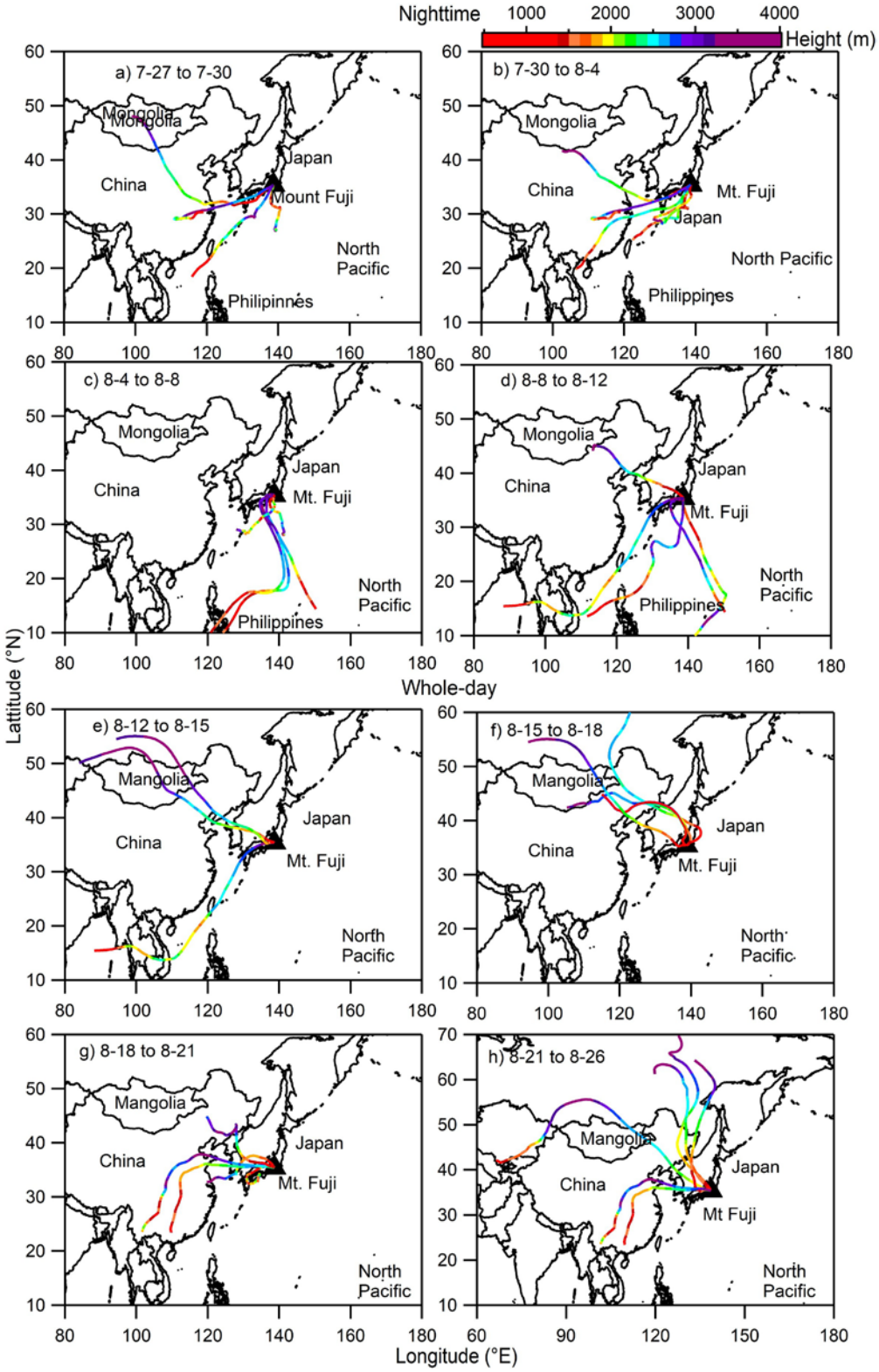
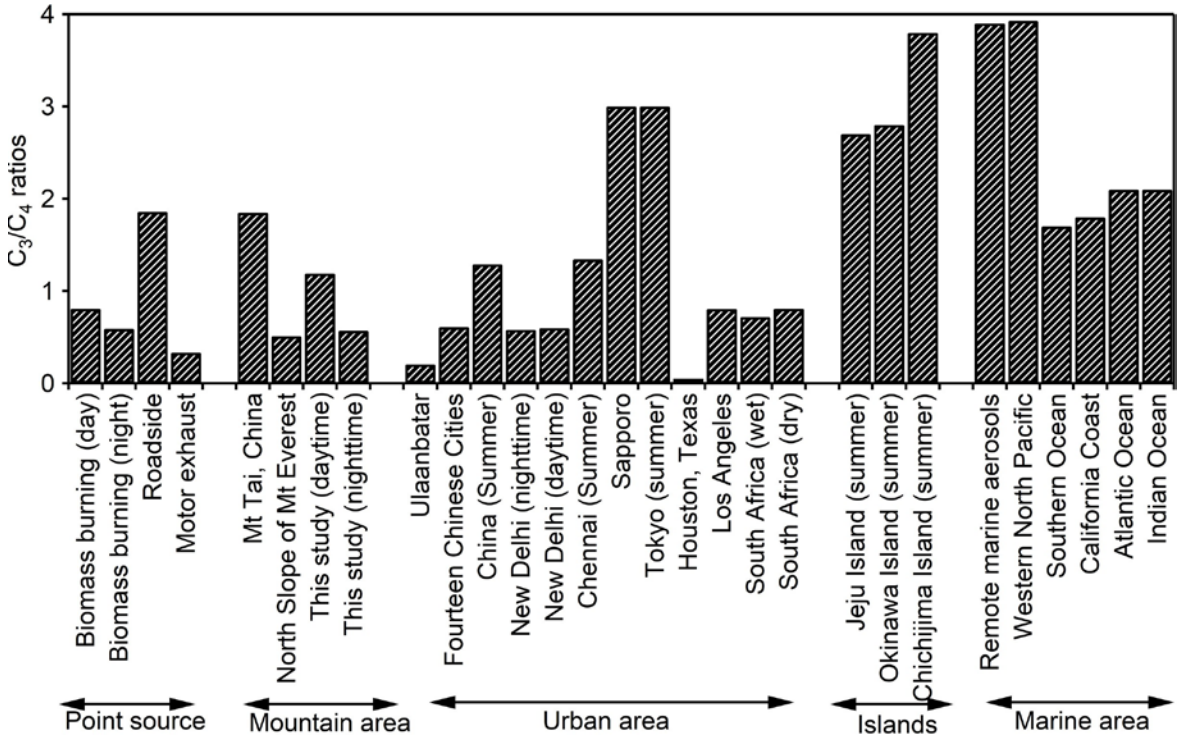


Figure 6. Five-day backward trajectory analysis for (a) July 27-30, (b) July 30- August 4, (c) August 4-8, (d) August 4-12, (e) August 12-15, (f) August 15- 18, (g) August 18- 21, and (h) August 18-21. Backward trajectories at 3800m above sea level were drawn with the NOAA HYSPLIT model.



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929 Figure 7. Comparison of C_3/C_4 ratio in aerosols collected from Mt. Fuji with the different
930 locations in the world.

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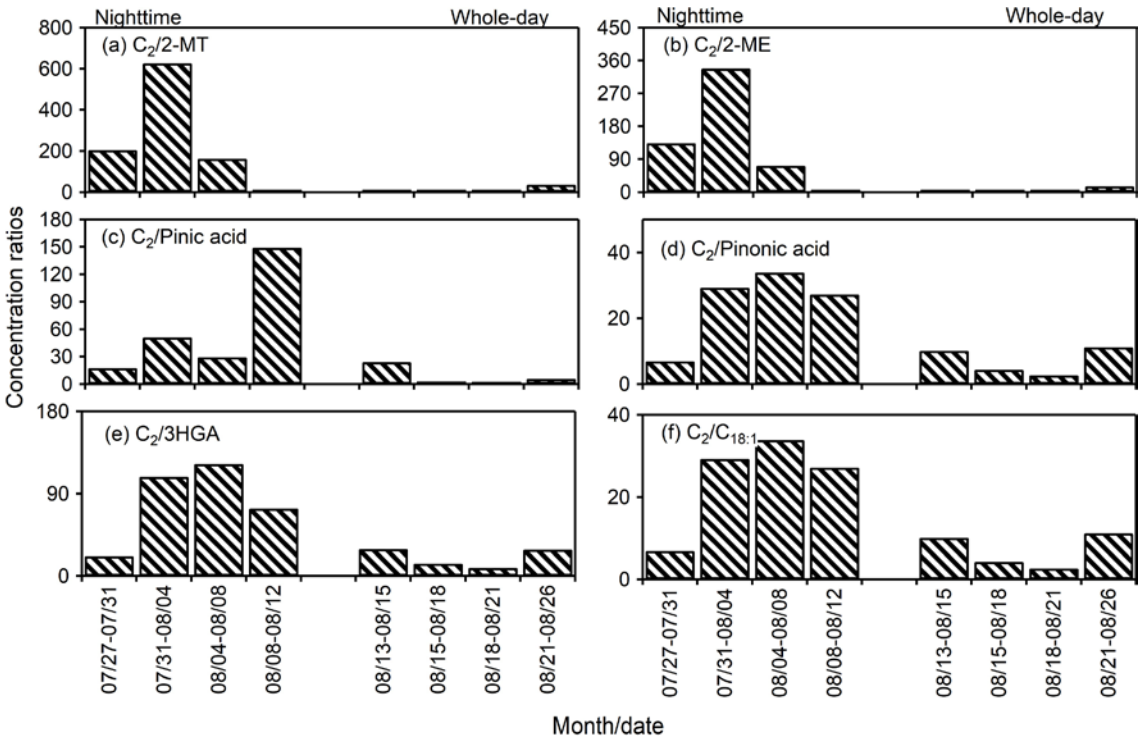

Figure 8. Nighttime and whole-day variations in concentration ratios of oxalic acid to isoprene and monoterpene SOA tracers (a) C_2/2-methylthreitol (2-MT), (b) C_2/2-methylerythreitol (2-ME), (c) C_2/pinic acid, (d) C_2/pinonic acid, (e) C_2/3HGA and (f) $C_2/C_{18:1}$ in aerosols collected from Mt. Fuji, Japan.