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Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China

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Abstract

To better understand the contribution of biogenic volatile organic compounds to the formation of secondary organic aerosol (SOA) in high mountain regions, ambient aerosols were collected at the summit of Mt. Tai (1534 m, a.s.l.), Central East China (CEC) during the Mount Tai eXperiment 2006 campaign (MTX2006) in early summer. Biogenic SOA tracers for the oxidation of isoprene, α/β -pinene, and β -caryophyllene were measured using gas chromatography/mass spectrometry. Most of the biogenic SOA tracers did not show clear diurnal variations, suggesting that they are formed during long-range atmospheric transport or over relatively long time scales. Although isoprene- and α/β -pinene-derived SOA tracers did not correlate with levoglucosan (a biomass burning tracer), β -caryophyllinic acid showed a good correlation with levoglucosan, indicating that crop residue burning may be a source for this acid. Total concentrations of isoprene oxidation products are much higher than those of α/β -pinene and β -caryophyllene oxidation products. The averaged ratio of isoprene to α/β -pinene oxidation products ($R_{\text{iso/pine}}$) was 4.9 and 6.7 for the daytime and nighttime samples, respectively. These values are among the highest in the aerosols reported in different geographical regions, which may be due to the large isoprene fluxes and relatively high levels of oxidants such as OH in CEC. Using a tracer-based method, we estimated the concentrations of secondary organic carbon (SOC) derived from isoprene, α/β -pinene, and β -caryophyllene to be 0.4-3.1 $\mu\text{gC m}^{-3}$ (average 1.6 $\mu\text{gC m}^{-3}$) during the daytime and 0.1-4.2 $\mu\text{gC m}^{-3}$ (1.7 $\mu\text{gC m}^{-3}$) during the nighttime. These values correspond to 2.9-23% (10%) and 3.2-28% (9.8%) of the total OC concentrations, in which isoprene-derived SOC accounts for 58% and 63% of total SOC during the daytime and nighttime, respectively. This study suggests that isoprene is a more significant precursor for biogenic SOA than α/β -pinene and β -caryophyllene at high altitudes in CEC.

Keywords: Biogenic VOCs; Secondary organic aerosol; Isoprene; α/β -Pinene; 2-Methyltetrols

1. Introduction

Vegetation releases large amounts of biogenic volatile organic compounds (BVOCs), including isoprene, monoterpenes, sesquiterpenes, and oxygenated hydrocarbons (Guenther et al., 1995; Goldstein and Galbally, 2007). On a global scale, emissions of biogenic VOCs (1150 Tg yr⁻¹) are suggested to be one order of magnitude larger than those of anthropogenic VOCs (Guenther et al., 2006). Considerable efforts have been devoted in the last decade to understand secondary organic aerosol (SOA) formation from the photooxidation of BVOCs (Hallquist et al., 2009 and references therein), because SOA is an important component in the Earth's atmosphere. For example, it may provide surfaces for heterogeneous reactions in the atmosphere, and can have an impact on the atmospheric radiation budget directly by scattering sunlight and indirectly by acting as cloud condensation nuclei (Kanakidou et al., 2005).

Isoprene is the most abundant non-methane hydrocarbon emitted into the Earth's atmosphere. Its annual global emission is estimated to be in the range of 400-600 teragrams of carbon (Tg C) (Guenther et al., 2006; Arneth et al., 2008). Despite its large flux, isoprene had not been generally considered to be an SOA precursor due to the high volatility of its known reaction products. However, Claeys et al. (2004) first identified two diastereoisomeric 2-methyltetrols in Amazonian rain forest aerosols as isoprene oxidation products. Since then, isoprene has been believed to be a large biogenic source of SOA mass. Monoterpenes and sesquiterpenes are also believed to be the major biogenic sources of SOA mass. Global bottom-up model estimates for biogenic SOA are in the range of 9–50 Tg C yr⁻¹ (Kanakidou et al., 2005), while recent top-down estimates, including isoprene SOA, are as high as 185 Tg C yr⁻¹ (Hallquist et al., 2009).

In forested areas, biogenic emissions may govern the air chemistry and SOA formation in summer when intense sunlight and high ambient temperatures are common. High loading of natural aerosols over boreal forests was reported in northern Europe (Tunved et al., 2006). In the past decade, the identification of SOA tracers of isoprene, monoterpenes, and sesquiterpene oxidation products has been conducted in chamber experiments (e.g., Hoffmann et al., 1997; Yu et al., 1999; Iinuma et al., 2007; Jaoui et al., 2007; Sato, 2008) and ambient aerosols from urban

(e.g., Hu et al., 2008; Fu et al., 2010; Stone et al., 2010), forested or mountain areas (e.g., Kavouras et al., 1998; Claeys et al., 2004; Cahill et al., 2006; Kleindienst et al., 2007; Lewandowski et al., 2007; Wang et al., 2008; Kourtchev et al., 2009), as well as the Arctic region (Fu et al., 2009). These studies provide insights into sources and processes that influence SOA production and their spatial and seasonal distributions.

However, information with regard to the BVOC oxidation products at high altitudes remains limited. High mountains may provide a unique situation for atmospheric chemistry because they sometimes exist in the free troposphere (FT) due to the downward movement of the planetary boundary layer (PBL) during the nighttime. Heald et al. (2005) reported a large, sustained source of SOA in the FT from the oxidation of long-lived volatile organic compounds. Henze and Seinfeld (2006) reported that inclusion of isoprene as a source of SOA in a global model substantially increases SOA concentrations in the FT, because isoprene, and especially its oxidation products, has much greater concentrations at higher altitudes than other biogenic SOA precursors. These studies highlight the need to investigate the organic molecular composition of atmospheric aerosols at high altitudes.

The objective of this research was to characterize the chemical compositions and abundance of SOA tracers produced by the oxidation of isoprene, α/β -pinene and β -caryophyllene, and to evaluate their contributions to organic carbon in the tropospheric aerosols over Mount Tai, Central East China (CEC).

2. Experimental section

2.1. Aerosol sampling

Mt. Tai (36.25°N and 117.10°E, 1534 m above sea level) is located in Shandong Province, Central East China (CEC, 30°N-40°N and 110°E-130°E), where the elevations in most of the flat region are less than 200 m. It lies in a deciduous forest zone, in which about 80% of the land is covered with vegetation. Almost 1000 species are known to grow in the mountain area (http://en.wikipedia.org/wiki/Mount_Tai). However, vegetation at the mountaintop is limited to

bushes, and the ground surfaces are mostly rocks. As part of the MTX2006 campaign, daytime/nighttime and three-hour aerosol samplings were performed from May 28 to June 28, 2006 at the balcony of the 2nd floor of the observatory (~10 m, above ground level) on the top of Mt. Tai using pre-combusted (450 °C for 6 h) quartz fiber filters and a high-volume air sampler at a flow rate of 1.0 m³ min⁻¹. Eighty-one aerosol samples (including 5 whole-day, 19 daytime (6:00-18:00, local time), 20 nighttime (18:00-6:00), and 37 three-hour samples) were collected during the campaign. Among them the results of daytime/nighttime samples (n=39) were presented here. The PBL height at Mt. Tai was estimated using a WRF/Chem model. The results showed that the PBL height reached a maximum of c.a. 4000 m at midday and a minimum of 200 m during the night to early morning period, with averages of 2200 m and 600 m during the campaign (Takigawa et al., unpublished data).

2.2. Extraction, derivatization, and GC/MS determination

Details of the sample extraction and derivatization have been presented elsewhere (Fu et al., 2008). Briefly, filter aliquots were extracted with dichloromethane/methanol (2:1, v/v), followed by TMS derivatization with 50 µl N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in the presence of 1% trimethylsilyl chloride and 10 µl of pyridine prior to GC/MS injection. GC/MS analyses of samples were performed on a Hewlett-Packard model 6890 GC coupled to Hewlett-Packard model 5973 mass-selective detector (MSD). The GC instrument was equipped with a split/splitless injection and a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ and then to 300 °C at 5 °C min⁻¹ with final isothermal hold at 300 °C for 16 min. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and scanned in the range of 50 to 650 Da. Data were acquired and processed with the Chemstation software.

Individual compounds (TMS derivatives) were identified by comparison of mass spectra with those of authentic standards or literature data (Claeys et al., 2004; Jaoui et al., 2007; Hu et al., 2008). Following fragment ions were used: m/z 219 and 277 for 2-methyltetrols, m/z 231 for C₅-alkene triols, m/z 219 and 203 for 2-methylglyceric acid, m/z 171 for pinic acid, m/z 349 for

3-hydroxyglutaric acid, m/z 405 for 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), and m/z 383 for β -caryophyllinic acid. Quantification was conducted using calibration curves by analyzing aliquots of a stock solution of authentic standards that had been derivatized using the procedure mentioned above. For the quantification of 3-hydroxyglutaric, *cis*-pinonic, and pinic acids, their GC/MS response factors were determined using authentic standards. *cis*-Norpinic acid was quantified using the response factor of *trans*-norpinic acid. β -Caryophyllinic acid (a diacid similar to pinic acid) was estimated using the response factor of pinic acid (Jaoui et al., 2007). 2-Methylglyceric acid, C₅-alkene triols, 2-methyltetrols and 3-methyl-1,2,3-butanetricarboxylic acid were quantitatively determined with a capillary GC (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m \times 0.2 mm i.d., 0.50 μ m film thickness), and a flame ionization detector (FID). The identification of the organic compounds quantified by GC-FID was confirmed by GC/MS analysis. The standard of *meso*-erythritol, a surrogate compound generally used for the quantification of 2-methyltetrols (e.g., Claeys et al., 2004; Ding et al., 2008; Kourtchev et al., 2009), was quantitatively determined by both GC/MS and GC-FID. The analytical error in the quantification of *meso*-erythritol between the two methods was <5%.

Field blank filters were treated as real samples for quality assurance. Target compounds were not detected in the blanks. Recoveries for the authentic standards or surrogates that were spiked onto pre-combusted quartz filters (n = 3) were $94 \pm 2.6\%$ for *meso*-erythritol, $91 \pm 5.5\%$ for 3-hydroxyglutaric acid, $64 \pm 5.9\%$ for *cis*-pinonic acid, $93 \pm 2.3\%$ for *trans*-norpinic acid, and $79 \pm 2.3\%$ for pinic acid. Relative standard deviation of the concentrations based on duplicate sample analysis was generally <10%.

OC was determined using a Sunset Lab EC/OC Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol. The concentrations of OC reported here are corrected for the field blanks. Duplicate analyses of filter samples showed uncertainties of $\pm 10\%$.

3. Results and discussion

3.1. Isoprene, α/β -pinene, and β -caryophyllene oxidation products

Six compounds were identified as isoprene SOA tracers in the tropospheric aerosols over Mt. Tai, including 2-methylglyceric acid, three C₅-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) (Table 1). Concentration ranges of 2-methyltetrols were 17-268 ng m⁻³ (average 98 ng m⁻³) during the daytime and 2.2-457 ng m⁻³ (123 ng m⁻³) during the nighttime with 2-methylerythritol being about 2.1-fold more abundant than 2-methylthreitol. The ratio is similar to those observed in other studies (e.g., Claeys et al., 2004a; Ion et al., 2005; Cahill et al., 2006). The levels of 2-methyltetrols are comparable to those reported in aerosols from Mt. Changbai, Northeast China (22-282 ng m⁻³) (Wang et al., 2008), and are slightly higher than those reported in the Amazon (Claeys et al., 2004), Hungary (Ion et al., 2005), Finland (Kourtchev et al., 2008a), Germany (Kourtchev et al., 2008b), and United States (Cahill et al., 2006; Ding et al., 2008).

C₅-Alkene triols, which are unique isoprene SOA tracers under low-NO_x conditions (Surratt et al., 2006), were detected in all samples with an average concentration of 18 ± 12 ng m⁻³ for both daytime and nighttime samples, which are lower than those (~50 ng m⁻³) reported in subtropical Hong Kong (Hu et al., 2008), but are higher than those reported in other studies from midlatitudes, e.g., a Californian pine forest, USA (3.47 ng m⁻³) (Cahill et al., 2006) and Jülich, Germany (1.6-4.9 ng m⁻³) (Kourtchev et al., 2008b), and 2-3 orders of magnitude higher than those reported in the Arctic (Fu et al., 2009). The concentration ranges of 2-methylglyceric acid, which is possibly formed by further oxidation of methacrolein and methacrylic acid from isoprene (Claeys et al., 2004b; Surratt et al., 2006), were 11-96 ng m⁻³ (45 ng m⁻³) during the daytime and 3.7-96 ng m⁻³ (40 ng m⁻³) during the nighttime in the Mt. Tai aerosols.

Pinonic, norpinic, and pinic acids were detected as monoterpene oxidation products. These acids are produced by photooxidation of α/β -pinene via reactions with O₃ and OH radicals (e.g., Hoffmann et al., 1997; Yu et al., 1999; Iinuma et al., 2004). Concentrations of pinonic, norpinic, and pinic acids in this study ranged from 0.21-22 ng m⁻³, 0.07-2.0 ng m⁻³ and 0.36-6.3 ng m⁻³,

respectively (Table 1). The concentrations of pinonic acid in the Mt. Tai aerosols were about 2 times higher than those of pinic acid. A similar pattern has been reported in other studies (e.g., Kavouras et al., 1999). However, higher concentrations of pinic acid than pinonic acid have been reported in the aerosols from a coniferous forest in Germany (Plewka et al., 2006) and Research Triangle Park (RTP), USA (Kleindienst et al., 2007).

Two novel α -pinene SOA tracers were identified in aerosols as 3-hydroxyglutaric acid (3-HGA) (Claeys et al., 2007) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007). Both 3-HGA and MBTCA are generated by the smog chamber experiments of α -pinene under UV-radiation in the presence of NO_x . Concentration ranges of 3-HGA were 2.9-42 ng m^{-3} (average 16 ng m^{-3}) during the daytime and 0.86-43 ng m^{-3} (15 ng m^{-3}) during the nighttime. Concentration ranges of MBTCA were 2.3-14 ng m^{-3} (6.7 ng m^{-3}) and 2.0-15 ng m^{-3} (4.9 ng m^{-3}) during the daytime and nighttime, respectively.

Because of their high reactivity and relatively low vapor pressure, sesquiterpenes have been the least studied BVOCs. Among sesquiterpenes emitted from the plants, β -caryophyllene is one of the most abundant species and most frequently reported (Duhl et al., 2008). β -Caryophyllinic acid, an ozonolysis or photo-oxidation product of β -caryophyllene (Jaoui et al., 2007), was identified in both daytime (1.8-35 ng m^{-3} , average 12 ng m^{-3}) and nighttime (1.2-39 ng m^{-3} , 12 ng m^{-3}) samples without any significant differences. These values are similar to those reported in the aerosols from Hong Kong (Hu et al., 2008) and Research Triangle Park, North Carolina (Lewandowski et al., 2007), but are about 2 orders of magnitude higher than those reported in the Arctic aerosols (Fu et al., 2009).

3.2. Temporal variations

In the previous study of the Mt. Tai aerosols (Fu et al., 2008), the temporal variation of levoglucosan, a tracer for biomass burning, showed two major peaks: one during 5-7 June (Event 1, E1) and the other during 12-14 June (Event 2, E2), as well as one minor peak on 27 June (Event 3, E3). Similar patterns were observed for other biomass burning tracers such as β -sitosterol, vanillic acid, and syringic acid (Fu et al., 2008). Thus, E1 and E2 were identified as major episodes of field burning of agricultural residues such as wheat straws in the CEC.

Figure 1 presents the overall temporal variations of the polar organic tracers. The isoprene oxidation tracers showed very similar temporal trends each other (Figure 1a-d). In addition to the peaks at E1, E2 and E3 when levoglucosan maximized, 2-methyltetrols showed some other peaks during 1-2 and 19-22 June. Similar concentration peaks can also be found in the temporal trends of α/β -pinene oxidation products such as 3-HGA and MBTCA (Figure 1), as well as malic acid (Fu et al., 2008). Malic acid can be produced by the photochemical oxidation of succinic acid in the atmosphere (Kawamura and Ikushima, 1993). Furthermore, isoprene SOA tracers such as 2-methylthreitol and 2-methylerythritol generally showed diurnal variations with higher concentrations at night (Figure 1). This feature became prominent during 29 May-3 June when a clear diurnal cycle was found (Figure 1c and 1d). In contrast, α/β -pinene SOA tracers such as pinic and pinonic acids do not show the similar diurnal patterns but exhibit rather opposite trends with lower concentrations at night (Figure 1h).

A positive correlation was found between the concentrations of 2-methyltetrols and C₅-alkene triols ($R^2 = 0.54$, Figure 2a) in the Mt. Tai samples. However, the concentration ratios of 2-methyltetrols to C₅-alkene triols significantly varied (Figure 3), suggesting that their formation pathways may be different. Wang et al. (2005) reported that these polyols are formed through diepoxy derivatives of isoprene, which can be converted into 2-methyltetrols through acid-catalyzed hydrolysis. Alternatively, the formation of C₅-alkene triols was explained through rearrangement reactions of hydroxyperoxy radicals that are formed in the initial photooxidation of isoprene (Surratt et al., 2006). In addition, the correlation coefficients (R^2) between the concentrations of 2-methyltetrols and C₅-alkene triols were 0.81 for nighttime samples versus 0.50 for daytime samples. This difference may suggest that the atmospheric behaviors of 2-methyltetrols and C₅-alkene triols were more consistent in the FT than in the boundary layer.

The temporal variations of α/β -pinene oxidation tracers (Figure 1e-i) were different from those of isoprene oxidation tracers (Figure 1a-d). Cahill et al. (2006) also reported a poor correlation between monoterpene oxidation products and 2-methyltetrols in mountain aerosols. As mentioned above, pinic acid and pinonic acid exhibited similar diurnal variations with

higher concentrations during the daytime. 3-HGA and MBTCA, however, did not reveal such patterns. This difference suggests that the time scales of the formation of these compounds are longer, which is in agreement with later-generation oxidation products of α -pinene. Kourtchev et al. (2009) also reported that there were no clear diurnal variations observed for 3-HGA and MBTCA at a forested site of K-pusztá, Hungary. However, in their study, the diurnal pattern of pinic acid showed higher concentrations at night and was explained by the fresh formation (dark ozonolysis of α -pinene) and/or enhanced gas-to-particle partitioning at the cooler nighttime temperatures.

Interestingly, pinonic, norpinic, and pinic acids showed a peak during 8-10 June, which was not found for other polar tracers. In fact, a rain event occurred in the evening of 7 June, although the precipitation was rather small (0.8 mm). Air mass trajectory analysis showed that the source region of air masses that arrived over Mt. Tai had shifted from the South to the North China during this period (Fu et al., 2008). Based on the levels of CO, ozone (Li et al., 2008), and levoglucosan (Fu et al., 2008), as well as air mass trajectories, we consider that a fresh air mass had intruded from the north over Mt. Tai during 8-10 June. This interpretation is further supported by the exceptionally high NO_x/NO_y ratio during the period (Kanaya et al., 2009). As expected, MBTCA and 3-HGA, which are later-generation photooxidation products of α -pinene, did not show a peak during this episode. The enhanced concentrations of pinic and pinonic acids, which are earlier-generation photooxidation products compared to MBTCA and 3-HGA (Szmigielski et al., 2007; Kourtchev et al., 2009), suggest that the photooxidation of α -pinene was not completed. The concentration ratio of 3-HGA plus MBTCA to pinic acid ($(3\text{HGA} + \text{MBTCA})/\text{pinic}$) also showed the lowest value during 8-10 June (Figure 3). In addition, such a ratio was generally higher during the nighttime than daytime, indicating that the later-generation oxidation products were more abundant and thus the aerosols were more aged during the nighttime when the summit of Mt. Tai was in the free troposphere.

Temporal variations of β -caryophyllinic acid (Figure 1j) showed two major peaks at E1 and E2. These peaks are substantially different from those of isoprene or α/β -pinene oxidation tracers (Figure 1a-i). However, they are similar to that of levoglucosan (Fu et al., 2008).

Interestingly, β -caryophyllinic acid and levoglucosan showed a positive correlation ($R^2 = 0.52$, Figure 2b), indicating that this acid mainly originated from biomass burning in early summer or from the same source regions. However, no correlations were found between levoglucosan and isoprene or α/β -pinene SOA tracers. This result is reasonable because the emissions of isoprene and monoterpenes are insignificant for most of the widely planted crop species (Kesselmeier and Staudt, 1999). Although little is known about the specific sesquiterpene emissions of wheat straws, crop species such as corn and potato have been found to emit sesquiterpene species including β -caryophyllene (Duhl et al., 2008 and references therein). Studies have found that sesquiterpene emissions are positively correlated with ambient temperatures (Duhl et al., 2008). Thus, the enhanced field burning activities of wheat straws in the CEC during early summer may release levoglucosan and sesquiterpenes such as β -caryophyllene to a certain quantity through either combustion processes or increasing leaf temperature.

As reported in a previous study, dehydroabietic acid, a smoke marker of coniferous trees, showed a major peak during E3 (Fu et al., 2008), suggesting that E3 was associated with the biomass burning source that may be different from E1 and E2. During E3, air mass trajectory analysis showed that most of the air masses came from South China where the field burning of wheat straws was almost finished, but the harvest of wheat was still active in the north. Thus, the concentration peak of isoprene and α/β -pinene SOA tracers during E3 (Figure 1) likely originate from forest fires in South China, since they enhance the emissions of BVOCs (Blake et al., 1994; Andreae and Merlet, 2001).

3.3. Hierarchical cluster analysis (HCA)

In order to get a general view on the sources of biogenic SOA tracers detected in the tropospheric aerosols over Mt. Tai, HCA was applied to the present dataset together with the data of OC, levoglucosan, and malic acid. HCA is a classification method used to divide the data into clusters. The software SPSS was used as a statistical analysis program. HCA was performed with the Ward's method using the standardized squared Euclidean distance as a grouping criterion. As shown in Figure 4, three clusters (1, 2 and 3) can be distinguished for both daytime and nighttime aerosols. During the daytime, cluster 1 is composed of

3-hydroxyglutaric acid, malic acid, β -caryophyllinic acid, OC, and levoglucosan. Thus, cluster 1 is mainly associated with the emissions from biomass burning. 3-Hydroxyglutaric acid was strongly correlated with malic acid ($R^2 = 0.91$, Figure 2c), indicating a similar formation pathway or similar source regions. Although 3-hydroxyglutaric acid can be generated in chamber experiments from the oxidation of α -pinene in the presence of NO_x (Claeys et al., 2007), its formation mechanism is still unclear. Gómez-González et al. (2008) suggested that the isomer of 3-hydroxyglutaric acid, 2-hydroxyglutaric acid may also result from the oxidative decay of unsaturated fatty acids (UFAs), which is similar to malic acid.

In this study, the temporal variations of 3-hydroxyglutaric acid showed concentration peaks during biomass burning events 1 and 2. Such peaks were also found for malic acid (Fu et al., 2008). However, the active field burning of wheat straws should not enhance the emission of α -pinene, the precursor of 3-hydroxyglutaric acid. Alternatively, the significantly high loadings of organic aerosols during E1 and E2 (averaged OC level was about $57 \mu\text{gC m}^{-3}$) may influence the gas/particle partitioning of these compounds. In addition, the co-emissions of UFAs and α -pinene from biogenic sources may also be one of the potential reasons to explain the positive correlation between malic acid and 3-HGA observed in this study. Cluster 2 contains pinonic and pinic acids that are associated with the photooxidation of α -pinene. Cluster 3 contains 2-methylglyceric acid, C_5 -alkene triols and 2-methyltetrols, which are produced by the photooxidation of isoprene. Two α/β -pinene SOA tracers (norpinic acid and MBTCA) are also in cluster 3. Although these compounds may have the source regions similar to those of isoprene oxidation products, we cannot provide a reasonable explanation for the results at this moment.

For the nighttime samples, cluster 1 contains the same pattern as that during the daytime. Cluster 2 contains pinonic, pinic, and norpinic acids that are derived from the photochemical oxidation of α -pinene. Cluster 3 contains isoprene oxidation products together with MBTCA, which is a later-generation photooxidation product of α/β -pinene as mentioned above. It should be noted that in Figure 4, only norpinic acid moved from daytime cluster 3 that is characterized by isoprene SOA tracers to nighttime cluster 2 that is associated with α/β -pinene SOA tracers

(pinic and pinonic acids), indicating that norpinic acid may have formation pathways different from pinic and pinonic acids during the daytime. As shown in Figure 1f-h, pinonic and pinic acids, rather than norpinic acid, showed relatively higher production during the daytime.

3.4. Enhanced contribution of measured isoprene oxidation products

In the Mt. Tai aerosols, total concentrations of isoprene SOA tracers ($161 \pm 99 \text{ ng m}^{-3}$ during the daytime and $180 \pm 146 \text{ ng m}^{-3}$ during the nighttime) are 5-6 times higher than those of α/β -pinene SOA tracers (daytime $33 \pm 12 \text{ ng m}^{-3}$ vs. nighttime $27 \pm 13 \text{ ng m}^{-3}$) (Table 1). This feature is different from the previous studies as summarized in Table 2, in which we propose a concentration ratio of total measured isoprene to α/β -pinene oxidation products ($R_{\text{iso/pine}}$) as a tracer to evaluate the relative contribution of isoprene and α/β -pinene oxidation to SOA formation. The averaged $R_{\text{iso/pine}}$ values in this study were 4.9 during the daytime and 6.7 during the nighttime, which are higher than those reported from other regions (Table 2). For example, $R_{\text{iso/pine}}$ values from different sites in China and Sierra Nevada, USA are slightly lower (2.8-5.4), but are significantly lower in aerosols from North Carolina, USA (0.89), Jülich, Germany (0.80), Rishiri Island, Japan (0.54), and Hong Kong, China (0.46). The ratios are further lower in PM_{10} samples from Hyytiälä, Finland (0.24-0.34). Interestingly, the lowest values (0.08-0.24) were observed in the Canadian high Arctic, especially before the polar sunrise (Fu et al., 2009). These comparisons indicate that organic aerosols over Mt. Tai are highly influenced by the isoprene oxidation products.

Average contributions of isoprene oxidation products to OC were found to be 0.47% during the daytime and 0.51% during the nighttime, which were 4-6 times higher than those of α/β -pinene oxidation products (0.11% during the daytime and 0.08% during the nighttime) (Table 1). The contributions of β -caryophyllinic acid to OC were 0.044% during the daytime and 0.036% during the nighttime. These results further suggest that the isoprene-derived SOA are more abundant than other biogenic SOA in the atmosphere at high altitudes in Central East Asia. Because the mountaintop exists in the FT at night, higher contribution of isoprene to SOA formation during the nighttime ($R_{\text{iso/pine}} = 6.7$) than daytime (4.9) may indicate that a large fraction of organic aerosol derives from isoprene oxidation in the FT (Heald et al., 2005).

Another possibility is that isoprene SOA tracers may be less efficiently removed than α/β -pinene SOA tracers in the FT during nighttime.

Gas/particle partitioning of SOA tracers can be affected by relatively lower temperatures at night (10-25 °C) when the summit of Mt. Tai is within the free troposphere. Lower temperatures in the FT can lead to the condensation of semivolatile products and/or adsorption on the pre-existing particles. Moreover, loss pathways such as wet deposition are less important compared to lower altitudes (Carlton et al., 2009). In the present study, concentrations of isoprene SOA tracers, especially 2-methyltetrols showed higher levels during the nighttime (average 123 ng m⁻³) than daytime (98.0 ng m⁻³) (Table 1 and Figure 1). 2-Methyltetrols are known to be present predominantly in the particle phase (Claeys et al., 2004). If lower ambient temperatures were the main factor to control higher concentrations of isoprene SOA tracers at night, the α/β -pinene SOA tracers should also exhibit higher concentrations at night. However, their concentrations were lower during the nighttime than daytime (Table 1 and Figure 1h). This behavior suggests that the higher nighttime levels of isoprene oxidation products over Mt. Tai can not be simply explained by the lower ambient temperatures.

The higher concentrations of isoprene oxidation products may actually be associated with greater emissions of isoprene than α/β -pinene and β -caryophyllene in the studied region. Central East China is not only the biggest source region of anthropogenic trace gases in China (Li et al., 2008; Zhao et al., 2009), but also one of the most important source regions of isoprene in the world during the summer (Guenther et al., 1995). Aerosol accumulation mode number concentrations in CEC are postulated to be among the highest in the world (Andreae and Rosenfeld, 2008). During MTX2006, the averaged mixing ratios of isoprene over Mt. Tai were about double those of α/β -pinene (Suthawaree et al., 2010). The emissions of biogenic VOCs were mainly from nearby trees or the local biosphere on the mountain slopes, over which the air masses have traveled as the daytime upslope wind (Kanaya et al., 2009).

Biogenic VOCs are quickly oxidized by OH, O₃ and/or NO₃ (and occasionally chlorine atoms) in the atmosphere. Lifetimes of isoprene are on a scale of hours with respect to OH and NO₃, and days with O₃. Monoterpenes generally react with oxidants more quickly than isoprene

does, with lifetimes of minutes to days. Sesquiterpenes generally have shorter lifetimes of minutes to hours (Atkinson and Arey, 2003). In the atmosphere, ozonolysis is a minor contributor to isoprene SOA formation compared to the reaction with OH, while terpenes are mainly oxidized by O₃. The midday peak concentration of OH during MTX2006 predicted by a photochemical box model was about $5.0 \times 10^6 \text{ cm}^{-3}$ with a maximum of $1.6 \times 10^7 \text{ cm}^{-3}$, and the 24-hour average concentration was about $1.8 \times 10^6 \text{ cm}^{-3}$ (Kanaya et al., 2009). Inomata et al. (2010) reported the mixing ratio of isoprene was almost zero at night, while that of monoterpenes was above zero even at night during the MTX2006 campaign. Interestingly, the diurnal variation of isoprene showed a peak early in the afternoon (12:00-14:00, local time). Methylvinylketone (MVK) and methacrolein (MACR), which are earlier-generation products of isoprene, peaked late in the afternoon, after the peak for isoprene (Inomata et al., 2010). The time lag of several hours in the mixing ratio of the earlier-generation products of MVK and MACR indicates a potential production of later-generation products of isoprene at night. This may partly explain the higher nighttime concentrations of isoprene SOA tracer.

The chemical mechanisms for SOA formation differ between day/night and between air mass compositions with e.g. different OH, ozone, and NO_x levels (Hallquist et al., 2009), as well as the aerosol acidity (Surratt et al., 2007). For example, a recent laboratory study has shown that SOA formation from isoprene can be significantly enhanced in the presence of acidified sulfate seed aerosol (Surratt et al., 2010). Furthermore, the SOA yield from cloud-processing of isoprene oxidation products could be enhanced in regions with high NO_x and isoprene emissions (Ervens et al., 2008). During the sampling period, brown clouds (polluted clouds) were occasionally observed uplifting from the mountain waist to the mountaintop during late afternoon to early evening. This process may further support the enhanced contribution of isoprene oxidation products in the present study because cloud-produced SOA can vent to free troposphere due to convective mixing (Carlton et al., 2009). However, the aqueous phase SOA production from isoprene is influenced by factors such as cloud contact time and initial VOC/NO_x ratio (Ervens et al., 2008), which remains an area for further study.

Except for Mt. Tai and an urban region of Hong Kong, the $R_{\text{iso/pine}}$ values seem to depend on latitude (Table 2). Higher $R_{\text{iso/pine}}$ values are observed at lower latitudes such as in South China (Hainan, 5.4), followed by those at mid-latitudes such as northeastern China (Mt. Changbai), USA, Japan, and Germany. As mentioned above, the lowest values are found at higher latitudes such as Finland and the Canadian high Arctic at Alert. This latitudinal trend is in accordance with the global distribution of isoprene emission rate estimated by a global model in which tropical woodlands have high fluxes of isoprene ($> 1 \text{ g C m}^{-2} \text{ month}^{-1}$) throughout the year (Guenther et al., 1995). These investigators stated that high summertime isoprene fluxes are also common in some temperate zones including eastern China. In contrast, the highest monoterpene emission rates in July are predicted for the western United States, eastern Canada, central Europe, and parts of the Amazon basin. The low $R_{\text{iso/pine}}$ value in Finland is further supported by the Finland country mean ratio R of emitted isoprene carbon to monoterpene carbon ($R = 0.16$) reported by Lindfors and Laurila (2000). Thus, we propose here that the $R_{\text{iso/pine}}$ value could be used to give a first indication on the relative contributions of isoprene and α/β -pinene to biogenic SOA formation at different locations.

3.5. Estimated contributions of BVOCs to secondary organic carbon

Contributions of BVOCs to secondary organic carbon (SOC) were estimated using a tracer-based method reported by Kleindienst et al. (2007). Using the measured concentrations of tracer compounds in the Mt. Tai aerosols and the laboratory-derived tracer mass fraction (f_{soc}) factors of 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for α -pinene, and 0.0230 ± 0.0046 for β -caryophyllene (Kleindienst et al., 2007), we calculated the contributions of these precursors to ambient OC (Table 1). α -Pinene and β -caryophyllene are found to be rather minor contributors to SOC during MTX2006 (Figure 5). It should be noted that the tracer-based method is a simplification of a truly complex system of the real atmosphere (Stone et al., 2010). The uncertainties of this approach range from 20 to 48%, based on the standard deviation of f_{soc} mentioned above (Kleindienst et al., 2007). In addition, Kleindienst et al. (2007) derived mass fractions of SOA tracers by using ketopinonic acid as the surrogate for all SOA tracers; however, either authentic standards or different surrogates were used in this study, as mentioned in

Section 2.2.

The contributions of α -pinene to SOC ranged from 0.06 to 0.24 $\mu\text{gC m}^{-3}$ (average 0.14 $\mu\text{gC m}^{-3}$) during the daytime and 0.02 to 0.24 $\mu\text{gC m}^{-3}$ (0.12 $\mu\text{gC m}^{-3}$) during the nighttime (Table 1). For β -caryophyllene, the contributions were 0.08-1.5 $\mu\text{gC m}^{-3}$ (0.54 $\mu\text{gC m}^{-3}$) and 0.05-1.7 $\mu\text{gC m}^{-3}$ (0.51 $\mu\text{gC m}^{-3}$), respectively. Hu et al. (2008) mentioned that acidic isomers of β -caryophyllinic acid could be formed from the photooxidation of other sesquiterpenes having an endocyclic C=C bond, which might co-elute with β -caryophyllinic acid. Therefore, the estimated contribution of β -caryophyllene SOC may represent a broader class of sesquiterpenes. The isoprene-based tracers (2-methylglyceric acid and 2-methyltetrols) were calculated to be 0.20-2.4 $\mu\text{gC m}^{-3}$ (0.92 $\mu\text{gC m}^{-3}$) during the daytime and 0.04-3.6 $\mu\text{gC m}^{-3}$ (1.1 $\mu\text{gC m}^{-3}$) during the nighttime. These values are similar to those reported at Research Triangle Park, North Carolina (Kleindienst et al., 2007), but are higher than those reported in urban regions such as Hong Kong (0.20 $\mu\text{gC m}^{-3}$) (Hu et al., 2008) and Mexico (0.22 $\mu\text{gC m}^{-3}$) (Stone et al., 2010), and are about 2-3 orders of magnitude higher than those reported in the Canadian high Arctic ($1.7 \pm 0.63 \text{ ngC m}^{-3}$) (Fu et al., 2009).

The total SOC derived from isoprene, α -pinene and sesquiterpene in the Mt. Tai aerosols ranged from 0.42 to 3.1 $\mu\text{gC m}^{-3}$ (average 1.6 $\mu\text{gC m}^{-3}$) during the daytime and 0.11 to 4.2 $\mu\text{gC m}^{-3}$ (1.7 $\mu\text{gC m}^{-3}$) during the nighttime, which account for $10 \pm 5.8\%$ and $9.8 \pm 7.0\%$ of OC in the day- and nighttime samples, respectively (Table 1). As shown in Figure 5, total SOC% in OC was maximized (28%) during 18-21 June when the mixing ratio of isoprene was the highest (Inomata et al., 2010). In contrast, a minimum (2.9%) was found during 8-10 June when a clean air mass came from the north through the FT. Isoprene is clearly found to be the largest SOC contributor (followed by β -caryophyllene and α/β -pinene) in the Mt. Tai aerosols (Figure 5), accounting for 58% and 63% of BVOC-derived SOC during the daytime and nighttime, respectively. This finding is consistent with the results reported by Kleindienst et al. (2007) that isoprene was the largest contributor in the summer aerosols collected at Research Triangle Park, North Carolina. However, in Hong Kong where the annual emissions of monoterpenes ($3.5 \times 10^9 \text{ g C a}^{-1}$) were higher than that of isoprene ($1.3 \times 10^9 \text{ g C a}^{-1}$), α/β -pinene was found to be

the largest contributor to SOC, followed by β -caryophyllene and isoprene (Hu et al., 2008). These results indicate that the secondary organic aerosol compositions at different regions largely depend on factors such as the local vegetation, plant species, meteorological conditions, and regional chemistry.

4. Summary and conclusion

Biogenic SOA tracers of isoprene, α/β -pinene, and β -caryophyllene (e.g., 2-methyltetrols, pinic acid, and β -caryophyllinic acid) were measured in tropospheric aerosols collected at the summit of Mt. Tai, Central East China (CEC). Their total concentrations account for 0.19-1.6% (average 0.63%) and 0.23-2.0% (0.63%) of the OC in the mountain aerosols during the daytime and nighttime, respectively. β -Caryophyllinic acid showed a temporal pattern similar to those of OC and levoglucosan. This compound may originate from the biomass burning activities that maximize in CEC during early summer. However, isoprene and α/β -pinene SOA tracers showed different temporal patterns. Earlier-generation products such as 2-methyltetrols, pinonic acid, and pinic acid generally showed diurnal patterns with daytime maxima, while 2-methylglyceric acid, 3-hydroxyglutaric acid and MBTCA did not exhibit such patterns. This difference suggests that the time scales of the formation of the latter compounds are relatively longer, supporting the fact that they are later oxidation products of BVOCs. A positive linear correlation was found between 3-hydroxyglutaric acid and malic acid, suggesting that they were formed and/or transported from very similar source regions.

The contributions of isoprene, α/β -pinene, and β -caryophyllene to SOC formation were estimated using the ambient concentrations of biogenic SOA tracers. On average, the isoprene-derived SOC is about 7 and 2 times higher than those of α -pinene- and β -caryophyllene-derived SOC, respectively. The averaged ratio of isoprene to α/β -pinene oxidation products ($R_{\text{iso/pine}}$) was 4.9 during the daytime and 6.7 during the nighttime. These values are among the highest in the aerosols reported in different regions. Higher contributions of isoprene oxidation products to SOA formation in CEC may be explained by larger isoprene

emissions, together with relatively high levels of oxidants (e.g., OH) in summer. Such a high isoprene-derived SOA observed in the high altitudinal aerosols over Mt. Tai is consistent with previous findings from a model study that isoprene oxidation products have much greater concentrations at higher altitudes (Henze and Seinfeld, 2006), or from aircraft observation that reveal very high OC mass loadings over the Northwest Pacific during the ACE-Asia campaign (Heald et al., 2005). Further field studies such as aircraft measurements of biogenic SOA tracers over East Asia are needed.

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Table 1. Concentrations of biogenic SOA tracers measured in the tropospheric aerosols over Mt. Tai, Central East China (ng m^{-3}).

Species	Daytime (n=19)					Nighttime (n=20)				
	average	std ^a	min	max	% C in OC	average	std	min	max	% C in OC
OC ($\mu\text{gC m}^{-3}$)	19	10	5.1	48	-	21	17	2.5	67	-
Tracer for isoprene SOA										
2-methylglyceric acid	45	27	11	96	0.13	40	26	3.7	96	0.10
ΣC_5 -alkene triols ^b	18	12	4.2	46	0.06	18	15	2.6	64	0.06
2-methylthreitol	32	23	4.9	84	0.09	42	39	0.72	153	0.11
2-methylerythritol	66	48	12	184	0.20	81	72	1.5	304	0.23
subtotal	161	99	36	400	0.47	180	146	11	617	0.51
SOC _{isoprene} ^c ($\mu\text{gC m}^{-3}$)	0.92	0.58	0.20	2.4	6.2	1.1	0.85	0.04	3.6	6.7
Tracer for α/β-pinene SOA										
3-hydroxyglutaric acid	16	9.4	2.9	42	0.039	15	12	0.86	43	0.034
<i>cis</i> -pinonic acid	6.8	6.1	0.41	22	0.029	4.5	4.2	0.21	17	0.018
<i>cis</i> -norpinic acid	0.87	0.51	0.15	1.8	0.003	0.7	0.50	0.07	2.0	0.003
pinic acid	2.9	1.8	0.72	6.3	0.012	2.3	1.4	0.36	4.9	0.009
MBTCA ^d	6.7	3.5	2.3	14	0.023	4.9	3.0	2.0	15	0.018
subtotal	33	12	14	56	0.11	27	13	4.1	55	0.082
SOC _{α/β-pinene} ($\mu\text{gC m}^{-3}$)	0.14	0.05	0.06	0.24	0.94	0.12	0.06	0.02	0.24	0.74
Tracer for β-caryophyllene SOA										
β -caryophyllinic acid	12	9.0	1.8	35	0.044	12	11	1.2	39	0.036
SOC _{β-caryophyllene} ($\mu\text{gC m}^{-3}$)	0.54	0.39	0.08	1.5	2.9	0.51	0.50	0.05	1.7	2.4
total tracers	206	106	58	452	0.63	219	160	16	681	0.63
total SOC ($\mu\text{gC m}^{-3}$)	1.6	0.79	0.42	3.1	10	1.7	1.2	0.11	4.2	9.8

^a std: standard deviation.

^b C_5 -alkene triols: *cis*-2-methyl-1,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene.

^c The total mass concentrations of SOC produced by isoprene (2-methylglyceric acid and 2-methyltetrols were used), α/β -pinene, and β -caryophyllene were calculated using a tracer-based method reported by Kleindienst et al. (2007).

^d MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

Table 2. Concentration ratios of total isoprene SOA tracers to α/β -pinene SOA tracers ($R_{\text{iso/pine}}$) measured in the Mt. Tai aerosols compared to those reported in other studies.

Location	Type of aerosol	Isoprene SOA tracers		α/β -Pinene SOA tracers		$R_{\text{iso/pine}}$	Reference
		Tracers ^a	Aver. Conc. ^b	Tracers ^a	Aver. Conc.		
Mt. Tai, China	TSP, nighttime	1, 2, 3	180	4, 5, 6, 7, 8	27	6.7	This study
Mt. Tai, China	TSP, daytime	1, 2, 3	161	4, 5, 6, 7, 8	33	4.9	This study
Hainan, China	PM _{2.5} , 24 h	1, 2, 3	51	5, 7, 8	9.4	5.4	(Wang et al., 2008)
Changbai, China	PM _{2.5} , daytime	1, 2, 3	140	7, 8	38	3.7	(Wang et al., 2008)
Sierra Nevada, USA	TSP	1, 2, 3	57	4, 5, 6	18.3	3.1	(Cahill et al., 2006)
Changbai, China	PM _{2.5} , nighttime	1, 2, 3	114	7, 8	41	2.8	(Wang et al., 2008)
RTP, NC, USA	PM _{2.5}	1, 3	137	4, 7, 8, 9, 10, 11, 12	154	0.89	(Lewandowski et al., 2007)
Jülich, Germany	PM _{2.5}	1, 2, 3	20.5	4, 5, 7, 8	25.6	0.80	(Kourtchev et al., 2008b)
Rishiri Is., Japan	TSP	1, 2, 3	9.7	4, 5, 6, 7, 8	18	0.54	(Fu et al., unpublished data)
Hong Kong, China	PM _{2.5}	1, 2, 3	91.5	7, 8, 9, 10, 11, 12	199	0.46	(Hu et al., 2008)
Hyytiälä, Finland	PM ₁ , daytime	1, 2, 3	22.4	4, 5, 7, 8	65	0.34	(Kourtchev et al., 2008a)
Hyytiälä, Finland	PM ₁ , nighttime	1, 2, 3	15.6	4, 5, 7, 8	65	0.24	(Kourtchev et al., 2008a)
Alert, Canada	TSP, light spring	1, 2, 3	0.31	4, 5, 6, 7, 8	1.3	0.24	(Fu et al., 2009)
Alert, Canada	TSP, dark winter	1, 2, 3	0.26	4, 5, 6, 7, 8	3.2	0.08	(Fu et al., 2009)

^a Tracers: (1) 2-methyltetrols; (2) C₅-alkene triols; (3) 2-methylglyceric acid; (4) pinic acid; (5) norpinic acid, (6) pinonic acid; (7) 3-hydroxyglutaric acid; (8) MBTCA; (9)

3-hydroxy-4,4-dimethylglutaric acid; (10) 3-isopropylpentanedioic acid; (11) 3-acetylpentanedioic acid; (12) 3-acetylhexanedioic acid. ^b averaged concentration in ng m⁻³.

Figure captions

Fig. 1. Temporal variations of biogenic SOA tracers measured in the Mt. Tai aerosols during May-June, 2006. Event 1 (E1), E2, and E3 mean significant biomass burning periods reported in a previous study (Fu et al., 2008). The open and shaded circles represent the daytime and nighttime samples, respectively (The daytime/nighttime data during 2-5 June, 23 June and 25 June were obtained by the calculation of the unpublished data on three-hour samples).

Fig. 2. Relations between (a) 2-methyltetrols and C₅-alkene triols, (b) β-caryophyllinic acid and levoglucosan, and (c) 3-hydroxyglutaric acid and malic acid.

Fig. 3. Temporal trends of the concentration ratios of C₅-alkene triols to 2-methyltetrols, and the sum of 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) to pinic acid. The shaded circles/squares represent the nighttime samples.

Fig. 4. Hierarchical cluster analysis of biogenic SOA tracers, levoglucosan, malic acid and organic carbon (OC) in the Mt. Tai aerosols at (a) daytime, and (b) nighttime.

Fig. 5. Estimated contributions of different biogenic VOCs to SOC, and the temporal variations of the percentage of total SOC in OC.

Fig. 1 (Fu et al., 2010)

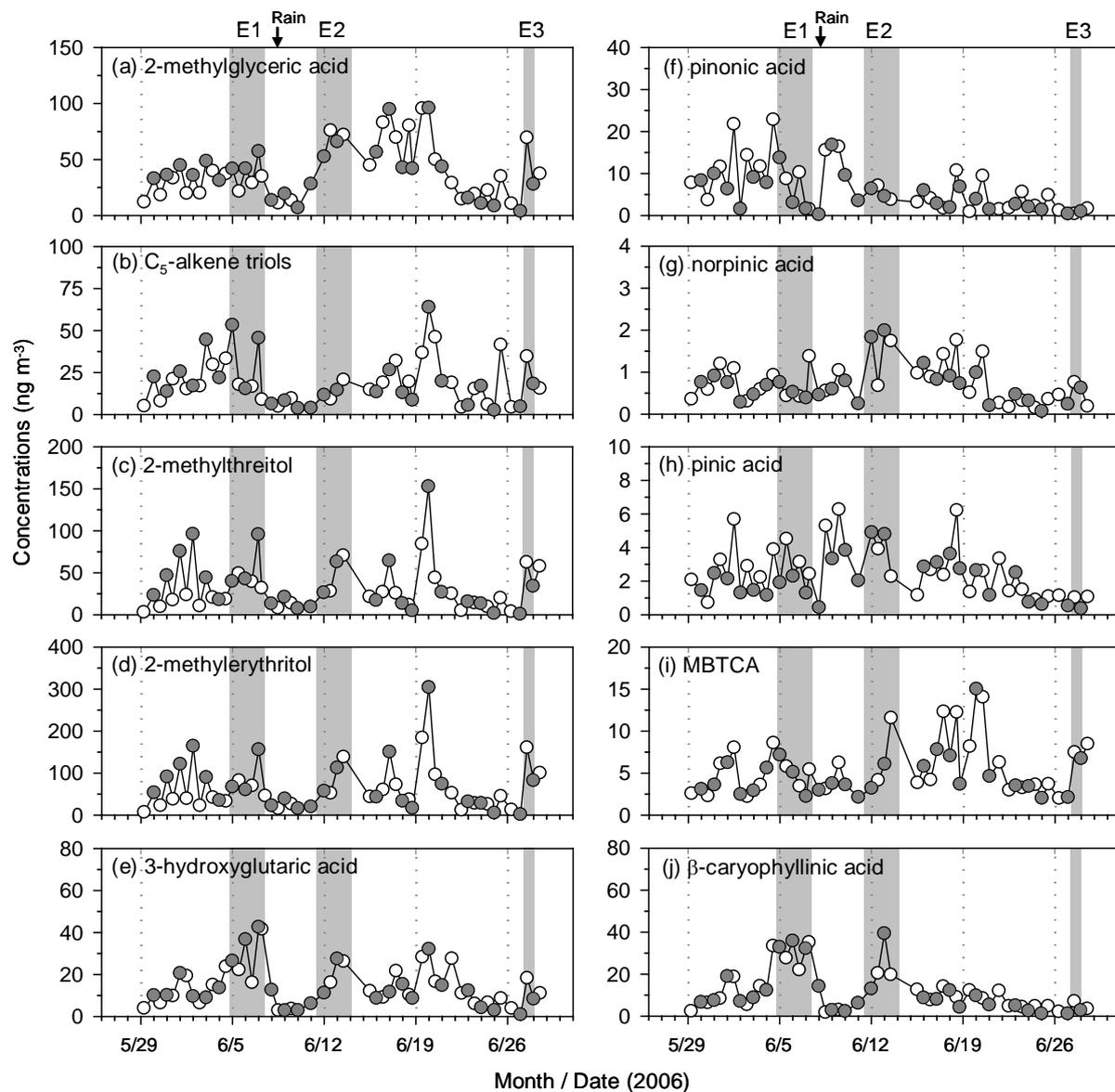


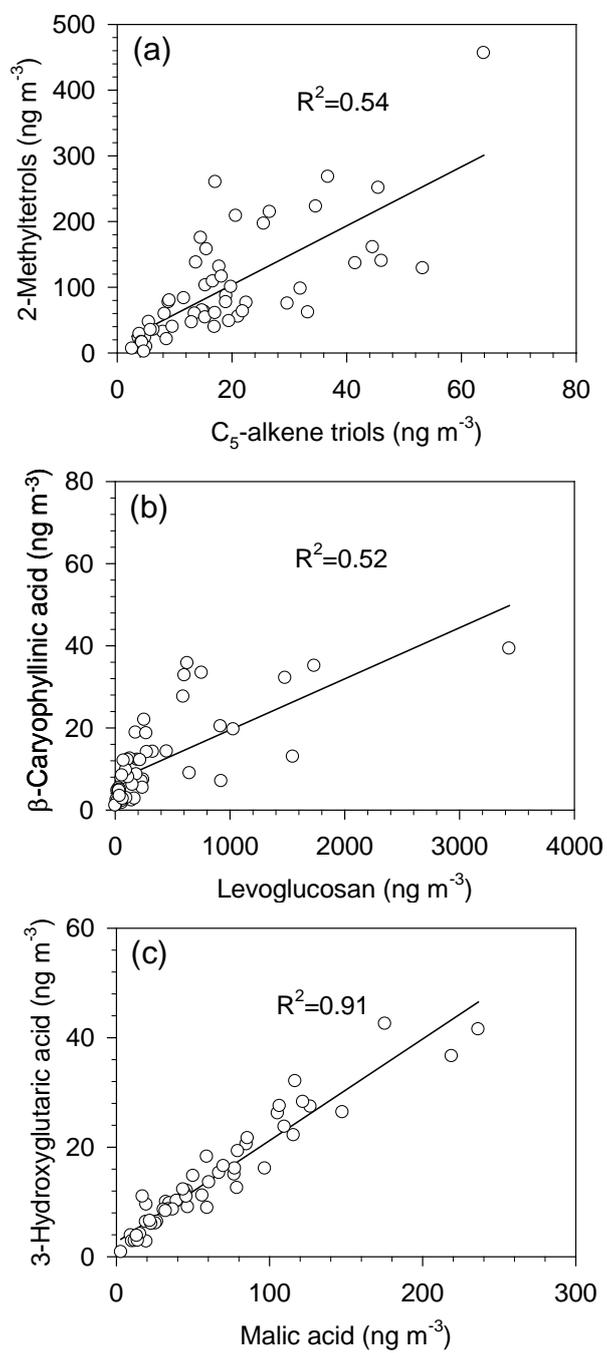
Fig. 2 (Fu et al., 2010)

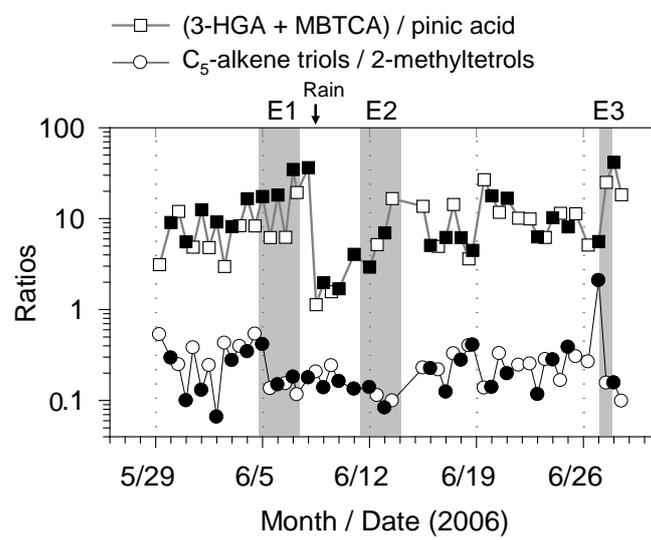
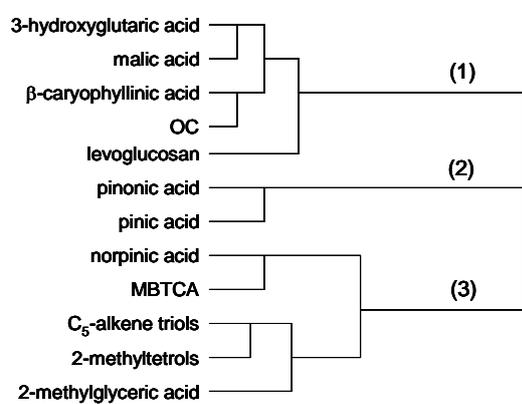
Fig. 3 (Fu et al., 2010)

Fig. 4 (Fu et al., 2010)

(a) daytime



(b) nighttime

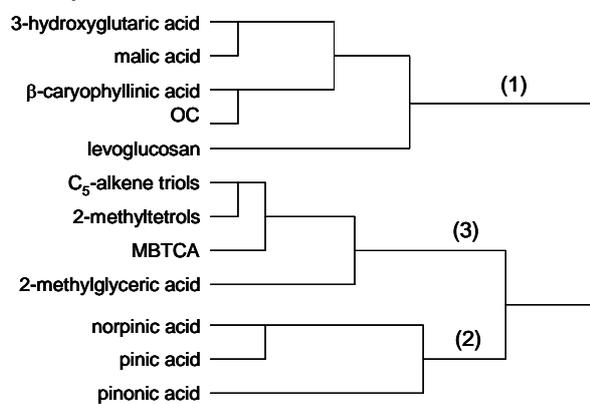


Fig. 5 (Fu et al., 2010)