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Summertime contributions of isoprene, monoterpenes, and sesquiterpene oxidation to the formation of secondary organic aerosol in the troposphere over Mt. Tai, Central East China during MTX2006

P. Q. Fu[1], K. Kawamura[1], P. Pochanart[2], H. Tanimoto[3], Y. Kanaya[2], and Z. F. Wang[4]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan
[2]Frontier Research Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan
[3]National Institute for Environmental Studies, Tsukuba, Japan

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[4]LAPC/NZC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

Correspondence to: P. Q. Fu (pqfu@pop.lowtem.hokudai.ac.jp)

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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 of isoprene, monoterpenes, and β-caryophyllene oxidation products were measured using gas chromatography/mass spectrometry. All the biogenic SOA tracers showed no clear diurnal variations, suggesting that they are formed during long-range atmospheric transport. Although isoprene- and monoterpene-derived SOA tracers did not correlate with levoglucosan (a biomass burning tracer), β-caryophyllinic acid showed a good correlation with levoglucosan, indicating that biomass burning may be a source for this compound. Total concentrations of isoprene oxidation products are much higher than those of monoterpene and β-caryophyllene oxidation products. The ratio of isoprene to monoterpene oxidation products ($R_{\mathrm{iso/mono}}$) was found to co-vary with ozone and NO_x during the summer campaign. The average $R_{\mathrm{iso/mono}}$ value was 6.94 at daytime and 10.0 at nighttime. These values are among the highest in the aerosols studied in different regions, which may be due to the large isoprene fluxes, high O_3 and NO_x levels and relatively high OH concentrations in CEC. Using a tracer-based method, we estimated the average concentrations of secondary organic carbon (SOC) derived from isoprene, monoterpenes, and β-caryophyllene to be 1.76 μgC m^{-3} at daytime and 1.85 μgC m^{-3} at nighttime. These values correspond to 11.2% and 11.0% of the total OC concentrations, in which isoprene-derived SOC are 7.4% and 8.0% at day- and night-time, respectively. This study suggests that isoprene is a more significant precursor for biogenic SOA than monoterpenes and β-caryophyllene in high altitude in CEC.

1 Introduction

Secondary organic aerosol (SOA) is an important component in the Earth's atmosphere. It may provide surfaces for heterogeneous reactions in the atmosphere, and can impact on the atmospheric radiation budget directly by scattering sunlight and indirectly by acting as cloud condensation nuclei (Kanakidou et al., 2005; Pöschl, 2005). The photooxidation of biogenic volatile organic compounds (BVOCs) that are emitted from vegetation to the atmosphere is an important source of SOA. On a global scale, emissions of BVOCs are suggested to be one order of magnitude larger than those of anthropogenic VOCs (Seinfeld and Pandis, 2006). Monoterpenes and sesquiterpenes are believed to be the largest biogenic sources of SOA mass, with global model estimates ranging from 12–70 Tg yr^{-1} (Kanakidou et al., 2005). Claeys et al. (2004a) first identified two diastereoisomeric 2-methyltetrols in Amazonian rain forest aerosols as photooxidation products of isoprene. They estimated its SOA production to be 2 Tg yr^{-1} globally. Isoprene is the most abundant non-methane hydrocarbon (c.a. 600 Tg yr^{-1}) emitted into the Earth's atmosphere (Guenther et al., 2006). Even its small SOA yield could enhance the predicted SOA formation seriously.

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 (Yu et al., 1999; Edney et al., 2005; Böge et al., 2006; Jaoui et al., 2007; Ma et al., 2007; Szmigielski et al., 2007a, b) and ambient aerosols from urban (Xia and Hopke, 2006; Hu et al., 2008), forested or mountain areas (Kavouras et al., 1998, 1999; Claeys et al., 2004a; Ion et al., 2005; Kourtchev et al., 2005, 2008b, 2009; Cahill et al., 2006; Kleindienst et al., 2007a; Wang et al., 2008), as well as the Arctic region (Fu et al., 2009). However up to date, information with regard to the BVOCs oxidation products in high altitudes is still 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) at nighttime. Recently, Heald et al. (2005) reported a large, sustained source of SOA in the FT from the oxidation of long-lived volatile organic compounds. A global model study showed that at higher altitudes, the isoprene oxidation products have much greater concentrations than other biogenic SOA precursors (Henze and Seinfeld, 2006).

The objective of this research was to characterize the chemical compositions and abundance of SOA tracers from isoprene, α-/β-pinene and β-caryophyllene oxidation, and to evaluate their contributions to organic carbon in the tropospheric aerosols over Mount Tai, Central East China (CEC). During the Mount Tai eXperiment 2006 (MTX2006) field campaign, simultaneous studies of ozone, nitrogen oxides ($NO_x=NO+NO_2$) and hydroxyl radical (OH) were conducted, which help us to better understand the atmospheric behaviors of biogenic SOA tracers in the troposphere over high mountains.

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 deciduous forest zone, in which about 80% are covered with vegetation. Almost 1000 species are known to grow in the mountain area. However, vegetations at the mountaintop are limited to bushes and the ground surfaces are mostly covered with rocks. As part of MTX2006 campaign, daytime/nighttime and three-hour aerosol sampling were performed from 28 May to 28 June 2006 at the balcony of the 2nd floor of observatory ($\sim$10 m, above ground level) on the top of Mt. Tai using pre-combusted ($450°$C for 6 h) quartz fiber filters and high-volume air sampler.

2.2 Extraction, derivatization, and GC/MS determination

Details of the sample extraction and derivatization are presented elsewhere (Fu et al., 2008). Briefly, filter aliquots were extracted with dichloromethane/methanol (2:1, v/v), followed by concentration, and derivatization with $50\,\mu$l N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in the presence of 1% trimethylsilyl chloride and $10\,\mu$l 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 was equipped with a split/splitless injection and a DB-5MS fused silica capillary column ($30\,\text{m} \times 0.25\,\text{mm}$ i.d., $0.25\,\mu$m 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 on the electron impact (EI) mode at 70 eV and scanned from 50 to 650 Da. Data were acquired and processed with the Chemstation software.

Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data (Claeys et al., 2004b; Jaoui et al., 2005; Hu et al., 2008; Kourtchev et al., 2008b; Wang et al., 2008). For the quantification of *cis*-pinonic, norpinic and pinic acids, their GC/MS response factors were determined using authentic standards. 3-Methyl-1,2,3-butanetricarboxylic, 3-hydroxyglutaric, and β-caryophyllinic acids were estimated using the response factors of pimelic, malic and pinic acids, respectively. 2-Methylglyceric acid, C_5-alkene triols and 2-methyltetrols were quantified using the response factor of *meso*-erythritol. Field blank filters were treated as the real samples for quality assurance. Target compounds were not detected in the blanks. Recoveries for the authentic standards or surrogates that were spiked into pre-combusted quartz filters (*n*=3) were 94±2.6% for *meso*-erythritol, 69±6.3% for malic acid, 64±5.9% for *cis*-pinonic acid, 93±2.3% for *trans*-norpinic acid, and 79±2.3% for pinic acid. The data reported here were not corrected for the recoveries. Relative standard deviation of the concentrations based on duplicate analysis was

generally <10%.

2.3 O_3 and NO_x measurement

O_3 was measured by an instrument based on ultraviolet absorption (Thermo, model 49C). NO_x ($NO+NO_2$) were detected by a customized instrument based on a commercially available instrument (Thermo, model 42CTL). The sensitivity to NO was determined against a premixed gas of NO/N_2 (2.004 ppmv, Taiyo Nippon Sanso Corporation). The detection limit of the instrument is specified to be 0.1 ppbv for NO and 0.2 ppbv for NO_2. Detailed information about the measurements of O_3 and NO_x are presented elsewhere (Kanaya et al., 2009; Pochanart et al., 2009).

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 C_5-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) (Table 1). Concentration ranges of 2-methyltetrols were 20.2-333 ng m^{-3} (average 128 ng m^{-3}) at daytime and 4.71–550 ng m^{-3} (148 ng m^{-3}) at nighttime with 2-methylerythritol being about 2.1-fold more abundant than 2-methylthreitol (Table 1). The ratio is similar to those observed in other studies (Claeys et al., 2004a; Ion et al., 2005; Cahill et al., 2006). The levels of 2-methyltetrols reported here are comparable to those reported in 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., 2004a), Hungary (Ion et al., 2005), Finland (Kourtchev et al., 2008a), Germany (Kourtchev et al., 2008b), and United States (Cahill et al., 2006; Clements and Seinfeld, 2007; Ding et al., 2008).

C_5-alkene triols, which are recently reported as photooxidation products of isoprene (Wang et al., 2005), were detected in all samples with an average concentration of

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$32.7\pm20.8\,\mathrm{ng\,m^{-3}}$ at daytime and $32.0\pm26.9\,\mathrm{ng\,m^{-3}}$ at nighttime, which are comparable to those ($\sim50\,\mathrm{ng\,m^{-3}}$) 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 ($3.47\,\mathrm{ng\,m^{-3}}$) (Cahill et al., 2006) and Jülich, Germany (1.6–$4.9\,\mathrm{ng\,m^{-3}}$) (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 12.7–$110\,\mathrm{ng\,m^{-3}}$ ($51.5\,\mathrm{ng\,m^{-3}}$) at daytime and 4.28–$110\,\mathrm{ng\,m^{-3}}$ ($45.7\,\mathrm{ng\,m^{-3}}$) at 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 O_3 and OH radicals (Hoffmann et al., 1997; Yu et al., 1999; Glasius et al., 2000; Iinuma et al., 2004). They have been observed in smog chamber experiments (Jang and Kamens, 1998; Yu et al., 1999; Glasius et al., 2000) and reported in the ambient aerosols (Kavouras et al., 1999; Ding et al., 2008; Kourtchev et al., 2008b; Fu et al., 2009). Concentrations of pinonic, norpinic, and pinic acids in this study ranged from 0.21–$21.8\,\mathrm{ng\,m^{-3}}$, 0.07–$1.99\,\mathrm{ng\,m^{-3}}$ and 0.36–$6.27\,\mathrm{ng\,m^{-3}}$, respectively (Table 1). Even though the vapor pressure of pinonic acid is about 2 orders of magnitude higher than pinic acid, the concentrations of pinonic acid in the Mt. Tai aerosols were about 2 times more abundant than pinic acid. Similar patterns have been reported in other studies (Kavouras et al., 1999; Kavouras and Stephanou, 2002; Cahill et al., 2006; Bhat and Fraser, 2007; Yan et al., 2008). 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., 2007a).

Two novel compounds were recently identified in aerosols as 3-hydroxyglutaric acid (3-HG) (Claeys et al., 2007) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007a). Both 3-HG and MBTCA are generated in smog chamber experiments of α-pinene with an irradiation of UV in the presence of NO_x. Concentration

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ranges of 3-HG were 1.39–18.9 ng m^{-3} (average 7.02 ng m^{-3}) at daytime and 0.39–19.4 ng m^{-3} (6.66 ng m^{-3}) at nighttime. Concentration ranges of MBTCA were 3.94–24.2 ng m^{-3} (11.5 ng m^{-3}) at daytime and 3.47–25.9 ng m^{-3} (8.36 ng m^{-3}) at nighttime.

Regarding 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 at both daytime (1.76–35.2 ng m^{-3}, average 12.5 ng m^{-3}) and nighttime (1.22–39.4 ng m^{-3}, 11.7 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), 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. All the biogenic SOA tracers showed no clear diurnal trends, suggesting that they are formed over a relatively long period of time. The isoprene oxidation tracers showed very similar temporal trends each other (Fig. 1a–d). In addition to the peaks at E1, E2 and E3 when levoglucosan maximized, 2-methyltetrols showed some other peaks during 1–2 June and 19–22 June. Similar maxima can also be found in the temporal

trends of monoterpene oxidation products (Fig. 1e–i) and malic acid (Fu et al., 2008). Malic acid is a secondary oxidation tracer of succinic acid (Kawamura and Ikushima, 1993).

A good correlation was found between the concentrations of 2-methyltetrols and C_5-alkene triols (R^2=0.68, Fig. 2a) in the Mt. Tai samples. However, the concentration ratios of 2-methyltetrols to C_5-alkene triols significantly varied (Fig. 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 C_5-alkene triols was explained through rearrangement reactions of hydroxyperoxy radicals that are formed in the initial photooxidation of isoprene (Surratt et al., 2006).

The temporal variations of monoterpene oxidation tracers (Fig. 1e–i) were different from those of isoprene oxidation tracers (Fig. 1a–d). Cahill et al. (2006) also reported a poor correlation between monoterpene oxidation products and 2-methyltetrols in mountain aerosols. 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 have 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 clean air mass may have intruded from the north over Mt. Tai during 8–10 June. However, MBTCA and 3-HG did not show a peak during this period. Because pinic and pinonic acids are lower-generation photooxidation products of α-/β-pinene compared to MBTCA and 3-HG (Kourtchev et al., 2009), the enhanced concentrations of pinic and pinonic acids during 8–10 June over Mt. Tai suggest that the photooxidation of α-/β-pinene was not completed. Concentration ratio of 3-HG plus MBTCA to pinic acid ((3HG+MBTCA)/pinic) also showed the lowest value during 8–10 June (Fig. 3).

Temporal variations of β-caryophyllinic acid (Fig. 1j) showed two major peaks at E1 and E2. These peaks are substantially different from those of isoprene- or monoterpene-oxidation tracers (Fig. 1a–i). However, they are similar to those of OC, WSOC, and levoglucosan (Fu et al., 2008). Levoglucosan and β-caryophyllene oxidation products showed a positive correlation (R^2=0.52, Fig. 2b), indicating that β-caryophyllinic acid detected over Mt. Tai was mainly originated from biomass burning process in early summer. However, no correlations were found between levoglucosan and isoprene or monoterpene SOA tracers. This is reasonable because the emissions of isoprene and monoterpenes are insignificant for most of the widely planted crop species (Kesselmeier and Staudt, 1999), while the active 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. Another possibility is that a significant emission of OC during biomass burning may shift the gas/particle partitioning of β-caryophyllinic acid toward particle phase due to the adsorption by the preexisting OC.

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 the 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 monoterpene SOA tracers during E3 (Fig. 1) may originate from possible forest fire that may happen in the South China. Forest fires enhance the emissions of BVOCs.

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 using the squared Euclidean distance as a grouping criterion. As shown in Fig. 4, three clusters (1, 2 and 3) can be

distinguished for both day- and night-time aerosols. At daytime, cluster 1 is composed of 3-hydroxyglutaric acid, malic acid, β-caryophyllinic acid, OC, and levoglucosan. Thus, cluster 1 should be mainly associated with the emissions from biomass burning. 3-Hydroxyglutaric acid was strongly correlated with malic acid (R^2=0.91, Fig. 2c), indi-
5 cating a similar formation pathway. Cluster 2 contains pinonic and pinic acids that are associated with the photooxidation of α-/β-pinene. Cluster 3 contains 2-methylglyceric acid, C_5-alkene triols and 2-methyltetrols, which are produced by the photooxidation of isoprene. Two monoterpene SOA tracers (norpinic acid and MBTCA) are also in cluster 3, indicating that these compounds may be derived from same source regions
10 and/or have very similar atmospheric behaviors (such as gas/particle partitioning) with those of isoprene oxidation products.

At nighttime, cluster 1 contains the same pattern as those at daytime. Cluster 2 contains pinonic, pinic, and norpinic acids that are derived from the photochemical oxidation of α-/β-pinene. Cluster 3 contains isoprene oxidation products together with
15 MBTCA, which is a higher-generation photooxidation product of α-/β-pinene as mentioned above. It should be noted that in Fig. 4, only norpinic acid moved from daytime cluster 3 that is characterized with isoprene SOA tracers to nighttime cluster 2 that is associated with monoterpene SOA tracers (pinic and pinonic acids), indicating that norpinic acid may have formation pathways different from pinic and pinonic acids at
20 daytime.

3.4 Enhanced contribution of isoprene oxidation products

In the Mt. Tai aerosols, total concentrations of isoprene SOA tracers (202±123 ng m^{-3} at daytime and 226±182 ng m^{-3} at nighttime) are 1 order of magnitude higher than those of the monoterpene SOA tracers (daytime 29.1±11.2 ng m^{-3} vs. nighttime
25 22.5±9.85 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 isoprene to monoterpene oxidation tracers ($R_{\mathrm{iso/mono}}$) to evaluate the relative contribution of isoprene and monoterpenes to SOA. The averaged $R_{\mathrm{iso/mono}}$ values in this study were

6.94 at daytime and 10.0 at nighttime. They are much higher than those reported from other regions (Table 2). For example, $R_{iso/mono}$ values from different sites in China, India and Sierra Nevada, USA are slightly lower (2–6), but significantly lower in aerosols from NC, USA (0.89), Rishiri Island, Japan (0.85), and Jülich, Germany (0.80), and Hong Kong, China (0.46). The ratios are further lower in PM1 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 polar sunrise (Fu et al., 2009). These comparisons indicate that the Mt. Tai aerosols are highly influenced by isoprene oxidation products compared to monoterpene oxidation products.

Average contribution of isoprene oxidation products to OC was found to be 0.603% at daytime and 0.643% at nighttime, which were 6–8 times higher than those of monoterpene oxidation products (0.102% at daytime and 0.076% nighttime) (Table 1). The contributions of β-caryophyllinic acid to OC were 0.044% at daytime and 0.036% at nighttime. Because the mountaintop exists in the FT at night, higher contribution of isoprene to SOA formation at nighttime ($R_{iso/mono}$=10.0) than daytime (6.94) may indicate the presence of a large source of organic aerosol in the FT (Heald et al., 2005). This also suggests that the isoprene oxidation products are more abundant than other biogenic SOA precursors in the atmosphere of high altitudes (Henze and Seinfeld, 2006).

The enhanced SOA formation from isoprene may 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 summer (Guenther et al., 1995). Aerosol concentrations in accumulation mode are suggested to be the highest in CEC (Andreae and Rosenfeld, 2008). Biogenic VOCs are quickly oxidized by OH, O_3 and/or NO_3 (and occasionally chlorine atoms) in the atmosphere. Lifetimes of isoprene are on a scale of hours with respect to OH and NO_3, and days with O_3. 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). During MTX2006, the atmospheric concentrations of isoprene over Mt. Tai were about twice higher than those of α-/β-pinene (Suthawaree and Kato, 2009), indicating that both of them (especially isoprene) were not completely oxidized during the transport from their ground sources to the summit of Mt. Tai.

Another important factor is that the gas/particle partitioning of isoprene oxidation products can be affected by relatively low temperatures at the summit of Mt. Tai (10–25 °C) at nighttime, causing higher concentrations in aerosol phase. Concentrations of isoprene SOA tracers, especially 2-methyltetrols showed higher levels at nighttime (average 226 ng m^{-3}) than daytime (202 ng m^{-3}), although monoterpene SOA tracers showed an opposite trend (Table 1).

Figure 5 shows the temporal variations of $R_{iso/mono}$ values, together with O$_3$ and NO$_x$ concentrations. The $R_{iso/mono}$ values that are higher than the median value (=6.93, in red dashed line) are shaded. Interestingly, higher $R_{iso/mono}$ values are observed when O$_3$ and NO$_x$ concentrations are higher. The observed mean O$_3$ concentration was very high (82 ppbv) during the sampling period, and the data of 14 days showed hourly ozone mixing ratios exceeding 100 ppbv, that is, China's air quality standard (Grade II) (Li et al., 2008). Such a high level of O$_3$ at the summit of Mt. Tai in July 2003 has been reported by Gao et al. (2005). O$_3$ is mainly produced by photochemical reactions involving NO$_x$, CO and VOCs. Ozone-isoprene reaction is a minor contributor to isoprene SOA formation compared to the reaction with OH (Kleindienst et al., 2007b). The midday peak concentration of OH during MTX2006 predicted by a photochemical box model was about 5.0×10^6 cm^{-3} with a maximum of 1.6×10^7 cm^{-3}, and the 24-h average concentrations were about 1.8×10^6 cm^{-3} (Kanaya et al., 2009). The relatively high OH concentrations during the sampling period indicate that OH reaction would dominate the isoprene SOA formation.

Recently, Weber et al. (2007) found that biogenic SOA formation is correlated with anthropogenic tracers. Ervens et al. (2008) reported that SOA yield from cloud-processing of isoprene oxidation products could be enhanced in regions with high NO$_x$

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and isoprene emissions. These findings may further support the enhanced contribution of isoprene oxidation products in the present study. Alternatively, the co-variation of $R_{iso/mono}$ values with ozone and NO_x concentrations may suggest that under high NO_x and OH conditions, BVOCs, in particular, isoprene and their oxidation products can act as important precursors for the photochemical production of ozone rather than its consumption. This assumption is supported by a photochemical box model study that biogenic hydrocarbons do contribute to the ozone production during the same campaign (Kanaya et al., 2009). Other studies have reported that the oxidation of BVOCs by OH in the presence of NO_x can be the primary source of tropospheric ozone (Ryerson et al., 2001). By comparing the measured isoprene emissions with estimated emissions of anthropogenic VOCs, Goldstein et al. (1998) also stated that isoprene is more important for ozone production in Massachusetts during hot summer days when the highest ozone events occur.

Except for Mt. Tai and Hong Kong aerosols, the $R_{iso/mono}$ values seem to depend on latitude (Table 2). Higher $R_{iso/mono}$ values are generally observed in lower latitudes such as in South China (Hainan, 5.43) and tropical India (Chennai, 3.62), followed by those in mid-latitudes such as the northeastern China (Mt. Changbai), USA, Japan, and Germany. As mentioned earlier in this section, the lowest values are found in higher latitudes such as in 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 ($>1\,g\,C\,m^{-2}\,month^{-1}$) throughout the year (Guenther et al., 1995). They 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. Thus, we propose here that the $R_{iso/mono}$ value can be used as a tracer to estimate the contribution of isoprene and monoterpenes to biogenic SOA formation in various ecosystems.

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. (2007a). 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 monoterpenes and 0.0230±0.0046 for β-caryophyllene (Kleindienst et al., 2007a), we calculated the contributions of these precursors to ambient OC. As shown in Table 1 and Fig. 6, we found that monoterpenes and β-caryophyllene are rather minor contributors to SOC during MTX2006.

The contributions of monoterpenes to SOC ranged from 0.05 to 0.22 μgC m^{-3} (average 0.13 μgC m^{-3}) at daytime and 0.02 to 0.21 μgC m^{-3} (0.10 μgC m^{-3}) at nighttime (Table 1). For β-caryophyllene, the contributions were 0.08–1.53 μgC m^{-3} (0.54 μgC m^{-3}) and 0.05–1.71 μgC m^{-3} (0.51 μgC 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 endocylic 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 0.24–2.79 μgC m^{-3} (1.09 μgC m^{-3}) at daytime and 0.05–4.26 μgC m^{-3} (1.25 μgC m^{-3}) at nighttime. These values are similar to those reported at Research Triangle Park, NC (Kleindienst et al., 2007a) and Hong Kong (Hu et al., 2008), but are about 2–3 orders of magnitude higher than those reported in the Canadian High Arctic (Fu et al., 2009).

As shown in Table 1, the total SOC derived from isoprene, monoterpenes and sesquiterpene in the Mt. Tai aerosols ranged from 0.46 to 3.45 μgC m^{-3} (average 1.76 μgC m^{-3}) at daytime and 0.12 to 4.89 μgC m^{-3} (1.85 μgC m^{-3}) at nighttime, which account for 11.2% and 11.0% of the OC at day- and night-time, respectively. As shown in Fig. 6, the temporal variation of total SOC% in OC maximized (up to 32.5%) during 18–21 June when the daytime ambient temperature became highest. In contrast, a

minimum (3.27%) was found during 8–10 June when the clean air mass came from the north through the FT. Isoprene is clearly found to be the largest SOC contributor in the Mt. Tai aerosols (Fig. 6), accounting for 62.2% and 67.3% of BVOC-derived SOC at day- and night-time, respectively. This is consistent with the results reported by Kleindienst et al. (2007a) that isoprene was the largest contributor in the summer aerosols collected at Research Triangle Park, North Carolina.

4 Conclusions

In this study, biogenic SOA tracers of isoprene, monoterpenes, and β-caryophyllene were measured in tropospheric aerosols collected during a summer field campaign conducted at the summit of Mt. Tai (1534 m), Central East China. Their total concentrations exhibited no diurnal variations, ranging from 62.9 to 542 ng m^{-3} (average 244 ng m^{-3}) at daytime and 21.8 to 834 ng m^{-3} (260 ng m^{-3}) at nighttime, which account for 0.75% and 0.76% of OC in the mountain aerosols. β-Caryophyllinic acid showed a temporal pattern similar to those of OC and levoglucosan. This compound may originate from the biomass burning activities that maximized in Central East China during early summer. However, isoprene and monoterpene tracers showed different temporal patterns.

Due to the tracer-based calculation, the contributions of BVOCs to SOC were estimated using the ambient concentrations of biogenic SOA tracers. On average, the isoprene-derived SOC is about 10 and 2 times higher than those of monoterpene- and β-caryophyllene-derived SOC, respectively. Higher contribution of isoprene oxidation products to SOA formation may be explained by larger isoprene emissions in this region, together with relatively high levels of OH, O$_3$ and NO$_x$ in Central East China in summer. High levels of pollutants may enhance the SOA formation rates, which affect the gas/particle partitioning of the BVOCs oxidation products. This situation also changes the formation pathways of SOA tracers, and produces inorganic salts (i.e. ammonium sulfate) and organic acids (i.e. dicarboxylic acids) to alter the hygroscopic

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property of particle. Hence, high loading of organic aerosols (the averaged OC levels were 18.6 μg m^{-3} at daytime and 20.5 μg m^{-3} at nighttime) in the Mt. Tai aerosols may influence the gas/particle partitioning processes. Such a high isoprene-derived SOA observed in the high altitudinal aerosols over Mt. Tai is consistent with previous findings from model study that isoprene oxidation products have much greater concentrations at higher altitudes or from aircraft observation that very high OC values over Northwest Pacific during the ACE-Asia campaign.

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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 ($\mu g\,m^{-3}$)	18.6	10.4	5.1	47.5	–	20.5	16.8	2.5	67.2	–
Tracers for isoprene SOA										
2-methylglyceric acid	51.5	31.4	12.7	110	0.143	45.7	30.0	4.28	110	0.116
$\sum C_5$-alkene triols [b]	32.7	20.8	7.70	83.7	0.114	32.0	26.9	4.68	116	0.110
2-methylthreitol	38.6	27.4	5.96	102	0.111	50.4	47.0	0.86	184	0.137
2-methylerythritol	79.5	58.3	14.3	222	0.235	97.4	87.1	1.83	366	0.280
subtotal	202	123	44.8	500	0.603	226	182	15.5	777	0.643
$SOC_{isoprene}^{c}$ ($\mu gC\,m^{-3}$)	1.09	0.69	0.24	2.79	7.4	1.25	1.02	0.05	4.26	8.0
Tracers for monoterpene SOA										
3-hydroxyglutaric acid	7.02	4.28	1.31	18.9	0.018	6.66	5.26	0.39	19.4	0.015
cis-pinonic acid	6.82	6.05	0.41	21.8	0.029	4.49	4.16	0.21	16.8	0.018
norpinic acid	0.87	0.51	0.15	1.76	0.003	0.74	0.50	0.07	1.99	0.003
pinic acid	2.91	1.83	0.72	6.27	0.012	2.28	1.39	0.36	4.90	0.009
MBTCA [d]	11.5	6.10	3.94	24.2	0.040	8.36	5.13	3.47	25.9	0.031
subtotal	29.1	11.2	11.9	51.1	0.102	22.5	9.85	5.19	48.0	
$SOC_{monoterpenes}$ ($\mu gC\,m^{-3}$)	0.13	0.05	0.05	0.22	0.87	0.10	0.04	0.02	0.21	0.66
Tracer for β-caryophyllene SOA										
β−caryophyllinic acid	12.4	8.98	1.76	35.2	0.044	11.7	11.4	1.15	39.4	0.036
$SOC_{\beta-caryophyllene}$ ($\mu gC\,m^{-3}$)	0.54	0.39	0.08	1.53	2.91	0.51	0.50	0.05	1.71	2.37
total tracers	244	129	62.9	542	0.75	260	194	21.8	834	0.76
total SOC ($\mu gC\,m^{-3}$)	1.76	0.87	0.46	3.45	11.2	1.85	1.30	0.12	4.89	11.0

[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), monoterpenes, and β-caryophyllene were calculated using a tracer-based method reported by Kleindienst et al. (2007a).
[d] MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

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Table 2. Concentration ratios of total isoprene SOA tracers to monoterpene SOA tracers ($R_{iso/mono}$) measured in the Mt. Tai aerosols compared to those reported in other studies.

Location	Type of aerosol	Isoprene SOA tracers		Monoterpene SOA tracers		$R_{iso/mono}$	References
		Tracers [a]	Aver. Conc. [b]	Tracers [a]	Aver. Conc.		
Mt. Tai, China	TSP, nighttime	1, 2, 3	226	4, 5, 6, 7, 8	22.5	10.0	This study
Mt. Tai, China	TSP, daytime	1, 2, 3	202	4, 5, 6, 7, 8	29.1	6.94	This study
Hainan, China	$PM_{2.5}$, 24 h	1, 2, 3	51	5, 7, 8	9.4	5.43	(Wang et al., 2008)
Changbai, China	$PM_{2.5}$, daytime	1, 2, 3	140	7, 8	38	3.68	(Wang et al., 2008)
Chennai, India	PM_{10}, summer	1, 2, 3	34.3	4, 5, 6, 7, 8	9.5	3.62	(Fu et al., unpublished data)
Sierra Nevada, USA	TSP	1, 2, 3	57	4, 5, 6	18.3	3.10	(Cahill et al., 2006)
Changbai, China	$PM_{2.5}$, nighttime	1, 2, 3	114	7, 8	41	2.78	(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)
Rishiri Is., Japan	TSP	1, 2, 3	13.3	4, 5, 6, 7, 8	15.7	0.85	(Fu et al., unpublished data)
Jülich, Germany	$PM_{2.5}$	1, 2, 3	20.5	4, 5, 7, 8	25.6	0.80	(Kourtchev et al., 2008b)
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) C_5-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.
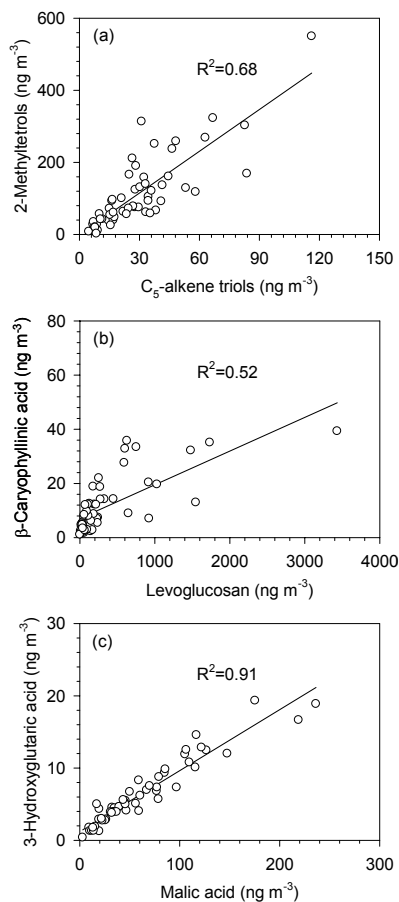[b] averaged concentration in $ng\,m^{-3}$.
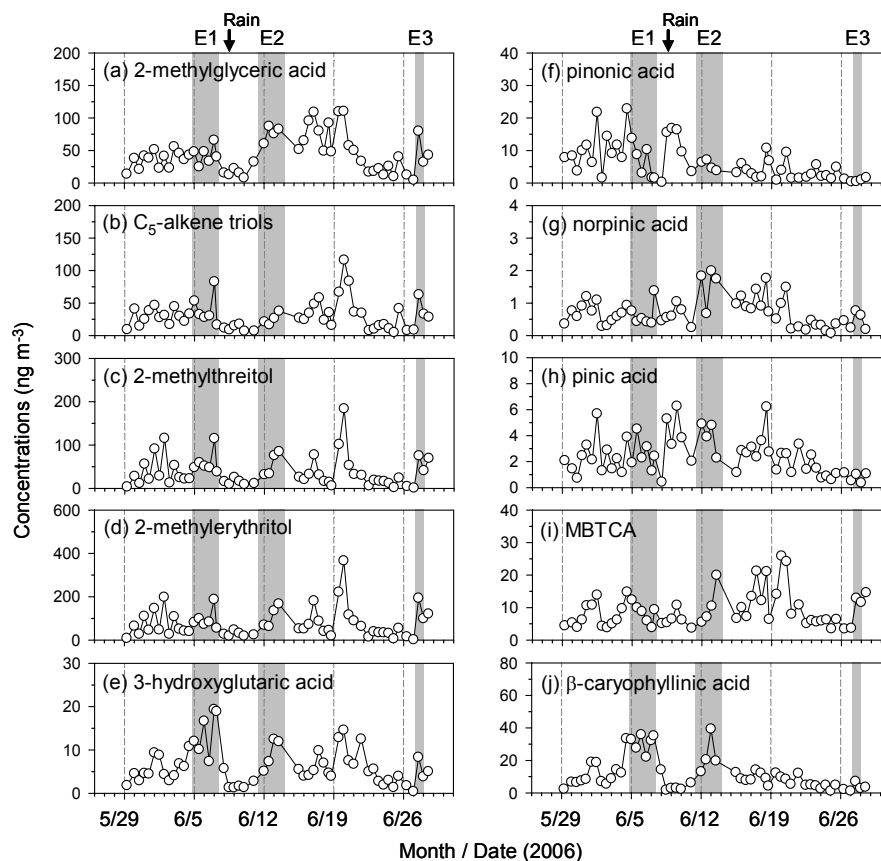
Fig. 1. Temporal variations of biogenic SOA tracers measured in the Mt. Tai aerosols during May–June, 2006. Event 1 (E1), E2, and E3 are significant biomass burning periods reported in a previous study (Fu et al., 2008).
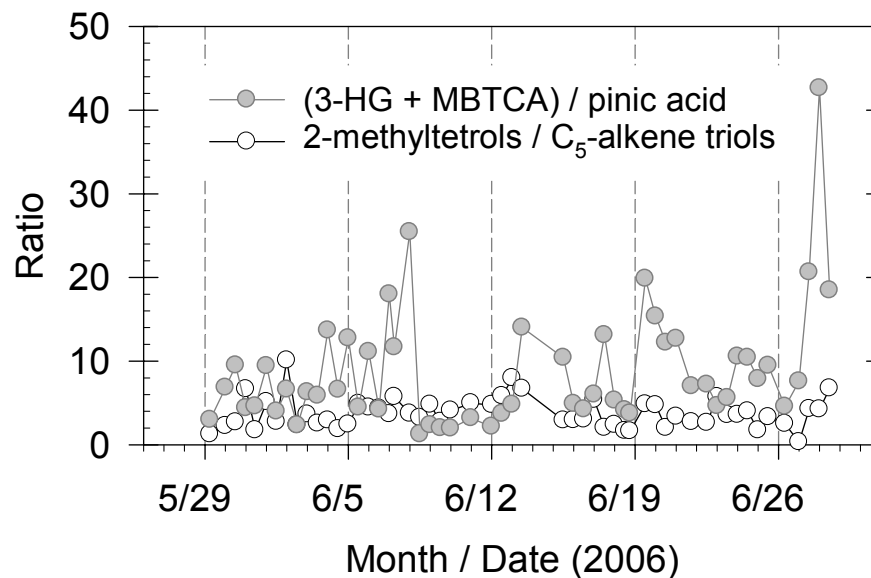
Fig. 2. Correlations between the concentrations of **(a)** C$_5$-alkene triols and 2-methyltetrols, **(b)** levoglucosan and β-caryophyllinic acid, and **(c)** malic acid and 3-hydroxyglutaric acid.

Fig. 3. Temporal trends of the concentration ratios of 2-metnyltetrols to C_5-alkene triols (white circle), and sum of 3-hydroxyglutaric acid (3-HG) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) to pinic acid (grey circle).

(a) daytime

3-hydroxyglutaric acid
malic acid
β-caryophylinic acid
OC
levoglucosan
pinonic acid
pinic acid
norpinic acid
MBTCA
C_5-alkene triols
2-methyltetrols
2-methylglyceric acid

(1)
(2)
(3)

(b) nighttime

3-hydroxyglutaric acid
malic acid
β-caryophylinic acid
OC
levoglucosan
C_5-alkene triols
2-methyltetrols
MBTCA
2-methylglyceric acid
norpinic acid
pinic acid
pinonic acid

(1)
(3)
(2)
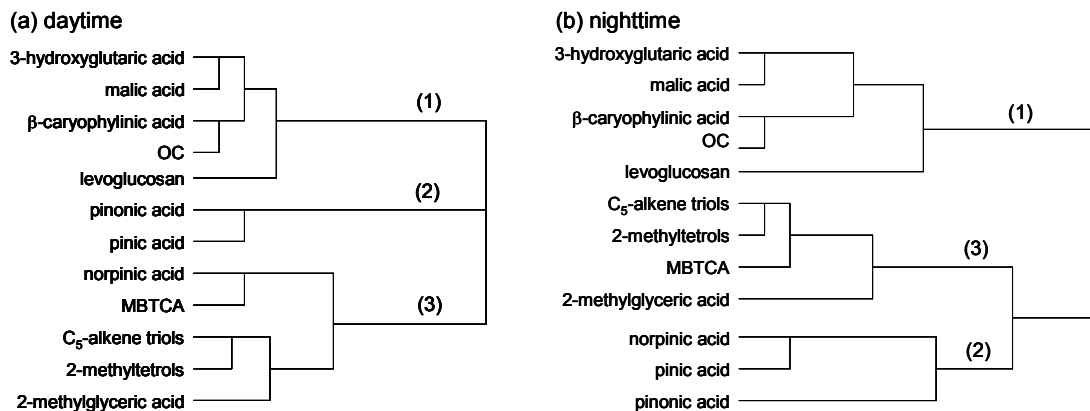
Fig. 4. Hierarchical cluster analysis of biogenic SOA tracers, levoglucosan, malic acid and organic carbon (OC) in the Mt. Tai aerosols during **(a)** daytime, and **(b)** nighttime.
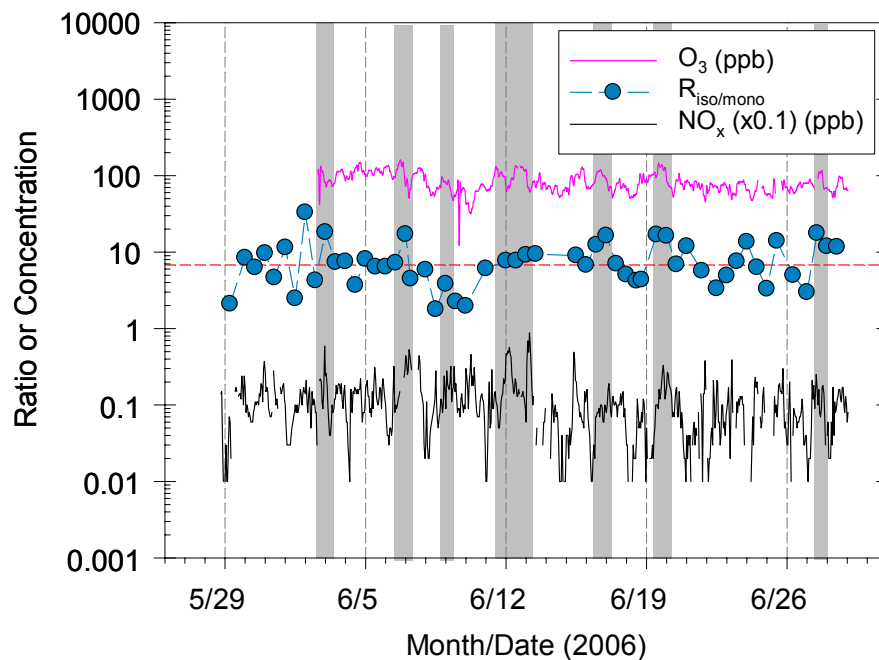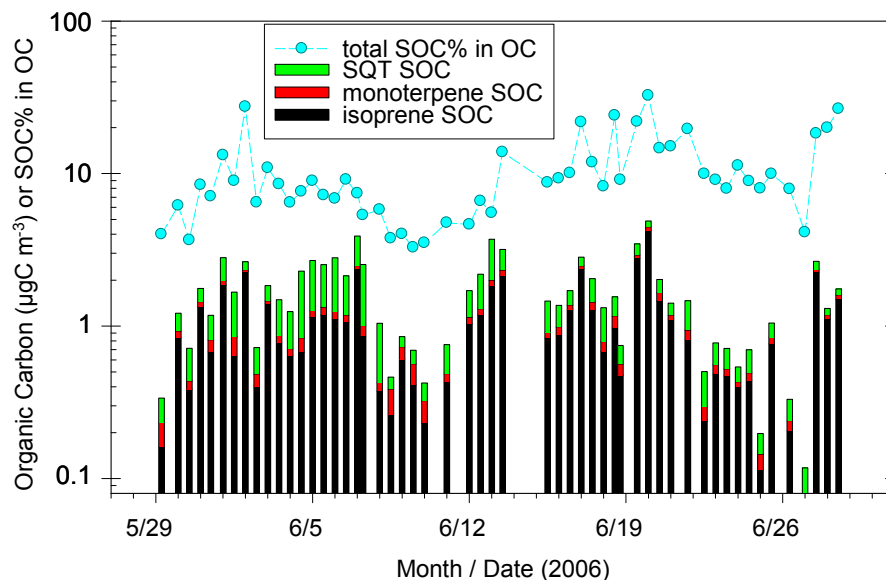
Fig. 5. Time series for the ratio of isoprene to monoterpenes oxidation products ($R_{iso/mono}$), and the observed concentrations of O_3 and NO_x in the troposphere over Mt. Tai during MTX2006. The dashed red line represents the median value of $R_{iso/mono}$=6.93.

Fig. 6. Estimated contributions of different biogenic VOCs to SOC, and the temporal variations of the percentage of total SOC in OC.