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Discussions

Emissions of biogenic volatile organic compounds and subsequent formation of secondary organic aerosols in a *Larix kaempferi* forest

T. Mochizuki[1,*], Y. Miyazaki[2], K. Ono[2], R. Wada[3], Y. Takahashi[4], N. Saigusa[4], K. Kawamura[2], and A. Tani[1]

[1]Graduate School of Nutritional and Environmental Sciences, University of Shizuoka, Shizuoka 422-8526, Japan
[2]Institute of Low Temperature Science, Hokkaido University, Hokkaido, 060-0819, Japan
[3]Department of Natural and Environmental Science, Teikyo University of Science, Yamanashi, 409-0193, Japan
[4]National Institute for Environmental Studies, Ibaraki, 305-8506, Japan
[*]now at: Institute of Low Temperature Science, Hokkaido University, Hokkaido, Japan

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Correspondence to: A. Tani (atani@u-shizuoka-ken.ac.jp)
and Y. Miyazaki (yuzom@lowtem.hokudai.ac.jp)

Abstract

We conducted simultaneous measurements of concentrations and above-canopy fluxes of isoprene and α-pinene, along with their oxidation products in aerosols in a *Larix kaempferi* (Japanese larch) forest in summer 2012. Vertical profiles of isoprene showed the maximum concentration near the forest floor with a peak around noon, whereas oxidation products of isoprene, i.e., methacrolein (MACR) and methyl vinyl ketone (MVK), showed higher concentrations near the canopy level of the forest. The vertical profile suggests large emissions of isoprene near the forest floor, likely due to *Dryopteris crassirhizoma* (a fern species), and the subsequent reaction within the canopy. The concentrations of α-pinene also showed highest values near the forest floor with maximums in the early morning and late afternoon. The vertical profiles of α-pinene suggest its large emissions from soil and litter in addition to emissions from *L. kaempferi* leaves at the forest site. Isoprene and its oxidation products in aerosols exhibited similar diurnal variations within the forest canopy, providing evidence for secondary organic aerosol (SOA) formation via oxidation of isoprene most likely emitted from the forest floor. Although high abundance of α-pinene was observed in the morning, its oxidation products in aerosols showed peaks in daytime, due to a time lag between the emission and atmospheric reactions of α-pinene to form SOA. Positive matrix factorization (PMF) analysis indicated that anthropogenic influence is the most important factor contributing to the elevated concentrations of molecular oxidation products of isoprene- (> 64 %) and α-pinene-derived SOA (> 57 %). The combination of the measured fluxes and vertical profiles of biogenic volatile organic compounds (BVOCs) suggests that the inflow of anthropogenic precursors/aerosols likely enhanced the formation of both isoprene- and α-pinene-SOA within the forest canopy even when the BVOC flux was relatively low. This study highlights the importance of intra-canopy processes that promote biogenic SOA formation in the presence of significant inflow of anthropogenic aerosols and their precursors.

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1 Introduction

Forest vegetation contributes substantially to emissions of a variety of biogenic volatile organic compounds (BVOCs), such as isoprene, monoterpenes, and sesquiterpenes, which are involved in plant growth, reproduction, and defence. BVOCs have significant effects on not only insects and other organisms but also atmospheric chemistry and physics. On a global scale, approximately 90 % of annual VOC emissions are derived from biogenic sources, with an estimated amount of about 1000 Tg year^{-1} (Guenther et al., 2012). This is significantly greater (ca. 10 times) than the emission of anthropogenic VOCs. Emission sources of BVOCs in the forest ecosystem include leaves, leaf litter, stems, and roots (Lin et al., 2007; Leff et al., 2008; Aaltonen et al., 2011; Noe et al., 2012). The emission strength and composition of BVOCs in the forest environment depend on vegetation types, seasons, and meteorological parameters such as temperature, solar radiation, and precipitation (Kesselmeier and Staudt, 1999; Guenther et al., 1993; Tani et al., 2002; Kuhn et al., 2004; Mochizuki et al., 2014). Moreover, physical and biological structures of the forest canopy may contribute to chemical loss and deposition of BVOCs within the canopy (Fuentes et al., 2007).

BVOCs are important precursors of organic aerosols (OAs) in the forest atmosphere. The formation of biogenic secondary OA (BSOA) and its transformation by atmospheric processes influence the physicochemical properties of atmospheric aerosols, such as particle hygroscopicity and cloud condensation nuclei (CCN) activity. Because the formation processes of BSOA and its amount are largely uncertain, prediction is difficult. Accurate modelling of BSOA formation requires reliable information about BVOC emissions and a robust understanding of the chemical processing of these precursors inside the forest canopy before entering the atmosphere above the canopy.

The characterization of OAs at the molecular level in forests remains challenging because of multiple contributing sources, variable oxidant concentrations and compositions, and the variable contributions of background gases and aerosols from regions outside forests (e.g., de Gouw and Jimenez, 2009). As discussed by Hallquist

et al. (2009), previous studies indicate that the production of BSOA is substantially greater than that of anthropogenic SOA (Kanakidou et al., 2005). Recent studies based on field and laboratory experiments suggest that VOC emissions from biogenic and anthropogenic sources may interact and enhance SOA formation (Goldstein et al., 2009; Emanuelsson et al., 2013). To evaluate the contribution of VOCs emitted by forest vegetation to SOA formation, accurate information about emissions and concentrations of VOCs along with concentrations of BSOAs is required. Understanding the formation processes of BSOAs and their controlling factors in forests needs extensive field studies, in which significant amounts of biogenic OA are required to determine clearly the diurnal variations of the biogenic signals. However, studies remain limited in terms of time-resolved, simultaneous measurements of BVOCs and their fluxes and OA at molecular levels in the forest atmosphere.

We conducted ambient measurements of concentrations and canopy-scale fluxes of isoprene and α-pinene along with their oxidation products in aerosols in a *Larix kaempferi* forest in the summer of 2012. Congeneric species of *Larix kaempferi* such as *Larix sibirica* and *Larix gmelinii* grow naturally and widely in boreal coniferous forests in Siberia and northern Europe. Therefore, the vegetation at the current study site might be representative and suitable for characterizing emissions and compositions of BVOCs in boreal forests. The goal of this study is to investigate controlling factors of BSOA formation from BVOC in a forest environment located near anthropogenic sources. Here, we characterize the vertical profiles and temporal variations of BVOCs at this forest site. We also present the analytical results of molecular tracer compounds for BSOA and explore the controlling factors of the SOA formation in the forest canopy at the measurement site.

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2   Experimental methods

2.1   Site description

Ambient samplings of gas and aerosol were conducted on 5, 10, and 15–17 July 2012 at the Fuji-Hokuroku Flux Research site (35°26′ N, 138°45′ E) (e.g., Mochizuki et al., 2014). The research site is located at the base of Mt. Fuji in Fujiyoshida city, Yamanashi, Japan (Fig. 1). The urban area of Fujiyoshida city is located about 8 km northeast of the site. The vegetation type is *Larix kaempferi* plantation, which was planted uniformly 55 years ago over 150 ha. Tree height was approximately 20–25 m. The site is surrounded by coniferous and broad-leaved mixed forests. A meteorological tower with 32 m height and a steel scaffold with 20 m height for tree survey were situated at the center of the forest site. The soil type is coarse-grained volcanic ash. The forest floor is covered mainly with *Dryopteris crassirhizoma*. Further details of the study site are given by Urakawa et al. (2015). During the entire study period, the ambient temperature at the measurement site ranged between 14.2 and 29.9 °C.

2.2   Measurements of VOCs and flux calculation

We measured vertical distributions of VOC concentrations at the five altitude levels of 2, 10, 16, 22 m (just below the forest canopy), and 28 m (above the canopy) using the meteorological tower. Ambient air was collected into stainless steel adsorbent tubes (φ 1/4 inch × 3.5 inch) filled with 200 mg of Tenax-TA (GL Science, Japan) and 100 mg of Carbotrap (Supelco, USA). The air was sampled at a flow rate of 100 mL min^{-1} for ∼ 3 h using a portable pump (MP-Σ30, Shibata Inc., Japan). The sampling was conducted every 3 h during daytime (6:00–9:00, 9:00–12:00, 12:00–15:00, and 15:00–18:00 LT). To prevent the degradation of VOCs by O$_3$, scrubbers coated with manganese dioxide (MnO$_2$) were applied upstream of the adsorbent tubes (Calogirou et al., 1996). Prior to the sampling, the adsorbent tubes were conditioned with purified helium (50 mL min^{-1}) at 300 °C for 10 min and were stored at approximately 5 °C.

Above-canopy fluxes of VOCs were calculated using a relaxed eddy accumulation (REA) method (Businger and Oncley, 1990):

$$F = b\sigma_w(C^+ - C^-) \tag{1}$$

where σ_w is the SD of vertical wind velocity (w), and C^+ and C^- are the VOC concentrations in the sample air when the measured vertical wind is upward and downward, respectively. b is an empirical coefficient that can be obtained from sensible heat flux using an eddy covariance method (Hamotani et al., 2001):

$$b = \frac{\overline{w'T'}}{\sigma_w(\overline{T^+} - \overline{T^-})} \tag{2}$$

where the overbar denotes an average value over sampling time and prime represents deviations from a mean value. T^+ and T^- are air temperature for air with upward and downward directions, respectively. An averaged value of the coefficient b was determined to be 0.38 ($r^2 = 0.98$).

The REA sampling was conducted at a height of 35 m using the portable REA sampling system (Mochizuki et al., 2014, and references therein). Three-dimensional wind speed and temperature were measured using a three-dimensional ultrasonic anemometer–thermometer (DA-600-3TV, Sonic, Japan). The measurement frequency of w and T was 10 Hz. The REA sampling was conducted for 55 min at an interval of 1 h from 06:00 to 18:00.

Individual VOCs were identified and quantified using a gas chromatograph (GC) coupled to a mass spectrometer (MS) (QP5050A, Shimadzu, Japan) with an SPB-5 capillary column (60 m × 25 mm, 1 µm film thickness, Supelco, USA) equipped with a thermal desorption system (Turbo Matrix ATD, Perkin Elmer Instruments, USA) (Mochizuki et al., 2014). Here, we quantified BVOCs including isoprene, monoterpenes, methacrolein (MACR), methyl vinyl ketone (MVK), as well as anthropogenic VOCs such as benzene, toluene, and methyl ethyl ketone (MEK).

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2.3 Aerosol sampling and analysis

Total suspended particulate matter (TSP) samplings were conducted at a height of 16 m, just beneath the larch canopy, using a high-volume air sampler (AS-810B, Kimoto Electric, Japan) mounted on the 20 m steel scaffold. The ambient particles were collected onto quartz-fiber filters (8 inch × 10 inch) (Tissuquartz 2500QAT-UP, Pallflex, USA) at a flow rate of 1200 L min^{-1}. The filters were precombusted at 450 °C for 6 h prior to the sampling in order to remove organic contaminants. The sampling was conducted every 3 h during daytime (06:00–09:00, 09:00–12:00, 12:00–15:00, and 15:00–18:00 LT) and 12 h during nighttime (18:00–06:00 LT). The aerosol samples were stored at approximately −20 °C until analysis.

For the chemical analysis of biogenic molecular marker compounds, a filter portion (24 cm^2) was extracted with dichloromethane/methanol. The –COOH and –OH functional groups in the extracts were reacted with N,O-bis-(trimethylsilyl) trifluoroacetamide with 1 % trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h to form trimethylsilyl (TMS) esters and TMS ethers, respectively. The TMS derivatives were analyzed using a capillary GC (HPGC6890, Hewlett-Packard, USA) coupled to a MS (5973 MSD, Agilent, USA) (Fu et al., 2009; Miyazaki et al., 2012). We determined the concentrations of oxidation products of isoprene–2-methylglyceric acid (2-MGA) and 2-methyltetrols (2-MTLs; the sum of 2-methylerythritol and 2-methylthreitol), as well as those of α-pinene–pinic acid, pinonic acid, 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), and 3-hydroxyglutaric acid (3-HGA).

Another portion (7.07 cm^2) of a filter was extracted with ultrapure water under ultrasonication for 15 min in order to measure inorganic ions. The extracts were filtered through a membrane disc filter (0.22 μm, Millipore Millex-GV, Merck, USA) and then introduced to the ion chromatograph (Model 761 compact IC, Metrohm, Switzerland) (Miyazaki et al., 2009). Sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions were measured using an SI-90 4E column (Shodex, Showa Denko, Japan) and a 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ eluent.

2.4   O$_3$ and NO$_x$ measurement

The concentrations of ozone (O$_3$) and nitrogen oxides (NO$_x$ = NO + NO$_2$) were measured every 1 min with an ultraviolet light absorption analyzer (49C, Thermo Scientific, USA) and a chemiluminescence analyzer (42i-TL, Thermo Scientific, USA), respectively, at a flow rate of 3.5 L min^{-1}. The ambient air was drawn sequentially from inlets placed at 2, 10, 16 m (under the forest canopy), and 28 m (above the forest canopy) altitude levels on the meteorological tower by automatically switching two-way Teflon solenoid valves every 4 min. The O$_3$ and NO$_x$ instruments were placed inside a shelter on the ground. To prevent degradation of O$_3$ and NO$_x$ by sunlight during the sampling of ambient air, the sampling lines of 1/4-inch PTFE tubing were covered with shade sheet.

3   Results and discussion

3.1   Vertical profiles and diurnal variations of VOC concentrations and fluxes

3.1.1   Isoprene and oxygenated VOCs

On average, isoprene accounted for 23 % of the total terpenoids measured in the present study. The vertical profile of isoprene (Fig. 2a) showed that the concentrations were largest near the forest floor ($\sim$ 2 m) at all sampling times. At the 16 m level, where the aerosol sampling was made, the concentrations of isoprene in daytime ranged between 157 and 703 ng m^{-3} with an average of 316 ng m^{-3} (Fig. 3a). This value is similar to those observed at a boreal forest site in Hyytiälä, Finland ($\sim$ 300 ng m^{-3}) (Hakola et al., 2003).

The diurnal profile of isoprene (Fig. 2a) showed the maximum concentration around noon at all altitude levels. This diurnal pattern is in agreement with the dependency of isoprene emission on ambient light and temperature (e.g., Guenther et al., 1993).

In our previous study, a fern species *D*. *crassirhizoma* growing on the forest floor was found to be a dominant emitter of isoprene at this forest site (Mochizuki et al., 2014). The leaf area index (LAI) in summer at this study site is about 2.8 (Okano and Arase, 2007), which is considerably lower than the typical value in forests with similar vegetation types (e.g., $\sim$ 5–6 in a *Pinus ponderosa L.* forest site, USA). This means that the forest canopy at the study site is not fully covered with leaves, allowing large amounts of solar radiation to reach the forest floor level in daytime. Sunlight transmittance through the forest canopy likely leads to the enhancement of isoprene emission from *D. crassirhizoma* on the forest floor.

Figure 2b shows vertical profiles of the sum of two isoprene oxidation products, methacrolein (MACR) and methyl vinyl ketone (MVK). The concentrations of MACR + MVK were generally higher above 25 m, although they did not exhibit clear vertical gradients within the forest canopy. These profiles result in substantially higher ratios of (MACR + MVK)/isoprene (1.2–1.6) near the forest canopy (22 m) compared to those at the 2 m height near the forest floor (0.5–0.9) (Fig. 2c). The MACR + MVK concentrations reached a maximum in the afternoon. The delay of a few hours in the increase of MACR + MVK concentrations likely represents the time scale required for isoprene degradation. Indeed, this time scale is similar to that reported for the known reaction of isoprene with a typical OH radical concentration of 2.0×10^6 molecules cm^{-3} ($\sim$ 2 h) (Atkinson and Arey, 2003). These results indicate dominant emission of isoprene from the forest floor vegetation, followed by degradation to form the first-order oxidation products MACR and MVK at the study site. It is noted that uptake of MACR and MVK by tree leaves has been suggsted as an important sink of oxygenated VOCs in the forest environment (Tani et al., 2010; Karl et al., 2010). However, the significance of the uptake of these VOCs by leaves is not clear from our data.

Diurnal variations in the above-canopy flux of isoprene showed that the flux of isoprene had distinct peaks around noon from 15 to 17 July when the ambient temperature exceeded 25 °C (Fig. 3e and f). The emission of isoprene is often presented as a function of temperature and light intensity (Guenther et al., 1993). The observed

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isoprene fluxes did indeed depend on both ambient temperature and photosynthetic photon flux density (PPFD) near the forest floor (Fig. 4a and b). To further analyse the meteorological responses of isoprene emissions, we calculated the temperature and light dependence of isoprene emissions, I_s, under standard conditions of temperature (30 °C) and PPFD (1000 μmol m^{-2} s^{-1}) using an algorithm proposed by Guenther et al. (1993). Figure 4c shows the observed isoprene flux plotted against functions describing the dependence of the PPFD (C_L) and ambient temperature (C_T) (r^2 = 0.53). I_s was calculated to be 6.0 nmol m^{-2} s^{-1}, which was lower than that reported for mixture of coniferous and deciduous forest in Europe (8.2–13.0 nmol m^{-2} s^{-1}) (Laffineur et al., 2011). This suggests that the isoprene fluxes at this forest site were characterized by lower sensitivity to temperature and light compared to other forest sites with similar vegetation types.

3.1.2 α-pinene

Our previous work reported that monoterpenes are emitted mainly by *L. kaempferi* at this forest site (Mochizuki et al., 2014). On average, α-pinene accounted for 44 % of the total terpenoid measured in the present study. Figures 2d and 3b depict the vertical and diurnal variations in the α-pinene concentrations, respectively. The highest concentrations of α-pinene were observed near the forest floor (2 m), and the concentrations decreased with increasing height at any time of the day (Fig. 2d). Similar vertical profiles of α-pinene have been reported for hemiboreal mixed forest sites by some previous studies (Holzinger et al., 2005; Noe et al., 2012). The clear vertical gradient indicates emission sources of α-pinene near the forest floor. In fact, emission of monoterpene from the soil surface including fallen needles/branches and roots has been suggested as an important source of α-pinene (e.g., Hayward et al., 2001; Lin et al., 2007; Aaltonen et al., 2011) and its oxidation products in aerosols (Faiola et al., 2014). The vertical gradient of α-pinene found in the present study suggests that α-

pinene is emitted not only from *L. kaempferi* leaves but also from the forest floor, such as from litter and/or roots.

The daytime concentrations of α-pinene ranged between 489 and 4395 ng m^{-3} with an average of 1444 ng m^{-3}. The observed range of the α-pinene concentrations was similar to those reported for Californian pine forest (60–1800 ng m^{-3}) (Goldstein et al., 2004) and for Hyytiälä, Finland (60–350 ng m^{-3}) (Spanke et al., 2001). The diurnal variations of α-pinene showed that the concentrations generally increased in the morning (06:00–09:00 LT) at the 16 m level (Fig. 3b). Indeed, increased concentrations of monoterpene in the morning have been observed at other forest sites (e.g., Holzinger et al., 2005). The emission of α-pinene from *L. kaempferi*, which depends solely on temperature (e.g., Guenther et al., 1993), may continue during night. This continued emission results in accumulation of α-pinene in the forest canopy. Moreover, the low wind speeds during the night (< 2 m s^{-1}) (Fig. 3g) indicate relatively stable atmospheric conditions with less vertical mixing within the forest canopy. This may cause stagnation of α-pinene followed by increased concentrations near the forest floor in the morning.

Similarly to isoprene, the above-canopy flux of α-pinene exhibited distinct peaks around noon on 15, 16, and 17 July (Fig. 3e). It is recognized that the emission of α-pinene depends on temperature alone (e.g., Guenther et al., 1993). In fact, the above-canopy flux of α-pinene was found to increase exponentially with temperature ($r^2 = 0.72$) (Fig. 4d). We determined the basal flux at the standard temperature T_s (30 °C), F_s, which was 0.88 nmol m^{-2} s^{-1} using the temperature-flux algorithm (Guenther et al., 1993). This value is close to the previous data in 2011 (Mochizuki et al., 2014) and the F_s value reported for *Pinus sylvestris* forest in Europe (1.3 nmol m^{-2} s^{-1}) (Rinne et al., 2000).

3.1.3 Influence of anthropogenic sources

Here, we examine the influence of anthropogenic air transported from outside the forest site. The concentrations of toluene, which is used as a tracer for anthropogenic sources, showed little vertical gradient except for the early morning (06:00–09:00 LT)

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(Fig. 2e). The vertical gradients of O_3 concentrations were relatively small during the daytime, indicating intense vertical mixing.

The O_3 concentrations showed clear diurnal profiles during the study period (Fig. 3d). In particular, the concentration increased during the early morning and reached a daily maximum of more than 60 ppbv in the early afternoon on 10 July. The dominant wind on that day during daytime was northeasterly and easterly (Fig. 3g), indicating inflow of air masses from the urban area (Fig. 1). On the other hand, the dominant wind direction on the other days was southerly and southwesterly, indicating transport of air from the forested and/or mountain areas. This was supported by lower concentrations of toluene, benzene, and NO_x on 5 July and 15–17 July.

3.2 Oxidation products of isoprene in the aerosol phase

Figure 5a presents temporal variations in the concentrations of molecular markers for isoprene oxidation products, 2-methylglyceric acid (2-MGA) and 2-methyltetrols (2-MTLs), at the 16 m level. The average concentrations of 2-MGA and 2-MTLs were 4.5 ± 3.6 and 14.0 ± 6.8 ng m^{-3}, respectively (Table 1). The average concentration of 2-MTLs was similar to that reported for a deciduous broadleaf forest in northern Japan in summer (~ 20 ng m^{-3}) (Miyazaki et al., 2014).

The concentrations of 2-MGA and 2-MTLs exhibited clear diurnal variations with a maximum in the afternoon. These temporal variations generally followed that of isoprene, suggesting local production of isoprene-derived OA within the forest canopy. It is noted that the concentrations of 2-MGA and 2-MTLs showed higher values (up to ~ 10 and ~ 30 ng m^{-3}, respectively) on 10 and 17 July. On these two days, the (MACR + MVK)/isoprene and 2-MTLs/isoprene ratios were two- to six-fold higher than those on the other days (Fig. 5b). On the other hand, the concentrations and above-canopy flux of isoprene were similar to or even lower than those on the others days (Fig. 3a and e). These results suggest that the atmospheric reactivity for isoprene oxidation was considerably higher on those specific days to produce OAs. This is supported by elevated concentrations of SO_4^{2-} and O_3 as shown in Figs. 5e and 3d, re-

spectively. In particular, the 2-MGA/isoprene and 2-MTLs/isoprene ratios increased with increasing levels of O$_3$ (Fig. 6a and b). In fact, anthropogenic influence on the observed aerosols was significant on 10 July, as evident from the substantially large concentrations of SO$_4^{2-}$ ($\sim$ 6400 ng m^{-3}), O$_3$ ($\sim$ 65 ppbv), and NO$_x$ ($\sim$ 3.5 ppbv) on that day. The processes for the isoprene oxidation producing OAs will be discussed in detail in Sect. 3.4.

3.3 Oxidation products of α-pinene in the aerosol phase

Figure 5c presents temporal variations in the concentrations of pinonic acid (PA) and 3-MBTCA at the 16 m altitude level. PA and 3-MBTCA showed enhanced concentrations in daytime (Fig. 5c), whereas the concentration of α-pinene was highest in the morning for most of the observational period, as shown in Fig. 3b. PA is formed by the ozonolysis and photooxidation of α- and β-pinene via reactions with O$_3$ and OH radicals (e.g., Yu et al., 1999). The reaction rate coefficients k (OH) for α-pinene (5.3×10^{-11} cm^3 s^{-1}) (Atkinson et al., 2006) result in OH lifetimes of 5 h for α-pinene, based on a typical average OH concentration of 1×10^6 cm^{-3}. This first-generation product of α- and β-pinene is further oxidized to higher-generation oxidation products through OH radical-initiated reactions. Further reaction of the initial oxidation products of pinene leads to highly oxidized polar compounds (e.g., 3-MBTCA) (Szmigielski et al., 2007; Kourtchev et al., 2009; Müller et al., 2012). The difference in the diurnal peaks of the concentrations of α-pinene and its oxidation products in aerosols can be explained by the timescale for such atmospheric reactions of α-pinene to form SOA.

Similar to the temporal variations of 2-MGA and 2-MTLs, the concentrations of PA and 3-MBTCA on 10 and 17 July were considerably higher than those on the other days. The elevated ratios of PA/α-pinene (up to $\sim$ 0.04) and 3-MBTCA/α-pinene (up to $\sim$ 0.06) on 10 July (Fig. 5d) compared to those on the other days suggest that the atmospheric reactivity of α-pinene was more pronounced on that day. This is also evident from Fig. 6c and d, which showed positive correlations of the 2-MGA/isoprene

and 2-MTLs/isoprene ratios with O_3 ($r^2 = 0.67$). In contrast to this, the concentrations and above-canopy flux of α-pinene on 10 July were markedly lower than those on 17 July. This suggests an importance of atmospheric reactivity for α-pinene to form SOA. Possible controlling factors for the production of α-pinene-derived SOA as well as isoprene-derived SOA are discussed in Sect. 3.4.

3.4 Controlling factors of biogenic SOA formation

To investigate the factors controlling biogenic SOA formation at the study site, we conducted a positive matrix factorization (PMF) (Paatero and Tapper, 1994). The PMF analysis was performed for the collected samples including VOCs and tracer compounds as well as inorganic species in aerosols. The PMF analysis resulted in the deduction of three interpretable factors. Figure 7 shows composition profiles for the three factors resolved by the PMF. Factor 1 (F1) was dominated by higher fractions of O_3 (53 %), NO_x (52 %), SO_4^{2-} (68 %), and toluene (60 %), indicating a larger influence of anthropogenic sources. Factor 2 (F2) was characterized by smaller fractions of these species and was dominated by oxidation products in aerosols, such as 2-MGA, pinic acid, 3-HGA, and 3-MBTCA. Factor 3 (F3) was dominated by isoprene (71 %) and α-pinene (70 %) and had a larger contribution of anthropogenic tracers such as benzene (41 %). Based on the results above, F1, F2, and F3 are referred here as "anthropogenically more influenced/photochemically more aged," "anthropogenically less influenced/photochemically more aged," and "anthropogenically more influenced/photochemically less aged," respectively (Fig. 8).

Figure 9 shows time series of the estimated relative contributions of the different factors to the concentrations of 2-MTLs and 3-MBTCA resolved by PMF on each day. It is noteworthy that the contributions of each factor to the elevated concentrations of 2-MTLs and 3-MBTCA are different between 10 and 17 July. On 10 July, F1 was a dominant factor to 2-MTLs (64 %) and 3-MBTCA (57 %). In contrast, contributions of F2 to 2-MTLs (75 %) and 3-MBTCA (90 %) were predominant on 17 July. As stated in the

previous sections, anthropogenic influence on the observed aerosols was significant on 10 July. The PMF result indicates that anthropogenic inflow and subsequent oxidation of both isoprene and α-pinene likely enhanced SOA formation within the forest canopy, despite the relatively low above-canopy fluxes of BVOCs.

OH-oxidation of isoprene is initiated by the addition of hydroxyl radical to the double bonds of isoprene. The alkyl radicals formed in the air react with oxygen (O_2) to form alkyl peroxyl radicals (HOC_5H_8OO), commonly called ISOPOO. ISOPOO radicals subsequently react with either NO (Tuazon and Atkinson, 1990), hydroperoxyl radicals HO_2 (Paulot et al., 2009), or organic peroxyl radicals RO_2 (Jenkin et al., 1998). Under high NO_x conditions, the dominant fate of ISOPOO is generally a reaction with NO. For SOA formed from isoprene oxidation, the existence of particle-phase acid-catalyzed reactions has been demonstrated, and this leads to the formation of 2-MTLs and high-molecular-weight products of SOA (Surratt et al., 2007). Edney et al. (2005) found that concentrations of 2-MGA and 2-MTLs increased significantly under acidic conditions.

Moreover, a recent field study indicated that a significant fraction of 2-MTLs exists in the gas phase (Isaacman et al., 2013). It is thus likely that volatilization of methyltetrols from the fine particles occurs and is followed by gas-particle repartitioning. In addition to the photooxidation of isoprene, Nozière et al. (2011) suggested that some fraction of 2-MTLs is likely of primary biological origin, which may be associated with production by plants, algae, and other living organisms. However, the average local wind speeds on 10 and 17 July were much lower ($< 2\,\mathrm{m\,s^{-1}}$) than those on 15–16 July (Fig. 3f), indicating that any primary biological origin contribution to the observed 2-MTLs was likely minor in this study.

With regard to α-pinene SOA, Emanuelsson et al. (2013) conducted photo-oxidation experiments with a mixture of biogenic and anthropogenic precursors. They suggested that even small contributuions of anthropogenic SOA can reduce the volatility of α-pinene-derived SOA. BSOA from α-pinene is formed already at low OH levels and vapors with high vapor pressures reach saturation, which contribute to the BSOA mass (Pankow, 1994). These vapors can react with OH, which leads to increasing second-

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generation products with low volatility, such as 3-MBTCA (Müller et al., 2012). Although OH measurement is not available in the present study, our data on 10 July indicates that mixed anthropogenic/biogenic SOA with OH likely resulted in the enhanced concentrations of 3-MBTCA (Fig. 9b). In summary, the present results suggest that the anthropogenic inflow and subsequent oxidation of isoprene and α-pinene promoted BSOA formation within the forest canopy despite the lower concentrations and above-canopy fluxes of those VOCs.

4   Conclusions

We measured concentrations and canopy-scale fluxes of isoprene and α-pinene simultaneously with their oxidation products in total suspended particles (TSP) at a *Larix kaempferi* forest site in summer. Isoprene and α-pinene accounted for 23 and 44 %, respectively, of the total terpenoids measured in this study. Vertical profiles of isoprene showed the highest concentrations near the forest floor with a maximum around noon, whereas concentrations of MACR and MVK were high near the *L. kaempferi* canopy. The profile suggests large emissions of isoprene near the forest floor, which is likely due to *Dryopteris crassirhizoma*, followed by reaction of the isoprene within the canopy. The concentrations of α-pinene also showed peaks near the forest floor with maximums in the early morning and late afternoon. The vertical profiles of α-pinene suggested high emissions of α-pinene from soil and litter in addition to emissions from leaves at the forest site.

Isoprene and its oxidation products in aerosols exhibited similar diurnal variations within forest canopy, providing an evidence of SOA formation via oxidation of isoprene emitted from *Dryopteris crassirhizoma* on the forest floor. PMF analysis indicated that factors in which anthropogenic influence was significant largely contributed to the elevated concentrations of isoprene SOA (> 64 %) and α-pinene SOA (> 57 %). The combined analyses of the fluxes and vertical profiles of BVOCs suggest that anthropogenic inflow and the subsequent oxidation of both isoprene and α-pinene likely enhanced

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BSOA formation within the forest canopy even though the BVOC fluxes were relatively low. This study emphasizes an importance of intra-canopy processes for biogenic SOA formation in the presence of significant inflow of anthropogenic aerosols and their precursors.

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Table 1. Concentrations of biogenic VOCs, biogenic SOA tracers, inorganic ions, and gas species measured in the *Larix kaempferi* forest.

Compounds/Species	Daytime concentration ($ng\,m^{-3}$)				Nighttime concentration ($ng\,m^{-3}$)			
	mean	SD	min	max	mean	SD	min	max
Biogenic VOCs ($ng\,m^{-3}$)								
Isoprene	316	139	157	703	NA	NA	NA	NA
α-pinene	1444	837	489	4395	NA	NA	NA	NA
Anthropogenic VOCs ($ng\,m^{-3}$)								
MEK	130	105	15	329	NA	NA	NA	NA
Benzene	485	415	34	1241	NA	NA	NA	NA
Toluene	637	411	144	1594	NA	NA	NA	NA
Oxidation products of isoprene ($ng\,m^{-3}$)								
MACR	146	44	71	252	NA	NA	NA	NA
MVK	163	62	70	320	NA	NA	NA	NA
Isoprene SOA tracers ($ng\,m^{-3}$)								
2-methylglyceric acid	4.5	3.6	0.2	11.3	1.4	1.3	0.1	3
2-methyltetrols	14.0	6.8	0.4	30.7	8.8	6.3	0.7	19
2-methylthreitol	4.2	2.9	0.2	9.5	2.2	1.9	0.2	4
2-methylerythritol	9.8	6.2	0.3	21.2	6.6	6.0	0.5	15
α-pinene SOA tracers ($ng\,m^{-3}$)								
Pinonic arid	12.7	7.7	1.7	28.0	3.1	2.6	0.9	6.8
Pinic arid	4.9	5.0	0.0	18.2	6.4	5.8	0.8	14.5
3-hydroxyglutaric arid	14.4	13.7	1.6	44.0	15.9	15.8	1.0	35.6
3-MBTCA	14.3	13.6	0.0	49.7	12.7	12.8	0.3	27.5
Inorganic ions ($ng\,m^{-3}$)								
SO_4^{2-}	2937	2065	617	6331	1875	1592	767	4237
NO_3^-	529	289	271	1562	200	136	95	385
O_3 (ppb)	29.4	16.2	4.6	63.0	13.5	11.0	4.0	30.8
NO_x (ppb)	1.5	0.8	0.6	3.3	1.0	0.3	0.6	1.3

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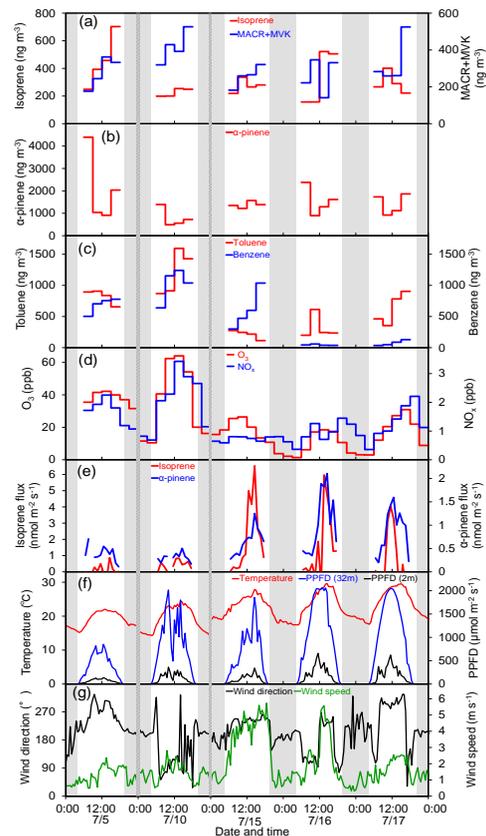Full Screen / Esc

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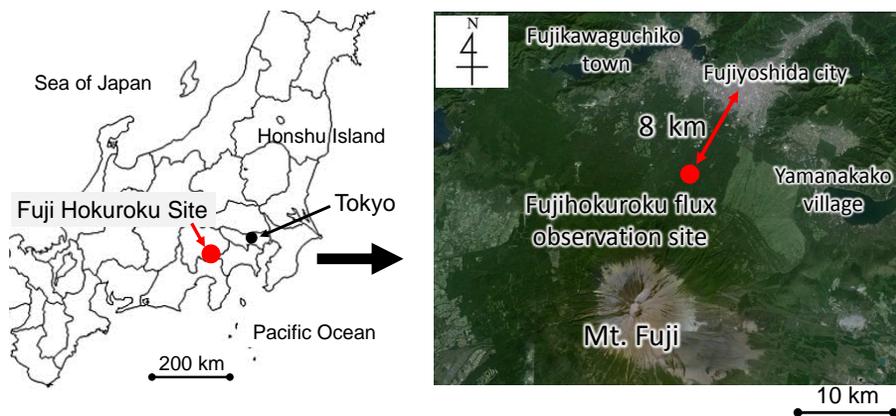
Figure 1. Location of the study site.
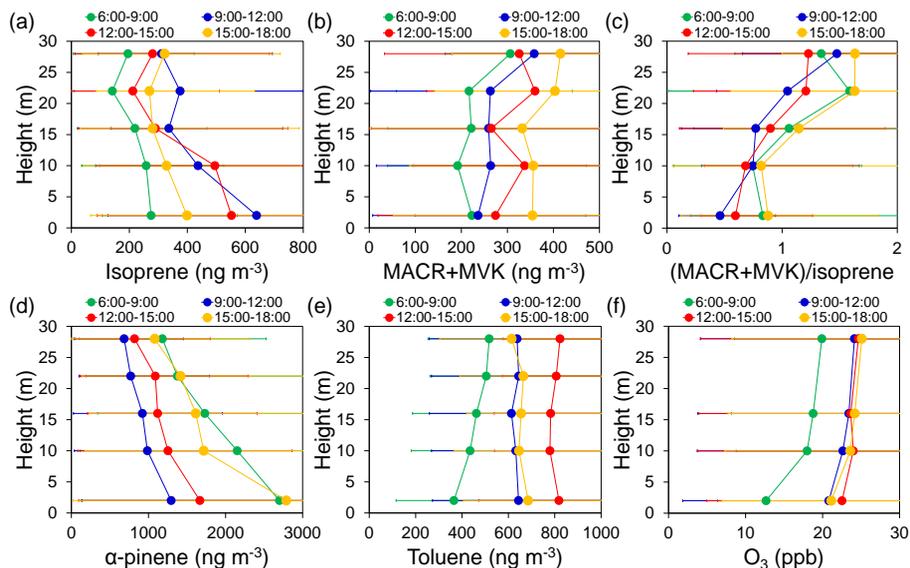
Figure 2. The average vertical profiles of **(a)** isoprene, **(b)** MACR + MVK, **(c)** (MACR + MVK)/isoprene, **(d)** α-pinene, **(e)** toluene, and **(f)** O$_3$ during the study period. Data shown are median values with interquartile range.

Figure 3. Diurnal variation of **(a)** isoprene, MACR, and MVK, **(b)** α-pinene, **(c)** toluene and benzene, **(d)** O_3 and NO_x, **(e)** isoprene and α-pinene fluxes **(f)** temperature and solar radiation, and **(g)** wind speed and wind direction. Shaded areas indicate nighttime.
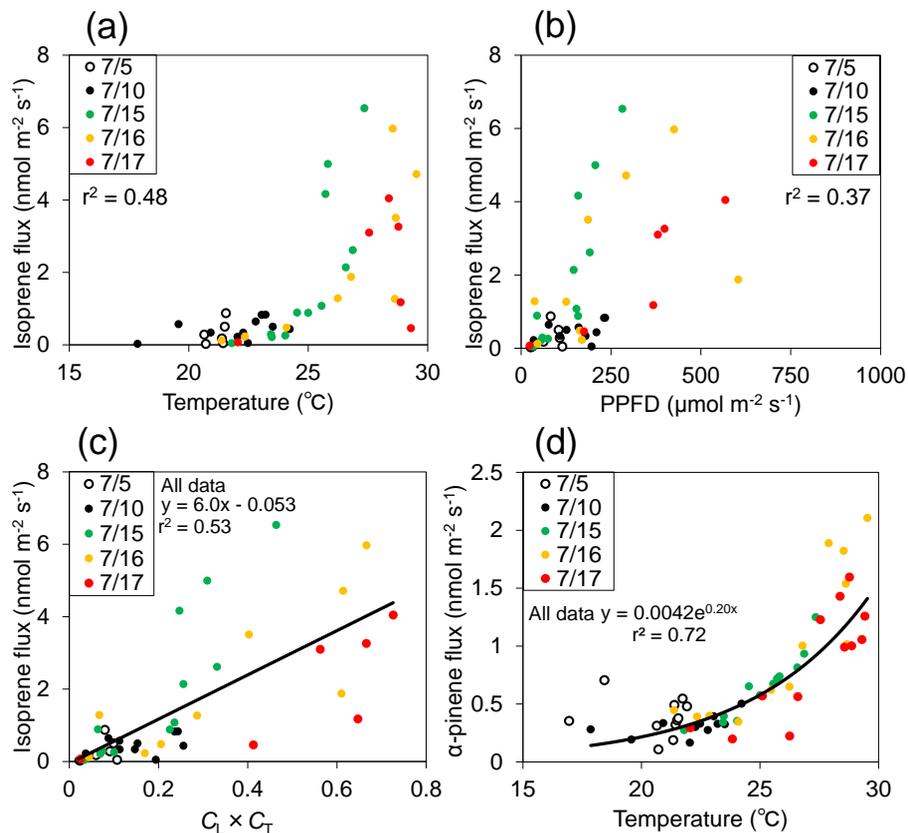
Figure 4. Isoprene fluxes against **(a)** the ambient temperature, **(b)** photosynthetic photon flux density (PPFD), and **(c)** temperature and light activity factor ($C_L \times C_T$) and **(d)** α-pinene flux against the ambient temperature.
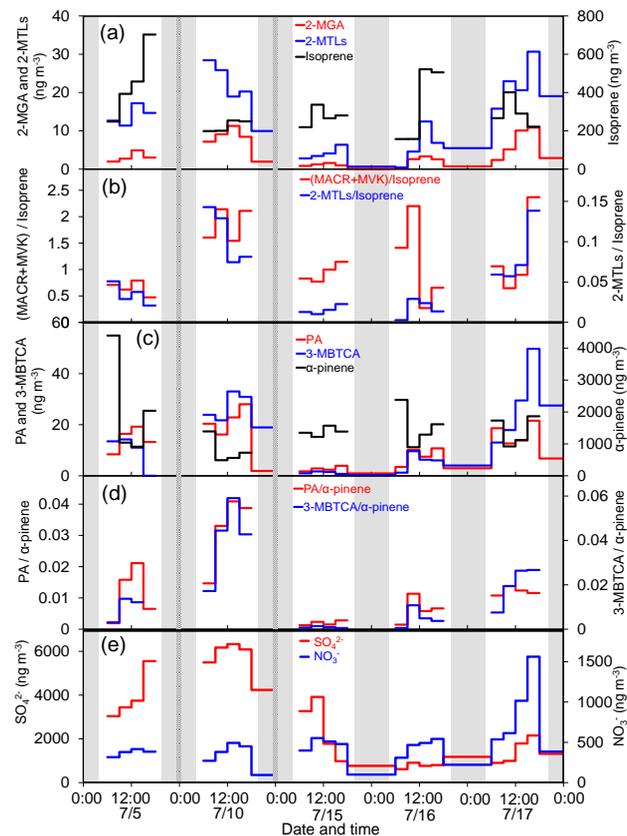
Figure 5. Diurnal variations of **(a)** 2-MGA, 2-MTLs, and isoprene, **(b)** the ratios of (MACR + MVK)/isoprene and 2-MTLs/isoprene, **(c)** PA, 3-MBTCA, and α-pinene, **(d)** the ratios of pinonic acid/α-pinene and 3-MBTCA/α-pinene, and **(e)** SO_4^{2-} and NO_3^- at the 16 m altitude level on 5, 10, and 15–17 July. Shaded areas indicate nighttime.

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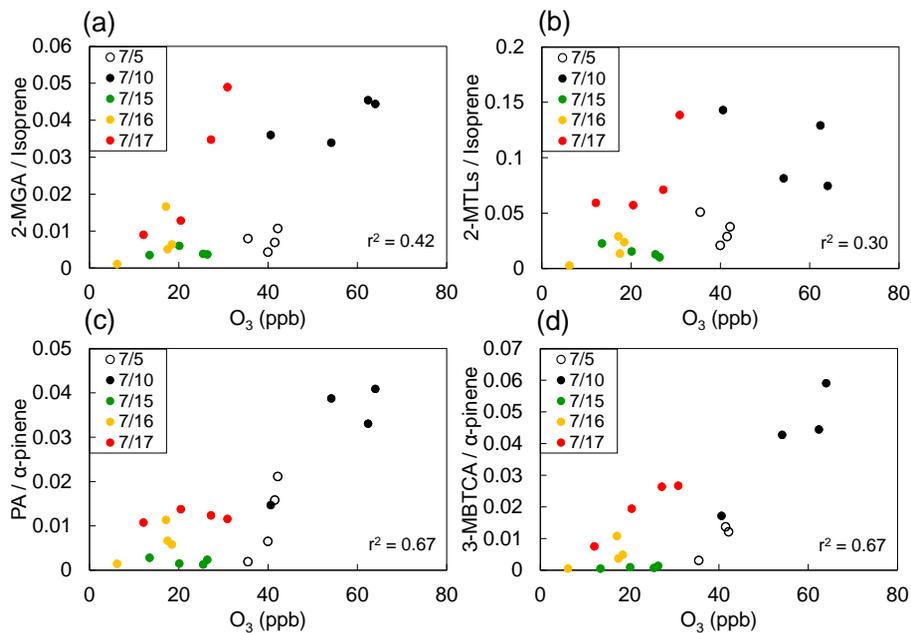
Figure 6. The ratios of **(a)** 2-MGA/isoprene, **(b)** 2-MTLs/isoprene, **(c)** PA/α-pinene, and **(d)** 3-MBTCA/α-pinene as a function of the O_3 mixing ratios.

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Figure 7. Three compositional factors isolated by PMF.

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Anthropogenically more influenced

Factor 3   Factor 1

Photochemically
less aged

Photochemically
more aged

Factor 2

Anthropogenically less influenced
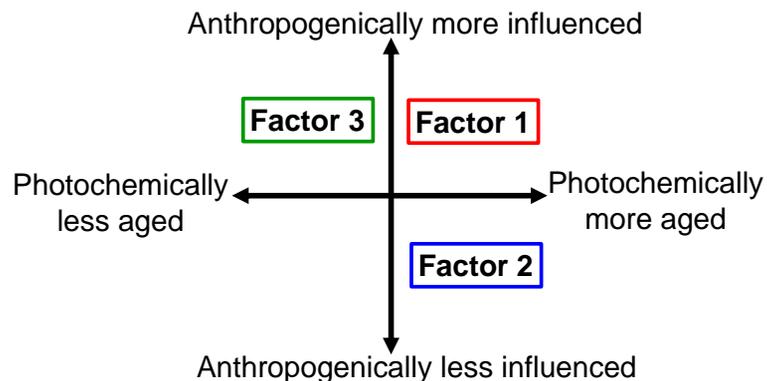
Figure 8. Schematic of each characteristic of the three PMF factors in terms of the degree of anthropogenic influence and photochemical aging.
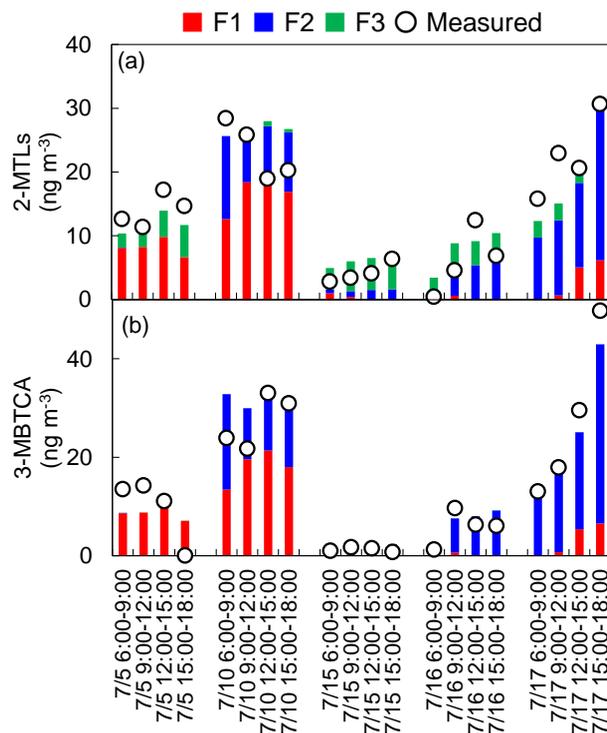
Figure 9. Time series of estimated relative contributions of different factors to the concentrations of **(a)** 2-MTLs and **(b)** 3-MBTCA resolved by PMF in each day. Open circles indicate the measured concentrations within the forest canopy.

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