Canopy fluxes of monoterpane, isoprene and isoprene oxidation products in a pine-oak forest

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Abstract

Monoterpenes and isoprene emitted from forest ecosystems contribute to the formation of secondary organic aerosols (SOAs) and photochemical oxidants (O₃) and affect an ecosystem’s carbon budget. Initial oxidation products of isoprene, methacrolein (MACR) and methyl vinyl ketone (MVK), are key intermediate compounds for the formation of SOAs and O₃, but the production and loss processes of MACR and MVK and its controlling factors within a forest have not been revealed. To address them within a forest and the behavior of related compounds, we measured vertical concentrations and fluxes of monoterpenes, isoprene, and MACR+MVK in a pine-oak forest during summer. Monoterpane concentrations were the highest near the forest floor. A higher isoprene concentration was observed at the height of the Quercus trees. High positive fluxes of monoterpenes and isoprene were observed during the day. The average flux of isoprene during the measurement period was 2.6 times higher than that of monoterpane. Quercus in the lower layer of the forest can be an important source of isoprene, even though the light intensity was estimated much lower than that of red pine canopy. The MACR+MVK concentrations did not show clear vertical gradient patterns. Both positive and negative MACR+MVK fluxes were observed and large positive MACR+MVK fluxes were occasionally observed under a relatively high O₃ concentration and isoprene flux around noon or during the afternoon, suggesting that they are produced more frequently by reaction with reactive species including O₃ at a higher temperature. Our results demonstrate that, to investigate sink and source dynamics of MACR+MVK above a forest, it is necessary to separately estimate production rate of MACR+MVK, which depends on isoprene emission from the target and surrounding forests, O₃ concentration, temperature, and its deposition rate, which is controlled by its concentration and micrometeorological factors.

Key words: Flux, Isoprene, Methacrolein, Methyl vinyl ketone, Monoterpane, Pine-oak forest

1. Introduction

Biogenic volatile organic compounds (BVOCs) are emitted from terrestrial ecosystems. Annual global BVOC emissions are estimated to be approximately 1000 Tg (Guenther et al., 2012). This amount is several times greater than that of annual global emission of anthropogenic volatile organic compounds (AVOC). Isoprene (C₅H₈) and monoterpane (C₅H₁₀) emissions comprise approximately 70% of the total emission of BVOCs at a global scale (Guenther et al., 2012). BVOC composition and emission depend on the vegetation type (e.g., Rinne et al., 2002; Fares et al., 2013; Mochizuki and Tani, 2017) and species and strains within genera (Tani and Kawawata, 2008; Miyama et al., 2018; Okumura et al., 2018).

Isoprene and monoterpenes can be easily oxidized by O₃ and OH radicals in the atmosphere. Their oxidation products lead to secondary organic aerosols (SOAs) in the forest atmosphere (e.g., Mochizuki et al., 2015; 2017). Biogenic secondary organic aerosols (BSOAs) can directly affect the radiation budget of the Earth’s atmosphere by scattering incoming solar radiation. As BSOAs are highly water-soluble, they contribute to the formation of cloud condensation nuclei (CCN) which also contribute to the radiation budget of the Earth’s atmosphere (Kanakidou et al., 2005). However, BVOCs contribute to the formation of photochemical oxidants such as ozone in the presence of NOₓ. An increase in the oxidant concentration can lead to degraded air quality and negatively affect human health (Ebi and McGregor, 2008).

Photochemical reaction of isoprene produces methacrolein (MACR) and methyl vinyl ketone (MVK), which are key intermediate compounds in the formation of SOAs (Surratt et al., 2006; Zhang et al., 2010) and photochemical oxidants (provided by California Air Resources Board). Tani et al. (2010) reported that leaves of several tree species were capable of MACR and MVK uptake. For ecosystem-scale flux measured using an eddy covariance method, Karl et al. (2010) observed the depositional flux of MACR+MVK on a tropical rain forest. Kalogridis et al. (2014) observed emission of MACR+MVK from a Mediterranean oak forest during the day (daily maximum: 0.40 nmol m⁻² s⁻¹). These results suggest that a source or sink of MACR and MVK depends on vegetation type. As measurement of MACR and MVK fluxes and distributions within a forest has...
not been studied except for in the aforementioned reports, the fate of MACR and MVK within a forest are rarely understood.

Isoprene and monoterpenes include 5 and 10 atoms of carbon, respectively, in each molecule. BVOC emitted from a forest may involve the loss of carbon to the atmosphere. Isoprene and monoterpenem emissions account for up to 5% of the net ecosystem exchange (NEE) depending on vegetation type and region (e.g., Bouvier-Brown et al., 2012; Mochizuki et al., 2014). There has been no study of the time-resolved variations in the ratio of carbon emitted as BVOCs to that fixed by NEE and on its controlling factors in a forest.

**Pinus densiflora** (Japanese red pine) is endemic to Japan and accounts for 8% of the total forest area in Japan. In the present study, to investigate the source and sink dynamics of monoterpenes, isoprene, and the initial isoprene oxidation products, we measured vertical profiles and above canopy fluxes of monoterpene, isoprene, and initial isoprene oxidation products in a pine-oak forest during summer. Here we also discuss the carbon ratio of BVOCs to NEE and its controlling factors in a pine-oak forest.

### 2. Experiment

Gas sampling was conducted on the 24th and 25th and from the 28th to 30th of August, 2012, at the Fujiyoshida forest meteorological research site (35°45′N, 138°7′E; elevation of 1040 m). This site is located in Fujiyoshida city, Yamanashi, Japan, on the Kenmarubi lava flow (slope: 3.5′) erupted about 1000 years ago. The forest area is approximately 3600 ha. The dominant tree species is *P. densiflora* (84.5% of total basal area). The tree density of *P. densiflora* is 920 ha⁻¹ in 1999. The tree age is approximately 100 years old and the mean canopy height is approximately 22 m. Some broadleaf trees including *Ilex pedunculosa* (5.4% of total basal area), *Quercus serrata* (2.2%), and *Quercus mongolica* (1.0%) also grow in this forest. The height of these trees is approximately 10 m. The soil type is basaltic lava. The forest floor is covered with leaf litter and organic matter. A meteorological tower of 32 m height was built at the forest site and temperature, photosynthetic photon flux density (PPFD), wind direction, and wind speed have been measured on the tower. Further details regarding the site information are provided in Mizoguchi et al. (2012) and Ohtsuka et al. (2013).

We did not measure the PPFD (μmol m⁻² s⁻¹) around the major trees in the lower layer of the forest. To estimate the PPFD at a height of 15 m (above the broadleaf trees), we used the following equation:

\[
P_{\text{PPFD}_15m} = \text{PPFD} \left( \frac{\text{PPFD}_{15m}}{\text{PPFD}} \right)^{\text{rPAI}}
\]

where PPFD₁₅ₘ is the calculated PPFD at a height 15 m above the ground, PPFD is the measured PPFD above the *P. densiflora* canopy, and PPFD₁₅ₘ is the measured PPFD at a height of 2 m. PPFD at a height of 2 m is measured at three points around the flux tower. Data of PPFD₁₅ₘ were the average of three points. rPAI is the relative plant area index (rPAI). The rPAI at a height of 15 m was determined to be 0.47 using the PAI values measured at 2 m and 15 m (Takanashi et al., unpublished data).

Vertical profiles of VOC concentration were measured at 2, 9, 17, 22, and 27 m above the ground on the meteorological tower. Ambient air was collected into stainless-steel tubes (Ø0.25 × 3.5 inches) filled with 200 mg of Tenax TA (GL Science, Japan) and 100 mg of Carbosieve (Supelco, USA) for 160 min at a flow rate of 100 ml min⁻¹ using a portable pump (MP-30, Shibata Inc., Japan). We applied MnO₂ filters upstream of the adsorbent tubes to avoid VOC degradation on the adsorbents (Calogirou et al., 1996). The samples were collected at 3-h intervals from 6:00 to 18:00. After sampling, the tubes were stored in a refrigerator at 4°C prior to analysis.

Canopy-scale VOC flux, \( F \ (\text{nmol m}^{-2} \text{s}^{-1}) \), was measured using a relaxed eddy accumulation (REA) method (Businger and Oncley, 1990) as follows:

\[
F = b \sigma_m (C^1 - C^*)
\]

where \( \sigma_m \ (\text{m s}^{-1}) \) is the standard deviation of the vertical wind speed; \( C^1 \) and \( C^* \ (\text{mol m}^{-3}) \) are the VOC concentrations in the upward and downward air, respectively, and \( b \) is an empirical coefficient value which is calculated from the sensible heat flux equation using an eddy covariance method. The \( b \) value was obtained as the slope of \( w^T \) against \( \sigma_m (T^1 - T^*) \) using all data during the measurement period and was determined to be 0.39 (\( r^2 = 0.99 \)). VOC fluxes were measured 27 m above the ground on the meteorological tower using a portable REA gas sampling system (Mochizuki et al., 2011; 2014). Ambient air was collected into adsorbent tubes for 55 min at a flow rate of 200 ml min⁻¹. The samples were collected at 1-h intervals from 6:00 to 18:00.

VOCs were identified and quantified using a capillary gas chromatography mass spectrometer (GC-MS) (QP5050A, Shimadzu, Japan) equipped with a thermal desorption system (Turbo matrix ATD, Perkin Elmer Instruments, USA). Isoprene and its oxidation products (MACR and MVK) and monoterpenes were identified and quantified. Details regarding the VOC analysis are provided in our previous publication (Mochizuki et al., 2015).

For monoterpane emission diffused out of monoterpane pools, the monoterpane flux is shown as the temperature-dependent algorithm (Guenther et al., 1993) as follows:

\[
M = M_i \exp \left( \beta (T - T_s) \right)
\]

where \( M \ (\text{nmol m}^{-2} \text{s}^{-1}) \) is the monoterpane flux; \( M_i \ (\text{nmol m}^{-2} \text{s}^{-1}) \) is the basal monoterpene flux at the standard temperature, \( T_s \ (30°C) \); \( \beta \ (\text{°C}^{-1}) \) is the empirical coefficient; and \( T \ (°C) \) is the ambient air temperature. Equation (3) is converted to equation (4) as follows:

\[
\ln M = \beta (T - T_s) + \ln M_i
\]

the coefficient \( \beta \) and \( M_i \) can be obtained as the slope and intercept at the y axis of the regression line between \( \beta (T - T_s) \) and \( \ln M \), respectively.

Isoprene flux is shown as the temperature and light intensity algorithm (Guenther et al., 1993) as follows:

\[
I = I_C C_T
\]

where \( I \ (\text{nmol m}^{-2} \text{s}^{-1}) \) is the isoprene flux at any temperature \( T \) and light intensity \( L \ (\text{PPFD}) \). \( I_C \ (\text{nmol m}^{-2} \text{s}^{-1}) \) is the basal isoprene flux at the standard temperature, \( T_s \ (30°C) \), and a
standard PPFD (1000 \( \mu \text{mol m}^{-2} \text{s}^{-1} \)). \( C_L \) and \( C_T \) (dimension less) are the light activity and temperature factors, respectively, as follows:

\[
C_L = \frac{\alpha C_L L}{\sqrt{1 + \alpha^2 L^2}} \tag{6}
\]

\[
C_T = \frac{\exp \left( \frac{C_{T1}(T - T_s)}{RT_s} \right)}{1 + \exp \left( \frac{C_{T2}(T - T_m)}{RT_m} \right)} \tag{7}
\]

where \( R \) is the gas constant (8.314 J L\(^{-1}\) mol\(^{-1}\)) and \( \alpha \) (0.0027), \( C_{L1} \) (1.066), \( C_{T1} \) (95,000 J mol\(^{-1}\)), \( C_{T2} \) (230,000 J mol\(^{-1}\)), and \( T_m \) (314 K) are empirically derived constants.

CO\(_2\) fluxes above the canopy were measured 27 m above the ground on the meteorological tower using the eddy covariance method and a closed-path infrared gas analyzer. NEE (\( \mu \text{mol m}^{-2} \text{s}^{-1} \)) was calculated by the CO\(_2\) flux plus the rate of change in CO\(_2\) storage in the canopy. Details regarding that calculation is described in Mizoguchi \textit{et al}, (2012).

O\(_3\) concentrations (ppb) were measured 17 m above the ground on the meteorological tower. O\(_3\) concentration was monitored using an ultraviolet light absorption analyzer (49C, Thermo Scientific, USA). Details of the sampling method and O\(_3\) analysis are described in Wada \textit{et al}, (2012).

We calculated 3-day air mass back trajectories at a height of 500 m using the Meteorological Data Explorer (METEX) provided by the National Institute for Environmental Studies.

3. Results and discussion

3.1 Variations in monoterpene and isoprene concentrations and fluxes

We identified isoprene and monoterpene such as \( \alpha \)-pinene, camphene, sabinene, myrcene, \( \beta \)-pinene, 3-carene, limonene and \( \beta \)-phellandrene in the pine-oak forest. Figure 1a shows the monoterpene vertical profiles. The monoterpene concentrations were the highest near the forest floor and the concentrations decreased with increasing height. Similar vertical profiles of monoterpene have been reported for Larix kaempferi forest (Mochizuki \textit{et al}, 2015) and Japanese red pine (Tani \textit{et al}, 2002). At the study site, \( P. \) densiflora roots extend into the basaltic lava and part of the root surfaces appear on the soil surface. The forest floor is mainly covered with \( P. \) densiflora leaf litter. Leaf litter and roots of \( P. \) densiflora are known to emit monoterpene (Miyama \textit{et al}, 2016; Tsuruta \textit{et al}, 2018). The clear vertical gradient indicates that monoterpene sources are not only leaves but also the forest floor in a pine-oak forest.

Figure 2a shows variations in the height-averaged monoterpene concentration below the canopy (2–17 m). High monoterpene concentrations were observed during the morning and the concentrations decreased during the day. The diurnal monoterpene concentration pattern differed from those of the ambient temperature and PPFD. \( P. \) densiflora has monoterpene storage organs and monoterpenes are emitted from the storage organs depending on the temperature (Yokouchi and Ambe, 1984). Monoterpenes were continuously emitted during the night and accumulated under and within the canopy from the night to the early morning when vertical mixing was low (Tani \textit{et al}, 2002), resulting in the highest concentration observed during the morning of all the measurement days. A higher monoterpene concentration was observed during the late afternoon compared to that around noon, suggesting that monoterpenes started to accumulate within canopy.

Figure 1b shows the isoprene concentration vertical profiles. The higher isoprene concentrations were observed at 9 m between 9:00 and 15:00. The tree height of \( Q. \) serrata and \( Q. \) mongolica is approximately 10 m above the ground. These trees have been reported to be strong isoprene emitters (Tani \textit{et al}, 2017). Isoprene emission depends on temperature and light intensity. Daily maximum values of the calculated PPFD at a height 15 m above the ground, PPFD\(_{15m}\), during the measurement period ranged from 277 to 412 \( \mu \text{mol m}^{-2} \text{s}^{-1} \) (Figure 2e), which were sufficiently high to promote isoprene emission from the \( Quercus \) trees (Tani and Kawawata, 2008). The vertical profile indicates that the main isoprene source at this site is these \( Quercus \) trees.

Figure 2b shows variations in isoprene concentration averaged within the height range under the canopy (2–17 m). Isoprene concentration was low during the morning and maximum around noon or during the afternoon. The diurnal isoprene concentration pattern was similar to those of the ambient temperature and PPFD. Isoprene is not emitted during the night (Guenther \textit{et al}.,...
and therefore a higher isoprene concentration caused by the storage effect was not observed during the early morning and late afternoon compared to that around noon, except for data collected on the 28th of August.

Monoterpene fluxes above the forest canopy started to increase during the morning with a maximum occurring between 11:00 and 14:00 (Figure 2a). The monoterpene flux showed a positive correlation with ambient air temperature \( r^2 = 0.61 \) (Figure 3a), whereas it showed a weak correlation with PPFD \( r^2 = 0.20 \) (Figure 3b). The basal monoterpene flux, \( M_b \), in the pine-oak forest was calculated to be 2.5 nmol m\(^{-2}\) s\(^{-1}\) (beta = 0.15) during summer using the equation 4. This value was comparable to those reported for \( P. densiflora \) forest in Nagano, Japan measured from May to August (1.8 nmol m\(^{-2}\) s\(^{-1}\)) (Tani et al., 2002) and \( P. sylvestris \) forest in Finland measured from May to August (2.0 nmol m\(^{-2}\) s\(^{-1}\)) (Rinne et al., 2000).

The isoprene flux above the \( P. densiflora \) canopy was high during the day (Figure 2b). Positive correlations between isoprene flux and ambient air temperature \( r^2 = 0.50 \) and between isoprene flux and PPFD \( r^2 = 0.45 \) were observed (Figures 4a and 4b). The basal isoprene flux, \( I_b \), was determined to be 13.3 nmol m\(^{-2}\) s\(^{-1}\) using the Equations 5–7 (Figure 4c). This value was comparable to that reported for a boreal aspen forest in Canada measured during summer (16 nmol m\(^{-2}\) s\(^{-1}\)) at 25°C (Fuentes et al., 1999) but lower than that reported for a French Mediterranean oak forest measured from May to June.

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Fig. 2. Diurnal and temporal variation of concentrations and fluxes of monoterpene (a), concentrations and fluxes of isoprene (b), concentrations and fluxes of MACR + MVK (c), \( O_3 \) (d), temperature and PPFD (e), and wind direction and wind speed (f).

Fig. 3. Monoterpene flux versus ambient temperature (a) and PPFD (b).
(30 nmol m\(^{-2}\) s\(^{-1}\)) (Kalogridis et al., 2014).

The average flux of isoprene during the measurement period (3.1 nmol m\(^{-2}\) s\(^{-1}\)) was 2.6 times higher than that of monoterpene (1.2 nmol m\(^{-2}\) s\(^{-1}\)). The \(I_s\) in this site was also higher than the \(M_s\). Our results suggest that Quercus in the lower layer of the forest can be an important source of isoprene, even though the light intensity was estimated much lower than that of red pine canopy.

### 3.2 Carbon budget

Because CO\(_2\) flux above the forest canopy cannot distinguish the contribution of \(P.\ densiflora\), broadleaf trees, and other components, the NEE shows the entire forest ecosystem response. NEE was negative during the day and had the lowest value around noon (Figure 5a). NEE was found to exponentially increase both with PPFD (\(r^2 = 0.61\)) and ambient temperature (\(r^2 = 0.21\)). To investigate the ratio of carbon emission in the form of monoterpene and isoprene, we calculated the ratio of monoterpene to NEE (monoterpene-C/NEE) and the ratio of isoprene to NEE (isoprene-C/NEE). The monoterpene-C/NEE ratio did not show clear diurnal variations (Figure 5b). However, the isoprene-C/NEE ratio started to increase during the morning with a maximum around noon (Figure 5b). The isoprene-C/NEE ratio was found to exponentially increase with increasing ambient air temperature (\(r^2 = 0.50\)) (Figure 6a) and PPFD (\(r^2 = 0.51\)) (Figure 6b). Such trends of the isoprene-C/NEE ratio are similar to the temperature and PPFD dependences of the isoprene flux. Our results indicate that temperature and PPFD are the key factors controlling the loss of carbon in the form of isoprene.

The average carbon ratio (monoterpene plus isoprene to NEE) in the pine-oak forest was 0.12%. The calculated carbon ratio

![Fig. 4. Isoprene flux versus ambient temperature (a), PPFD\(_{15n}\) (b), and temperature and light activity factor (\(C_x \times C_T\)) (c).](image)

![Fig. 5. Diurnal and temporal variation in NEE (a) and the carbon ratio of monoterpene and isoprene to NEE (b).](image)

![Fig. 6. Relationship of the carbon ratio of BVOC flux to NEE to temperature (a) and PPFD (b).](image)
was lower than that reported for a *P. ponderosa* forest (4%) (Bouvier-Brown *et al.*, 2012), broadleaf temperate forest (4.9%) (Seco *et al.*, 2015) and *L. Kaempferi* forest (0.9%) (Mochizuki *et al.*, 2014).

### 3.3 Concentrations and fluxes of isoprene oxidation products

Initial isoprene oxidation products, MACR and MVK, were detected in the atmosphere of the pine-oak forest. Figure 1c shows vertical profiles of the MACR+MVK concentrations. The MACR+MVK concentrations below the *P. densiflora* canopy were comparable to those above the canopy. A slightly lower concentration was observed at the height of the canopy. In a laboratory experiment, Tani *et al.* (2010) showed that gaseous MACR and MVK were absorbed by broadleaf tree leaves. However, absorption of MACR and MVK by coniferous trees including *P. densiflora* has not been reported.

The MACR+MVK concentration (average: 2 – 17 m) was the lowest during the early morning and increased until the afternoon (Figure 2c). It was highest during the early or late afternoon, consistent with or delayed by a few hours beyond the time when a peak isoprene concentration was observed. The MACR+MVK concentration showed a positive correlation with isoprene concentration ($r^2 = 0.29$) (Figure 7a). In addition, we found that such diurnal and temporal trends of MACR+MVK concentrations were similar to those of the O$_3$ concentrations (Figures 2c and 2d). Isoprene mainly reacts with O$_3$ and OH radicals during the day. Because we measured only O$_3$ of the two reactants, the O$_3$ concentration was used here as an indicator of the oxidant concentrations. The MACR+MVK concentration showed a significant correlation with the O$_3$ concentration ($r^2 = 0.51$) (Figure 7b). The forest site is located a few kilometers southwest of Fujiyoshida city and 80 kilometers west-southwest of the Tokyo metropolitan area. According to air mass back trajectories, all the air masses arriving at the forest site during the measurement period were not affected by the outflows of the metropolitan area (data not shown), suggesting that the majority of the sampled air was not influenced by urban air masses. As a result, the range of O$_3$ concentrations did not largely differ even though the local wind direction differed daily. O$_3$ seems to be locally produced via photochemical reaction near and in the forest area. Our results suggest that oxidant concentrations are important in the formation of MACR+MVK from isoprene within the forest.

Both the positive and negative values for MACR+MVK flux (range: -0.88 – 2.3 nmol m$^{-2}$ s$^{-1}$) were observed during the measurement period (Figure 2c). The average flux of MACR+MVK was calculated to be 0.23 ± 0.61 nmol m$^{-2}$ s$^{-1}$ and its median was 0.12 nmol m$^{-2}$ s$^{-1}$ (first quartile: -0.26 nmol m$^{-2}$ s$^{-1}$, third quartile: 0.64 nmol m$^{-2}$ s$^{-1}$). Large positive MACR+MVK fluxes (> 1.1 nmol m$^{-2}$ s$^{-1}$) were observed from 12:30 to 14:30 on the 24th and at 11:30 on the 25th and 30th of August. They were observed under a relatively high temperature, O$_3$ concentration, and isoprene flux (Figures 2d and 2e), meaning that MACR and MVK might have been more frequently produced by the reaction with reactive species including O$_3$ at a higher temperature (Atkinson and Arey, 2003). The positive fluxes mean that the MACR+MVK formation and transport rates above the canopy were higher than the MACR+MVK deposition rate in the forest.

However, small negative MACR+MVK fluxes were often observed during the measurement period. The negative values mean that the deposition rate of MACR+MVK in the forest was higher than the MACR+MVK formation and transport rates above the canopy. There are mixed forests consisting of isoprene-emitting deciduous broad-leaf trees near the site. The wind direction during daytime was from the east, south, and west (Figure 2f), indicating an inflow of air masses from the surrounding forested area in these directions. The MACR+MVK derived from isoprene emitted from the surrounding forests might have been transported and deposited in the pine-oak forest.

For field measurements, a small positive MACR+MVK flux was observed in an isoprene-emitting Mediterranean oak forest (0.12 nmol m$^{-2}$ s$^{-1}$) (Kalogridis *et al.*, 2014). However, Karl *et al.* (2010) reported that MACR+MVK typically deposited on a tropical rain forest. Forests including isoprene-emitting trees can be a source of MACR+MVK and its formation within the canopy and transport above the canopy may offset deposition in the forest. This may be different for different forest types and environments.

In the present study, the MACR+MVK flux did not correlate with either temperature ($r^2 = 0.08$) (see supplementary file: Figure S1a), PPFD ($r^2 = 0.04$) (Figure S1b), or O$_3$ concentration ($r^2 = 0.01$) (Figure S1c). The MACR+MVK flux showed a positive correlation with isoprene flux ($r^2 = 0.28$, $p < 0.01$) (Figure S1d), suggesting that a high isoprene flux contributes to a positive MACR+MVK flux within the forest. Comparison of change in storage of O$_3$ and MACR+MVK within the forest might give more detailed information regarding isoprene oxidation by
O₃, but we did not measure the profile of O₃ concentration within the forest. It is likely that the MACR+MVK flux above the forest canopy may depend on a variety of parameters including micro-meteorology and plant activity.

Our results suggest that, to investigate the sink and source dynamics of MACR+MVK within and above the forest, it is necessary to separately estimate 1) the MACR+MVK production rate, which depends on the isoprene emission rate of isoprene-emitting species within the forest, O₃ concentration, and temperature, and 2) its deposition rate in the forest, which is controlled by its concentration and micrometeorological factors. It is also important to consider the presence of isoprene-emitting species both in the target and surrounding forests. Because few reports are available regarding the MACR+MVK flux above a forest, more in-depth studies are needed to better understand the net flux of isoprene oxidation products within a forest.

4. Conclusions

We conducted atmospheric measurements of vertical concentrations and above-canopy fluxes of isoprene, initial isoprene oxidation products (MACR and MVK), and monoterpenes in a pine-oak forest during summer. The monoterpenes concentrations were highest near the forest floor and the isoprene concentration was the highest at the height of the Quercus trees. Upward monoterpenes and isoprene fluxes were observed. The monoterpenes flux showed a positive correlation with ambient air temperature. Positive correlations between isoprene flux and ambient air temperature and between isoprene flux and PPFD were observed. The average flux of isoprene during the measurement period (3.1 nmol m⁻² s⁻¹) was 2.6 times higher than that of monoterpenes (1.2 nmol m⁻² s⁻¹). Quercus in the lower layer of the forest can be an important source of isoprene, even though the light intensity was estimated much lower than that of red pine canopy. The average carbon emission ratio in the form of monoterpenes plus isoprene to NEE was calculated to be 0.12%. The MACR+MVK concentrations did not show clear vertical gradient patterns but had a positive correlation with the O₃ concentration. Both upward and downward MACR+MVK fluxes were observed. Large positive MACR+MVK fluxes were observed around noontime or during the afternoon and the flux had a positive correlation with the isoprene flux, suggesting that a high isoprene flux contributes to MACR+MVK production within the forest. However, the flux did not correlate with either temperature, PPFD, or O₃ concentration. Our results suggest that to evaluate the sink and source dynamics of MACR+MVK above a forest, it is necessary to separately estimate both upward MACR+MVK flux, which is caused by transport of MACR+MVK produced by isoprene oxidation within forests, and downward MACR+MVK flux, which is caused by MACR+MVK deposition on the target forest from surrounding forests.

Acknowledgement

We thank Dr. Yuichiro Nakai of the Forestry and Forest Products Research Institute for the courtesy of using the sampling site. This work was supported by JSPS KAKENHI Grant numbers JP2410958, JP17K19312, and JP19H04257.

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Acknowledgement

We thank Dr. Yuichiro Nakai of the Forestry and Forest Products Research Institute for the courtesy of using the sampling site. This work was supported by JSPS KAKENHI Grant numbers JP2410958, JP17K19312, and JP19H04257.

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