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*NOTE*

# Seasonal variation of isoprene basal emission in mature *Quercus crispula* trees under experimental warming of roots and branches

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Isoprene is a reactive volatile organic compound (VOC), the annual global biogenic emissions of which are the largest of the non-methane VOC. Since isoprene emissions are partly temperature-driven, understanding the relationship between isoprene emission and climate must be improved. Isoprene emission was measured in *Quercus crispula*, the second-most dominant isoprene-emitting tree species in Japan. Four mature *Q. crispula* trees were exposed to artificial warming of their roots and branches at approximately 5°C warmer than ambient temperatures. Four un-warmed control trees were also measured and compared for their emissions over the course of five months. Basal emission rates of isoprene (defined as a normalized emission rate under standard light and temperature conditions) was calculated and compared between warmed and control branches. The basal emission rates varied from 0.17 to 38.5 nmol $m^{-2}$ $s^{-1}$ (average; 10.4 nmol $m^{-2}$ $s^{-1}$) over the seasons. However, the basal emission rate did not significantly differ between warmed and control leaves.

Keywords: isoprene, biogenic volatile emission, *Quercus crispula*, experimental warming

## Introduction

Isoprene is the dominant non-methane biogenic volatile organic compound (BVOC), emitted globally each year, mainly from terrestrial among vascular plants. It is known to have an important role in atmospheric chemistry due to its high reactivity (Guenther *et al*., 2006). Because isoprene is highly reactive and has a limited atmospheric lifetime, information on its regional emission is very important. *Quercus crispula* is the second-most dominant isoprene emitting tree in Japan following *Quercus serrata* (National Survey on the Natural Environment, 1996), though there are few reports describing its emission characteristics (Bao *et al*., 2008; Tani and Kawawata, 2008). The emission of isoprene from plants is described by emission models such as the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther *et al*., 2006) which models the effects of changing phenological and environmental variables on isoprene and other BVOC given species-specific basal emission rates. The isoprene basal emission rate is defined as a constant emission factor representing the capacity of a given plant species to emit isoprene under standard environmental conditions (30°C, 1000 $\mu$mol $m^{-2}$ $s^{-1}$ of photosynthetic photon flux density (PPFD)). It is known that the basal emission rate of isoprene can be altered by the physiology of the plant, growth stage of leaves, etc. (Monson *et al*., 1994; Xiaoshan *et al*., 2000).

Previous experimental studies have shown that isoprene basal emissions generally increase with increasing temperatures (e.g., Pétron *et al*., 2001). This temperature response has also been analyzed by comparing emission rates across different seasons (after accounting for differences in light and temperature) (e.g., Monson *et al*., 1994) or by using potted plants exposed to different temperatures in greenhouses (e.g., Pétron *et al*., 2001). To our knowledge, no experiments have been performed to date in the mature oak canopies of Japan despite the fact that oaks are the dominant isoprene-emitting trees in Ja-

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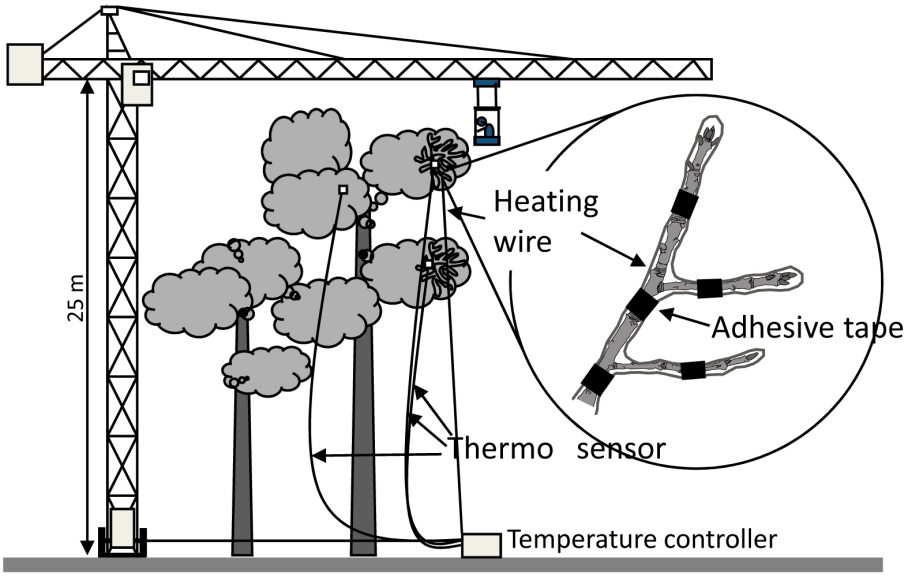


*Fig. 1. A overview of the construction crane used for the experiment and heating treatment using the wire heater on branch.*

pan. Nakamura *et al*. (2010) investigated the effect of warming on physiology of *Q*. *crispula* mature trees by putting wire heaters onto some branches and also into soil around the roots. The heaters were calibrated to maintain branch and root temperatures ~5°C higher than ambient conditions. The root/branch warming treatment was found to cause certain physiological effects in the *Q*. *crispula* trees (e.g., increase acorn production). Considering the physiological changes observed in the trees, the basal emission of isoprene was also expected to be altered by the continuously-raised temperatures. We investigated, for the first time, the isoprene basal emission rate of mature, experimentally-warmed *Q*. *crispula* trees throughout the growing season.

## Experiment

*Site description*

Tomakomai Experimental Forest, has an area of 2715 ha and consists of mature mixed deciduous woodland containing *Q*. *crispula* trees as the most dominant species. Monthly mean ambient temperatures range from minus 3.2 to 19.1°C. Annual precipitation is ~1450 mm (Hiura, 2005). A construction crane, located within the forest at ~42°42′43″ N, 141°33′52″ E has a gondola that enables access to approximately 0.5 ha of forest canopy (the jib length is 41 m at a height of 25 m).

*Experimental warming*

The artificial warming was applied to branches and soil surrounding the roots of four *Q*. *crispula* trees with heights of 18–20 m. Root warming was achieved by burying the wire heaters around the trunk of each tree in a 5 m × 5 m plot, while branch warming was accomplished by winding the heaters around individual branches (see Fig. 1 and Nakamura *et al*., 2010 for detail). One branch at the top of canopy and one branch at approximately 7 m below the canopy of three root-warming individuals were exposed to the warming. Branch warming was limited to branches of trees that were also experiencing the root-warming treatments. The branch warming and soil warming were continued from 1st December 2009 and 15th June 2007, respectively.

Soil and branch temperatures were controlled to be at approximately 5°C higher than the ambient temperatures using thermal sensors coupled with the controller at the site. Detailed definitions of terms used in this report are described in Appendix Table 1.

*Isoprene measurement*

Isoprene emission rate was measured from 8 trees in total during each sampling period. The emission was measured for four branches at the canopy top of four control trees (CC-u). Isoprene emissions from leaves in four branch classes on the four soil-warmed trees were also measured. The four classes were: branches without (CW) and with branch-warming (WW) at the upper (CW-u, WW-u) and lower (CW-l, WW-l) canopy heights so that each branch class contained four replicates. Isoprene emissions were measured by collecting air samples from a sample chamber (into which leaves were placed) equipped with a portable photosynthesis monitor (LI6400, LI-COR Bioscience, Lincoln NE, U.S.A.). To avoid potential contributions to measured emissions arising from

VOC present in ambient air, the inlet air supplied to the chamber was purified with an activated charcoal trap to remove VOCs and oxidants such as OH and ozone. Light intensity and leaf temperature in the chamber were controlled to be at 1000 $\mu$mol m$^{-2}$ s$^{-1}$ PPFD and around 20°C (actual temperatures ranged from 19.8 to 24.3°C, average: 20.9°C), respectively. Leaf temperature was measured in the chamber during sampling.

Isoprene in the sample air was collected and concentrated onto 6.35 mm diameter glass tubes filled with 200 mg of Tenax TA (GL Science, Shinjuku, Tokyo, Japan) and 100 mg Carbotrap (SUPELCO, Bellefonte PA, U.S.A.) adsorbents at a flow rate of 200 ml min$^{-1}$ for 10 minutes. Isoprene collected in the sampling tube was desorbed and injected into a gas chromatograph equipped with a flame ionization detector (GC-FID; 6890 Plus GC, Agilent Technologies Inc., Santa Clara CA, U.S.A.) using a thermo-desorption/cryo-focusing system (Chrompack CP4020, Agilent Technologies Inc.). Isoprene identification was qualified by comparing its GC retention time with the authentic standard gas (Takachiho Chemical Industrial Co. Ltd., Shibuya, Tokyo, Japan) and was quantified by comparing the GC peak area with the area obtained by the analysis of the standard gas (with a known concentration). The emission rate was calculated based on the amount of isoprene sampled, a leaf area of 6 $\times 10^{-4}$ m$^{-2}$, the dilution ratio of sampled air flow rate relative to total sampling chamber purge air flow rate, and sampling time and was presented in units of nmol m$^{-2}$ s$^{-1}$.

*Isoprene basal emission rate*

Isoprene emissions are very sensitive to light and temperature. To compare the capacity of a plant to emit isoprene under varying environmental conditions, among individuals, and/or under changing phenological states, a normalized emission rate is defined, which is assumed not to change when environmental conditions such as light and temperature change (although the actual measured emission rate would be expected to change in response to changing environmental conditions). The basal emission rate in the G93 algorithm (Guenther *et al*., 1993) and MEGAN (Guenther *et al*., 2006) is defined to be the emission rate under standard conditions of 1000 $\mu$mol m$^{-2}$ s$^{-1}$ of PPFD and 30°C leaf temperature. Because light intensity in the sampling chamber was controlled at 1000 $\mu$mol m$^{-2}$ s$^{-1}$ ($C_L$ = 1 in Eq. (1), below), only the temperature effect ($C_T$, from Eq. (2), below) was considered in the calculation of the basal emission rate. Actual leaf temperature varied from 19.8°C to 24.3°C due to the variation of temperature outside the sampling chamber. The basal emission rate was calculated by dividing the measured emission rate by $C_T$ calculated from Eq. (2) (below).

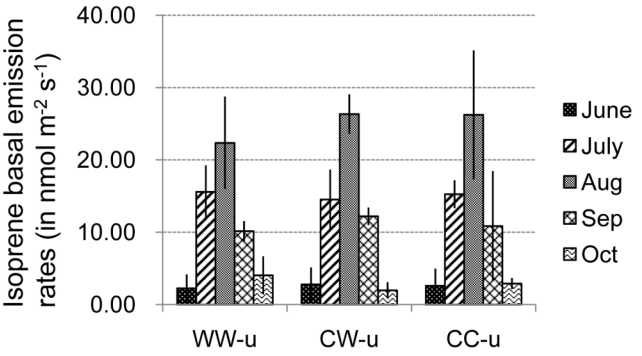


*Fig. 2. Seasonal variations in the averaged isoprene basal emission measured at upper branches for the control trees (CC-u) without any warming treatment (CW-u) and warmed trees (WW-u). Vertical bars present standard deviation of the basal emission among individuals.*

$$E = E_S C_L C_T \tag{1}$$

$$C_T = \frac{\dfrac{\exp\{C_{T1}(T - T_S)\}}{RT_S T}}{C_{T3} + \dfrac{\exp\{C_{T2}(T - T_M)\}}{RT_S T}} \tag{2}$$

where, $E$ and $E_S$ are the measured (actual) and basal emission rates of isoprene, respectively. $C_{T1}$, $C_{T2}$, $C_{T3}$, and $T_M$ are empirical coefficients = 95000 J mol$^{-1}$, 230000 J mol$^{-1}$, 0.961 (dimensionless), and 314 K, respectively.

The isoprene basal emission rate was calculated using Eq. (2) along with leaf temperature data collected during sampling, while the actual isoprene emission rate was measured from the chamber.

## Results and Discussion

*Differences in isoprene basal emission among different individuals and branch levels in the canopy*

The basal emission rates of isoprene collected from the 5 branch classes (WW-u, CW-u, WW-l, CW-l and CC-u) were compared among 4 individuals in each class. The coefficient of variation (CV) of the basal emission among individuals was 0.45 on average. On the other hand, CV of the basal emission over the seasons (5 months) was 0.87 in average. Therefore, we concluded that the difference of the basal emission among individuals is less important than the seasonal variation. Consistent with previously reported suggestions that isoprene emission is associated with heat tolerance (Darbah *et al*., 2010), the basal emission rates for branches on the canopy top were

generally higher (21–88%) than those of lower branches over the sampling periods (see Appendix Table 2).

*Effect of experimental warming on the isoprene basal emission rate*

*P* values from Student's *t*-test were calculated for each month to evaluate the effect of warming treatment on isoprene basal emission rate (see Appendix Table 3). The *P* values were compared for the basal emission rate between leaves from branches at a given branch height with and without warming treatment (e.g., CW-u vs. WW-u). Suggesting that the warming treatment did not significantly change the basal emission, most of the *P* values were larger than 0.05. As a result, the isoprene basal emission rate, which represents isoprene production capacity, did not significantly change with branch and soil warming.

*Seasonal variation of the isoprene basal emission rate*

As shown in Fig. 2, the isoprene basal emission exhibited a clear seasonal variation. Current typical BVOC emission models (e.g., MEGAN: Guenther *et al*., 2006) simulate seasonal changes in emission capacities through indicators of changing leaf biomass such as monthly-varying leaf area index (LAI) datasets. However, if LAI is not changing significantly month to month (i.e., as in the case with trees that retain leaves year-round or in areas where satellite-derived LAI datasets may not be reliable), there could be a significant overestimate during months when basal emission rates are lower (e.g., June, October), if isoprene emission rate is simulated using a constant basal emission capacity. The isoprene emission rate is estimated to be up to 61% higher in total with the constant basal emission rate. Because deciduous trees are important emission sources of isoprene, the seasonal variation in the isoprene basal emission should be considered to improve the emission model.

## Conclusion

The basal emission rate of isoprene did not show any significant change under 5°C of root and branch warming. Isoprene emission rates were measured from leaves of mature *Q. crispula* trees over five months. Isoprene basal emission rates, which represent isoprene production capacity of leaves, showed a clear seasonal variation.

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## Appendix

(see p. 167)

*Appendix Table 1. Detailed definitions of termes used in this report*

| | |
|---|---|
| Leaf temperature | Measured temperature of leaf in the sample chamber during isoprene sampling using a thermocouple equipped in the sample chamber. |
| Isoprene emission | Measured emission rate of isoprene at unit leaf area per unit time. |
| Isoprene basal emission | A normalized emission rate of isoprene calculated based on G93 algorithm under standard light and temperature conditions. |

*Appendix Table 2. Averages and standard deviations (SD) for isoprene emission rates of four mature Q. crispula trees measured and isoprene basal emission rate calculated based on G93 algorithm (in nmol $m^{-2}$ $s^{-1}$). Left three columns indicate warming treatment and level of the branches*

| Root warming | Branch level | Branch warming | | June 17–18 June, 2010 | | July 15–16 July, 2010 | | August 19–20 August, 2010 | | September 22–23 September, 2010 | | October 12–13 October, 2010 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Measured emission | Basal emission | Measured emission | Basal emission | Measured emission | Basal emission | Measured emission | Basal emission | Measured emission | Basal Emission |
| Control | Upper | Control | Average | 1.4 | 4.7 | 8.0 | 29.5 | 9.3 | 26.3 | 3.1 | 10.9 | 0.8 | 2.9 |
| Control | Upper | Control | SD | 1.3 | 4.4 | 1.0 | 3.7 | 3.2 | 8.9 | 2.2 | 7.6 | 0.2 | 0.8 |
| Warmed | Upper | Control | Average | 1.5 | 4.8 | 7.7 | 28.2 | 10.5 | 26.8 | 3.6 | 12.2 | 0.7 | 2.0 |
| Warmed | Upper | Control | SD | 1.2 | 3.7 | 2.2 | 8.3 | 2.4 | 2.8 | 0.3 | 1.2 | 0.4 | 1.1 |
| Warmed | Upper | Warmed | Average | 1.4 | 4.4 | 8.2 | 30.1 | 8.3 | 22.3 | 3.0 | 10.2 | 1.2 | 4.0 |
| Warmed | Upper | Warmed | SD | 1.4 | 4.4 | 1.9 | 7.3 | 2.1 | 6.3 | 0.4 | 1.4 | 0.8 | 2.6 |
| Warmed | Lower | Control | Average | 1.2 | 3.8 | 6.7 | 24.4 | 6.5 | 18.2 | 2.4 | 7.8 | 0.5 | 1.6 |
| Warmed | Lower | Control | SD | 1.1 | 3.3 | 1.7 | 6.1 | 1.8 | 5.7 | 1.2 | 3.7 | 0.4 | 1.2 |
| Warmed | Lower | Warmed | Average | 0.8 | 2.4 | 5.3 | 19.3 | 5.7 | 15.5 | 2.9 | 10.3 | 0.5 | 1.6 |
| Warmed | Lower | Warmed | SD | 0.4 | 1.3 | 1.6 | 5.6 | 1.3 | 3.0 | 1.2 | 4.6 | 0.3 | 1.0 |

*SD: Standard deviation of the isoprene basal emission among four individuals.*

*Appendix Table 3. P values calculated using Student's t-test for isoprene basal emission rates obtained from control leaves and leaves with warming treatment*

| Group 1 | | Group 2 | | Level of branch | June | July | Aug. | Sep. | Oct. |
|---|---|---|---|---|---|---|---|---|---|
| Branch | Root | Branch | Root | | | | | | |
| Control | Control | Warmed | Warmed | Upper | 0.43 | 0.45 | 0.30 | 0.43 | 0.20 |
| Control | Control | Control | Warmed | Upper | 0.47 | 0.45 | 0.25 | 0.36 | 0.11 |
| Control | Warmed | Warmed | Warmed | Upper | 0.39 | 0.22 | 0.22 | 0.07 | 0.08 |
| Control | Warmed | Warmed | Warmed | Lower | 0.26 | 0.20 | 0.15 | 0.02 | 0.44 |

*Tests have been conducted for isoprene basal emission rates obtained from leaves of four individuals in each group (e.g., CC vs. WW, see Subsection "Isoprene measurement" in text for definition of abbreviation).*