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EXPRESS LETTER

Factors affecting monoterpene emission from *Chamaecyparis obtusa*

TOMOKI MOCHIZUKI,[1] YUKIKO ENDO,[1] SOU MATSUNAGA,[2] JIE CHANG,[3] YING GE,[3]
CHENGAI HUANG[4] and AKIRA TANI[5]*

[1]Graduate School of Nutritional and Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan
[2]JATOP Department, Japan Petroleum Energy Center, 4-3-9 Toranomon, Minato-ku, Tokyo 105-0001, Japan
[3]College of Life Sciences, Zhejiang University, Hangzhou 310058, P.R. China
[4]Shaoxing University, Shaoxing 312000, P.R. China
[5]Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

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Monoterpenes are major compounds emitted by plants and contribute to the formation of photochemical oxidants and secondary organic aerosols in the troposphere. We measured monoterpene emissions from *Chamaecyparis obtusa*, a major coniferous tree species in Japan, in both the field and the laboratory. Short-term monoterpene emission from *C. obtusa* was typically dependent on temperature but barely dependent on light intensity. We calculated the basal emission rate E_s assuming $\beta = 0.09$ in the G93 model. Three individual trees showed similar, but large seasonal variations in E_s; e.g., 0.21–5.42 μg $g_{DW}^{-1}h^{-1}$ for a tree showing the highest emission rate. The emission rate was much higher in winter and autumn. Although E_s values averaged over 4 seasons indicated that *C. obtusa* is an intermediate emitter among coniferous trees, our results suggest that the large seasonal variation in E_s should be considered in estimating annual monoterpene emission from this species. Furthermore, we found a significant effect of branch-to-branch touching by vibration on monoterpene emission from this species, suggesting that wind effect should be considered in the future for more precise emission estimation.

Keywords: biogenic emission, seasonal variation, vibration, leaf temperature, light intensity

INTRODUCTION

Biogenic volatile organic compounds (BVOCs) include terpenoids (e.g., isoprene, monoterpenes, and sesquiterpenes), hexenal family compounds (hexenals, hexenols, and hexenyl esters), methanol, and acetone, and vegetation is the primary source of BVOCs. The annual global emission of BVOCs was estimated to range from 0.5 to 1.2 Pg C (Guenther *et al*., 1995), which is higher than that of anthropogenic VOC (AVOCs) (Singh and Zimmerman, 1992). In particular, terpenoids such as isoprene and monoterpenes emitted from vegetation are dominant.

Because of the higher atmospheric reactivity of terpenoids with OH radicals, O_3, and NO_3 radicals, the lifetimes of terpenoids are shorter than those of most AVOCs (Atkinson and Arey, 2003). These BVOCs contribute to the formation of photochemical oxidants in the troposphere (Guenther *et al*., 1995) and can adversely affect air quality. Terpenoids are also involved in the formation of particulate matter that is a precursor of aerosols in reactions with the ozone and OH radicals (Yokouchi and Ambe, 1985; Claeys *et al*., 2004). Yokouchi and Ambe (1985) reported that monoterpenes were oxidized in the atmosphere to produce pinonaldehyde and pinonic acid. Claeys *et al*. (2004) reported that the isoprene was oxidized in the atmosphere to form polyols. These compounds seem to be precursors of secondary organic aerosols (SOA). SOA may scatter light from the sun and, through reactions in the atmosphere, become the condensation nucleus of the cloud, somewhat inhibiting global warming (IPCC, 2007).

In areas or countries over which large portions are covered with BVOC emission sources, the emission may significantly cause production of photochemical pollutants and SOA, suggesting the importance of BVOC emission inventory over these regions. Therefore, it is necessary to obtain BVOC emission data for major tree species.

There is no BVOC emission inventory over Japan, although forests cover about 70% of the country. Only BVOC emission inventory for a local area of Japan, the

*Corresponding author (e-mail: atani@u-shizuoka-ken.ac.jp)

Kinki region, is available (Bao *et al*., 2008). The main coniferous tree species in Japan include *Cryptomeria japonica* (21% of the total vegetation area), *Chamaecyparis obtusa* (12%), and *Pinus densiflora* (8%). Major broad leaved trees include *Q. serrata* (14%), *Fagus crenata* (5%), and *Betula* sp. (3%). BVOC emission rates of *C. japonica* (Matsunaga *et al*., 2011), *P. densiflora* (Tani *et al*., 2002), and *Q. serrata* (Tani and Kawawata, 2008; Okumura *et al*., 2008) have been reported so far, but not yet for the other species including *C. obtusa*.

C. obtusa is endemic to Japan, but its variant *C. obtusa* var. *formosana* occurs in Taipei. Other tree species in *Chamaecyparis* spp. widely occur in East Asia and North America (e.g., *C. thyoides* and *C. lawsoniana*). BVOC emission data of *C. obtusa* can be used to estimate BVOC emission rates of these similar species and to establish a BVOC inventory for East Asia.

In the present study, we measured BVOC emission rates of *C. obtusa* over 4 seasons in the field and clarified that the normalized monoterpene emission rate was highest in winter and quite different between seasons. Furthermore, we investigated the effects of light and vibration on monoterpene emissions in laboratory experiments because these 2 stimuli were ubiquitous in natural conditions, and some reports showed their involvement in monoterpene emissions from other tree species (Yokouchi and Ambe, 1984; Yatagai *et al*., 1995).

Material and Method

Sampling of volatiles from C. obtusa at Tanashi

Monoterpenes were collected from *C. obtusa* at the Tanashi Experimental Station of University forests of The University of Tokyo (35°44′21″ N, 139°32′18″ E). The sample collections were conducted over 4 seasons (winter, 28–29 January; spring, 22–23 April; summer, 6–7 August; and autumn, 10 November 2009). Three individual *C. obtusa* trees (Hinoki I, Hinoki II, and Hinoki III hereafter) were used for the measurements. The trees were about 15 m high with a breast-height diameter of 0.2 m. To access branches at the canopy top, we built a 13-m-high tower between trees. Branches for the gas sampling were selected from the secondary branches. During the measurement periods, the weather conditions were sunny or cloudy.

The branch enclosure method was employed for the gas sampling, and the selected branches were individually enclosed in transparent 30 L PFA bags. Air purified by passing through activated charcoal was sent to the bag at a flow rate of 4 L min^{-1}. Using blank measurements, we verified that the purified air contained no monoterpenes. The flow rate was adjusted by a mass flow controller (SEC-E40, HORIBA STEC, Japan). The air was flowed out of 20 holes (3 mm diameter) made on a Teflon tubing ring to mix the inside air well (Matsunaga *et al*., 2011). Leaf temperature and photosynthetic photon flux density (*PPFD*) were measured by thin thermocouples and semiconductor light sensors (S1133, Hamamatsu Photonics, Japan) and were recorded every minute using a data logger (CR1000 Campbell Scientific Inc.).

Humidity in the bag was not monitored, but no water condensation was observed during the period of the measurements. To trap monoterpenes, stainless steel tubes (6.35 mm o.d.) filled with 200 mg Tenax TA (GL Science, Japan) and 100 mg Carbotrap (Supelco, USA) were used. The air inside the bag was collected at least 12 h after completion of the branch enclosures. The volatiles inside the bag were collected into the adsorbent tubes at a flow rate of 200 mL min^{-1} for 10 min using a portable pump (MP-Σ30, Shibata Inc., Japan). The sampling was conducted every 30 min during the daytime. The branches used for the measurement were excised and dried at 65°C for 72 h to weigh dry mass for obtaining the emission rates per unit dry weight. Therefore, different branches were chosen from 3 individuals every season.

Investigation of light dependency of the monoterpene emission

C. obtusa branches were obtained from 4 individuals (approximately 10 m high) grown in the Nihondaira mountains of the Shizuoka prefecture, Japan. The branches were cut off and immediately put into water-filled bottles during transport to the laboratory.

The leaf cuvette method using a portable photosynthesis measurement system (LI-6400XT, Li-Cor Inc, USA) was employed for the volatile sampling (Tani and Kawawata, 2008). The cuvette measures abaxial leaf temperature using thin thermocouples and can control it with its built-in Peltier heat exchanger. The measurement was conducted under *PPFD* of 1000, 100, and 0 μmol $m^{-2}s^{-1}$ at a 30°C leaf temperature. The CO_2 concentration in the cuvette was maintained at 400 ppm and the inflow rate to the cuvette was 750 ml min^{-1}. Monoterpenes were collected into the adsorbent tubes at 200 mL min^{-1} for 50 min. Blank measurement before and after the sampling was also conducted to confirm no target monoterpene emission from the cuvette materials and no re-emission of adsorbed monoterpenes. The sampling was initiated after the photosynthetic rate became almost constant.

Vibration experiment

To estimate the effect of wind stimulus on terpenoid emissions, *C. obtusa* sapling branches (3 years old) were manually vibrated for several ten seconds and terpenoid emissions were monitored with a proton transfer reaction mass spectrometer (PTR-MS, Ionicon GmbH, Austria). For comparison, another coniferous *C. japonica* (3 years old) and an herb *Melissa officinalis* were also used. The

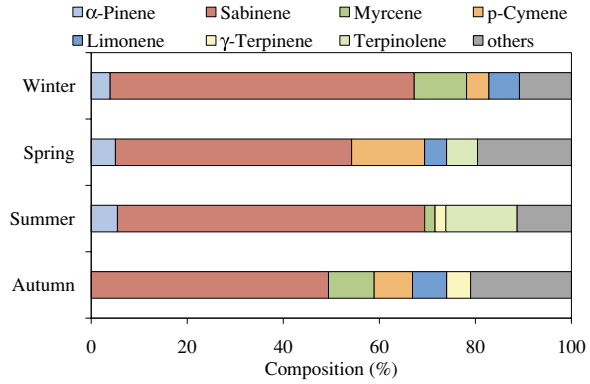

Fig. 1. Composition of monoterpenes emitted from Chamaecyparis obtusa across 4 seasons (Hinoki I).

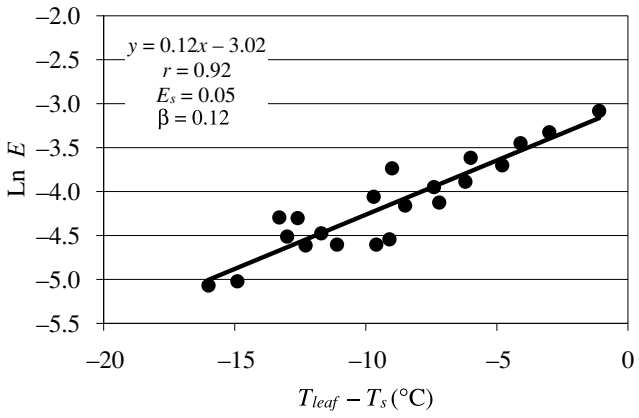

Fig. 2. Influence of leaf temperature on monoterpene emission rate of Chamaecyparis obtusa. The spring data of tree II is shown. E_s: the basal emission rate at the standard temperature T_s (30 °C). B: empirical coefficient. r: correlation coefficient.

measurement system was described in detail in our previous paper (Tani *et al*., 2007). An attached branch of the plants, of which the projected leaf area was 200–400 cm^2, was enclosed in a transparent PFA bag (40 L volume). The open side of the bag was tightly closed with a cable tie and the enclosed volume was less than 20 L. Ambient air was purified using a platinum catalyst heated to 400°C and then sent to the bag at a flow rate of 5 L min^{-1}. The inside air was introduced to the PTR-MS at a flow rate of 200 mL min^{-1}. The sample transfer line between the PTR-MS and the enclosure bag was heated at 80°C to prevent condensation of the water vapor and VOC adsorption onto the inner surface of the line. Four branches from different saplings were individually used for the measurement. They were swung manually by vibration of the branch base. The leaf top was swung within a 30-cm-wide at a frequency of 0.5 Hz for 10–60 s.

GC-MS analysis

Monoterpenes were identified and quantified with a gas chromatography mass spectrometer (GC-MS) (QP5050A, Shimadzu, Japan) equipped with a thermal desorption system (Turbo Matrix ATD, Perkin Elmer Instruments, USA). Details of the thermal desorption and GC-MS analysis were described previously (Tani *et al*., 2002; Tani and Kawawata, 2008).

PTR-MS analysis

The ratio of *E/N* in the drift tube of the PTR-MS instrument (where *E* is the electric field strength and *N* the buffer gas number density in the drift tube) was kept at 127 Td by maintaining the drift tube voltage, temperature, and pressure at 550 V, 40°C, and 1.95 mbar, respectively. Masses 81 and 137 and mass 155 were measured for estimating concentrations of total monoterpenes and oxygenated monoterpenes $C_{15}H_{18}O$, respectively (Tani *et al*., 2003).

Calculation of emission rates

The monoterpene emission rate E (μg $g_{DW}^{-1}h^{-1}$) was calculated from

$$E = \frac{C_s \times V_{in}}{DW} \quad (1)$$

where C_s is the monoterpene mixing ratio in the bag (μg mol^{-1}), V_{in} is the flow rate (mol h^{-1}), and DW is the dry leaf matter (g).

The equation presented by Guenther *et al*. (1993), the so-called G93 model, was used for normalizing the emission rate

$$E = E_s \exp\left\{\beta\left(T_{Leaf} - T_s\right)\right\} \quad (2)$$

where E is the monoterpene emission rate (μg $g_{DW}^{-1}h^{-1}$), E_s is the basal emission rate at the standard temperature T_s (30°C), T_{Leaf} is the leaf temperature, and β is an empirical coefficient. Equation (2) is modified as shown in Eq. (3)

$$\ln E = \beta\left(T_{Leaf} - T_s\right) + \ln E_s. \quad (3)$$

The coefficient β and basal emission rate E_s can be obtained as the slope and intercept at the *y*-axis of the regression line, respectively.

RESULTS

Monoterpene composition

Monoterpenes identified as compounds emitted from

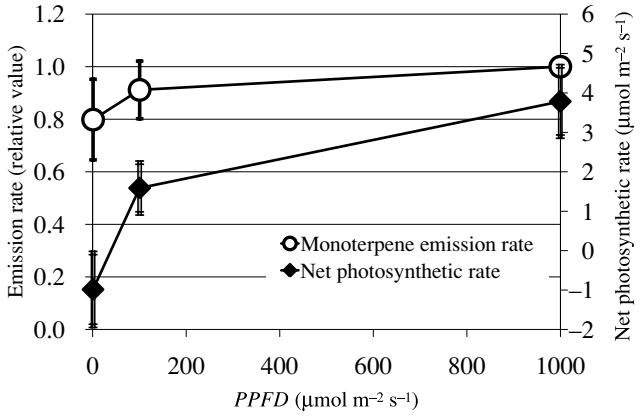

Fig. 3. Influence of light intensity on monoterpene emission rate of Chamaecyparis obtusa. Abaxial leaf temperature was maintained at 30°C. Bars indicate standard deviation (n = 4).

Hinoki I, II, and III included α-thujene, tricyclene, α-pinene, camphene, sabinene, myrcene, β-pinene, α-phellandrene, α-terpinene, *p*-cymene, limonene, β-phellandrene, γ-terpinene, and terpinolene (Fig. 1). Major compounds were sabinene, myrcene, and *p*-cymene, and their composition was similar between the 3 trees. Although the monoterpene composition showed a small seasonal variation, sabinene emission was predominant in all of the trees.

Influence of leaf temperature on monoterpene emission

Monoterpene emission rate *E* and leaf temperature T_{Leaf} of the three *C. obtusa* individuals were low in the morning and late afternoon and had maximum values around noon, suggesting good correlation between them. A similar tendency was observed for the 2 parameters in all seasons.

To investigate effect of leaf temperature on the emission rate *E* of *C. obtusa*, we plotted *E* against leaf temperature (Fig. 2). *E* was found to increase exponentially with leaf temperature in all cases except that for Hinoki III in autumn.

Influence of light intensity on monoterpene emission

We investigated whether the monoterpene emission of *C. obtusa* depended on light intensity under constant temperature conditions. The emission rate *E* was plotted against *PPFD* (Fig. 3). The photosynthetic rate *A* (Fig. 3) and stomatal conductance (data not shown) were deteriorated with a decrease in *PPFD*, but monoterpene emission rate *E* was not greatly deteriorated. *E* in the dark period was four-fifths that in the dark period.

Use of a leaf cuvette can keep the abaxial (bottom) leaf temperature constant. However, because *C. obtusa* leaves are relatively thick (~0.5 mm) and the light-emitting diodes of the cuvette irradiate downward onto the adaxial (upper) leaf surface, leaf temperature of the adaxial surface at high *PPFD* values might have been higher than that of the abaxial surface. This might result in overestimation of the total monoterpene emission at a leaf temperature of 30°C. Accordingly, our results indicate that light barely affects short-term monoterpene emissions of *C. obtusa*.

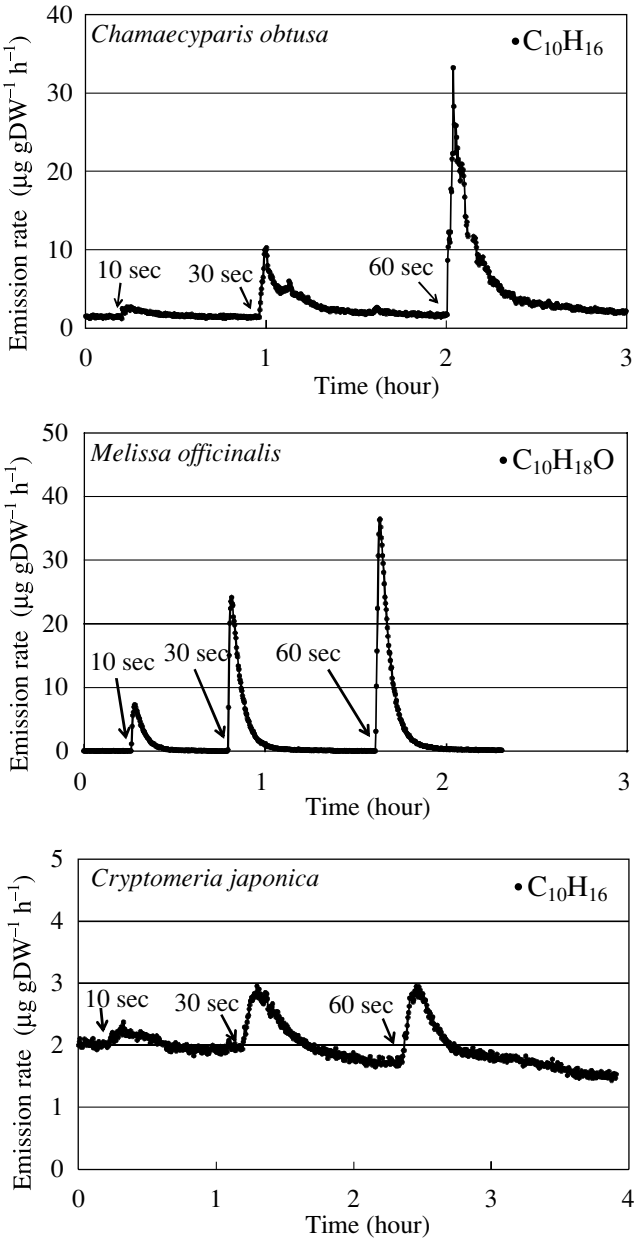

Fig. 4. Monoterpene emission rate from Chamaecyparis obtusa, Cryptomeria japonica, and Melissa officinalis affected by the vibration stimulus. Arrows indicate the time when the vibration stimulus was given for 10, 30 or 60 s.

Table 1. Basal emission rate E_s ($\mu g\ g_{DW}^{-1} h^{-1}$) and coefficient β calculated using the G93 model and the determined $E_{s0.09}$ value assuming $\beta = 0.09$ for the total monoterpene emission rate of Chamaecyparis obtusa

		β	E_s	r	RMS ($\ln E - \ln E'$)	$E_{s0.09}$	RMS ($\ln E - \ln E'_{0.09}$)
Winter	Hinoki I	0.08	4.36	0.79	0.10	5.42	0.11
	Hinoki II	0.11	2.32	0.56	0.36	1.43	0.35
	Hinoki III	0.35	131	0.97	0.14	0.56	0.42
Spring	Hinoki I	0.12	0.26	0.92	0.25	0.21	0.29
	Hinoki II	0.12	0.05	0.92	0.22	0.04	0.28
	Hinoki III	0.07	0.04	0.88	0.17	0.054	0.20
Summer	Hinoki I	0.15	0.22	0.95	0.16	0.21	0.25
	Hinoki II	0.13	0.1	0.88	0.31	0.096	0.32
	Hinoki III	—	—	—	—	—	—
Autumn	Hinoki I	0.16	0.81	0.76	0.31	0.36	0.35
	Hinoki II	0.1	0.35	0.96	0.11	0.33	0.10
	Hinoki III	0.024	0.13	0.21	0.37	0.29	0.42

E': the monoterpene emission rate estimated using the determined β and E_s values for the G93 model.
$E'_{0.09}$: the monoterpene emission rate estimated using the $E_{s0.09}$ value.
r: correlation coefficient.
RSM: root-mean-square error ($\mu g\ g_{DW}^{-1} h^{-1}$).

Influence of vibration on monoterpene emission

The branches of *C. obtusa* and *C. japonica*, and a species of herb *M. officinalis* emitted compounds whose ions produced by the proton-transfer reaction had masses of 81 and 137. They were identified by the GCMS analysis as ions originating from monoterpenes emitted by the former 2 plant species and from oxygenated monoterpenes, citronellal and citral, emitted by the herb. For the herb measurement, the protonated molecular ion with mass 155 originating from these 2 oxygenated monoterpenes was also observed in the PTR-MS analysis, and it showed a similar variation pattern to the ions with masses 81 and 137, which were fragment ions of the 2 oxygenated compounds (Tani *et al.*, 2003).

Soon after *C. obtusa* was vibrated for 10 sec, monoterpene emission increased by 1.5-fold and gradually decreased (Fig. 4). After it was vibrated for 30 sec, the emission increased by 8-fold within 3 min compared with the normal emission rate. The 60-sec vibration raised the emission by 20-fold. Similar results were observed for the 2 other measurements using different *C. obtusa* individuals.

On the other hand, monoterpene emission from *C. japonica* was not strongly stimulated by the vibration. The observed highest emission rate was 1.7 times as much as the normal emission rate. *M. officinalis*, which is known as a species that produces essential oils, was most greatly affected by the stimulus among the 3 species. The emission rate increased 330 times, at most, compared with the normal emission rate.

Basal emission rate

To obtain basal emission rate E_s and coefficient β, $\ln E$ was plotted against $T-T_s$ based on Eq. (3). The values of β and E_s can be obtained as the slope and intercept at the y-axis of the regression line, respectively. Different values of β and E_s were determined for the 4 seasons (Table 1).

The typical β value was 0.09 as suggested by Guenther *et al.* (1993), but β determined in our measurement was higher than 0.09 in most cases. Although β was determined using the least square method, high β values might be caused by small temperature ranges during the campaign periods. In fact, RMS error was not largely different for the determined β (RMS error: 0.23 ± 0.098) and β of 0.09 (RMS error: 0.28 ± 0.11). Therefore, the E_s values calculated assuming $\beta = 0.09$ for all the seasons were used for comparison of seasonal variation in E_s.

The E_s values of the 3 trees were highest in the winter followed by autumn and summer. Large differences in E_s, 10 times at most, were observed between trees, suggesting a large tree-to-tree difference.

DISCUSSION

The monoterpene composition of volatiles emitted

from *C. obtusa* leaves observed in the present study was similar to that in the leaf essential oils of this species (e.g., Katoh and Furuno, 2000). Although Kim *et al*. (2005) did not obtain the basal emission rate of monoterpenes emitted from *C. obtusa*, they reported a similar composition of emitted monoterpenes. Many of these monoterpenes are highly reactive with OH radicals, O_3, and NO_3 radicals (Atkinson and Arey, 2003), resulting in shorter lifetimes.

There have been some reports investigating whether short-term monoterpene emission from other coniferous tree species depends on light intensity. Many coniferous tree species including Slash pine (Tingey *et al*., 1980) and Scots pine (Tarvainen *et al*., 2005) were not light dependent. In contrast, *C. obtusa* (Yatagai *et al*., 1995) and *P. densiflora* (Yokouchi and Ambe, 1984) were reported to be light dependent. However, in the articles reporting short-term light-dependent monoterpene emission, chamber air temperature rather than leaf temperature was kept constant. Leaf temperature is commonly raised by high light intensity, and therefore these experiments could not distinguish between light and temperature effects. To date, there have been no reliable reports confirming short-term light-dependent monoterpene emission from coniferous trees. Our experimental results under constant leaf temperature conditions have revealed that short-term monoterpene emission from *C. obtusa* is barely affected by light. It should be noted that long-term light conditions affect the production of photosynthates, and as a result, it may be a long-term controlling factor for monoterpene production and emission. This effect was considered when establishing a process-based model of monoterpene emissions (Schurgers *et al*., 2009).

The vibration stimulus created by swinging branches has not been examined in real time for any tree species. The monoterpene emission rates were greatly accelerated by vibration but the degrees of the emission increase differed between plant species. *M. officinalis* has oil glands on its abaxial leaf surfaces. The swing vibration might directly stimulate these oil glands and force emissions. *C. japonica* was least affected by the vibration, probably as a result of a hidden monoterpene storage organ or resin duct inside the leaves. *C. obtusa* also has no monoterpene storage organ on its leaf surfaces. Resin ducts inside the leaves serve as monoterpene pools. However, emission from the unique-shaped or scale leaves of *C. obtusa* may be more readily accelerated by the vibration than from the spirally arranged, needle-like (0.5–1 cm), and hard leaves of *C. japonica*. Monoterpene emissions from *C. obtusa* and *M. officinalis* seem to linearly increase with vibration stimulus duration in some measurements. However, this tendency was not observed in all cases, and therefore, a more detailed investigation is required.

Although the wind-generated vibration stimulus is possible in field conditions, short-term monoterpene emissions from conifer leaves have been reported to be temperature-dependent (Tingey *et al*., 1980; Guenther *et al*., 1993). Since *C. obtusa* has monoterpene storage organs inside its leaves, monoterpene evaporation from the storage organs seems to increase as leaf temperature increases.

Apart from the effect of wind, we calculated the basal emission rate E_s, assuming $\beta = 0.09$, using the G93 model. The average E_s value over the 4 seasons was 0.82 μg $g_{DW}^{-1}h^{-1}$. The E_s values of other coniferous trees were summarized by Kesselmeier and Staudt (1999). The E_s values of *Cupressaceae* spp., *Taxodiaceae* spp., and *Pinaceae* spp. were 0.1–1.7 μg $g_{DW}^{-1}h^{-1}$, 0–8.5 μg $g_{DW}^{-1}h^{-1}$, and 0.5–6.9 μg $g_{DW}^{-1}h^{-1}$, respectively. The E_s value of *C. obtusa* obtained in this study was in the intermediate range.

Holzinger *et al*. (2006) showed that precipitation can largely enhance the emission from *Pinus ponderosa L.* for several days. In our study, precipitation was recorded 1 day before the spring measurements were taken. No precipitation was recorded within 3 days before measurements were taken in the other seasons. Spring monoterpene emissions were lowest despite the rain. Different E_s values between seasons has been reported for Scots pine (Janson, 1993; Tarvainen *et al*., 2005; Hakola *et al*., 2006; Holzke *et al*., 2006), *Pinus desiflora* (Tani *et al*., 2002) and *C. japonica* (Matsunaga *et al*., 2011). E_s values of Scots pine increased in spring and reached its peak in early summer. It was reported to decrease thereafter (Hakola *et al*., 2006; Holzke *et al*., 2006) or become high again to resist low temperatures (Janson, 1993). For the other monoterpene emitters, E_s was reported to be highest in summer in all cases (e.g., Kim, 2001; Tani *et al*., 2002) except for a report that E_s for *C. japonica* was high in fall and winter and lowest in summer (Matsunaga *et al*., 2011). To explain these seasonal variations in E_s, Steinbrecher *et al*. (2009) proposed the use of a correction factor considering seasonal variation of monoterpene synthesis and emission from storage organs in an emission model.

In this study, seasonal variation in E_s of *C. obtusa* was also observed, and the variation pattern of the 3 individuals was similar to each other. Because of suppressed evaporation of monoterpenes from their pools under low temperature conditions in winter, the monoterpene pools might become larger in the leaves, which would raise their emission potential. In spring, *C. obtusa* goes into the reproductive growth stage. A larger portion of photosynthetic products might be used for the reproductive growth, and a smaller portion is used for biosynthesis of the monoterpenes. In summer, due to high temperatures and dry conditions, the photosynthetic rate is not high and monoterpene evaporation from the pools is forced, which

makes the monoterpene pools smaller. This may be the reason why low E_s values were observed in spring and summer. This was also suggested for *C. japonica* by Matsunaga *et al*. (2011). The different E_s values in different seasons may give a more precise estimate of the annual monoterpene emission rate.

Conclusion

Short-term monoterpene emission from *C. obtusa* was temperature-dependent but barely dependent on light intensity. Three individual trees showed similar but large seasonal variation in the basal emission rate E_s; E_s was much higher in winter and autumn. Although E_s values averaged over 4 seasons indicated that *C. obtusa* is an intermediate emitter among coniferous trees, our result suggests that large seasonal variation in E_s should be considered in estimating annual monoterpene emission from this species. Since *Cupressaceae* spp. is widely distributed over East Asia and North America, the emission data obtained here can be used to develop a BVOC inventory for these regions. In the laboratory experiment, monoterpene emission from *C. obtusa* was accelerated by vibration stimulation, suggesting that the emission rate may be temporarily raised by wind-induced branch-to-branch contact stimulation. Therefore, our results also emphasize that the effect of branch-to-branch touching should be considered in the future for more precise emission estimation.

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