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Biogenic volatile organic compound emission potential of forests and paddy fields in the Kinki region of Japan

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Abstract

The standard biogenic volatile organic compound (BVOC) emissions from 10 Japanese plant species (*Quercus serrata*, *Quercus crispula*, *Fagus crenata*, *Quercus acutissima Carruthers*, *Quercus glauca*, *Quercus myrsinaefolia*, *Cryptomeria japonica*, *Chamaecyparis obtusa*, *Pinus densiflora*, and rice [*Oryza sativa*]) were measured. These species were selected due to their abundance in the estimated domain (47,000 km^2) of the Kinki region. BVOC emission experiments were conducted in a growth chamber where temperature and light intensity can be controlled. Temperature was set at the average summer temperature in Osaka and at 5 °C above average. Light intensity was set at 1000, 335, and 0 $\mu mol\,m^{-2}\,s^{-1}$ during day time. The amount of BVOC emission was high around noon due to the rise of ambient temperature. It was also found that the total emission rates and compositions of BVOC varied significantly among the plant species. *Q. serrata*, *Q. crispula*, *F. crenata*, *Q. acutissima Carruthers*, *Q. glauca*, and *Q. myrsinaefolia* emitted isoprene and showed emission dependence on light intensity and temperature. *C. japonica*, *P. densiflora*, *C. obtusa*, and *O. sativa* emitted monoterpenes and also showed emission dependence on temperature; however, only *C. japonica* and *P. densiflora* showed emission dependence on light intensity. Using BVOC emissions data from 10 plant species and forest data, BVOC emission potential maps were made. The emission of isoprene and monoterpenes from the Kinki region were estimated to be 596 and 54 $ton\,h^{-1}$, respectively. Seasonal and diurnal variations of BVOC emissions potential were also estimated. Of note, though the amount of monoterpenes from *O. sativa* is small, it contributes approximately 5% to the total monoterpene emissions due to the huge land area covered by paddy fields.

Keywords: BVOC; Isoprene; Monoterpene; Forest; Paddy field

1. Introduction

Nowadays it is recognized that biogenic volatile organic compounds (BVOCs) are emitted from plants. Several inventories suggested that the amount of BVOC is more than the anthropogenic volatile organic compounds (VOCs) on the global scale (Zimmerman, 1979; Lamb et al., 1987; Muller, 1992; Guenther et al., 1995). Among various species of BVOC, isoprene and monoterpenes are the abundant BVOC (Zimmerman et al., 1978). BVOCs play an important role in atmospheric chemistry because they can photochemically react with NO_x and enhance the production of ozone in the troposphere (Fehsenfeld, 1992; Rosselle, 1994; Simpson et al., 1995). Isoprene in BVOC is reported to be more reactive than most anthropogenic VOCs (Stockwell and Kuhn, 1998), because it plays an important role due to the generation of oxidant. In addition, it is reported that the increase in average temperature due to global warming (IPCC, 2001) may cause an increase in BVOC emission, and consequently, the photochemical oxidant concentration can rise when more BVOC reacts photochemically with NO_x (Pun et al., 2002; Hanna et al., 2001; Pierce et al., 1998). Therefore, it is important to monitor BVOC emissions in order to correctly assess photochemical oxidant concentrations in the future.

In spite of its adverse effects, there is no clear consensus as to the purpose of BVOC production by vegetation. Various hypotheses suggest that different plant species may

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produce BVOC for different reasons. Sharkey and Singsaas (1995) proposed that isoprene has a thermotolerance function. Ross and Sombrero (1991) have proposed that plants produce BVOC because these emissions protect them from photosynthetic damage. Similarly, Close and McArthur (2002) also reported that the phenolic compounds of plants function as a sunscreen. It has also been suggested that isoprene emission from plants can protect them from ozone exposure by direct quenching of ozone (Loreto et al., 2001b).

More than 70 kinds of BVOC are known to be emitted by plants (Isidorov et al., 1985; Winer et al., 1992); however, only a few kinds of BVOC are emitted by plants in large quantities. Among the BVOC emitted, isoprene is the most abundant—especially by deciduous trees (Guenther et al., 1995; Geron et al., 1995). The other BVOC emitted in significant quantities are monoterpenes, such as α-pinene, β-pinene, and limonene. Although BVOC emissions from various kinds of plants have already been measured in Europe and the USA, only a few of these species can be found in Japan. At present, there are very little data available for the BVOC emitted by plants commonly found in Japan.

Measurements of BVOC from leaves of cut branches have been reported (Isebrands, 1999) in USA, but they may be unreliable because there may be unexpected effects from cutting the sample plants. In this study, the entire plants were placed in a growth chamber to measure their BVOC emissions. Temperature and light intensity were manipulated to simulate the outside environment. The investigations presented in this paper focus on measuring BVOC emissions at standard condition [30 °C, photosynthetic active radiation (PAR): 1000 μmol m^{-2} s^{-1}].

BVOC emission potentials of several regions, such as Eastern US (Xu et al., 2002), Beijing, China (Wang, 2003), and Catalonia, Spain (Parra et al., 2004) have already been mapped. This study intends to estimate BVOC emission potential of the Kinki region in Japan. We measured BVOC emissions from the 10 most dominant plant species in the Kinki region (*Quercus serrata*, *Quercus crispula*, *Fagus crenata*, *Quercus acutissima Carruthers*, *Quercus glauca*, *Quercus myrsinaefolia*, *Cryptomeria japonica*, *Chamaecyparis obtusa*, *Pinus densiflora*, and *Oryza sativa*). This study monitored the 10 most abundant BVOC emitted by these plants (isoprene, α-pinene, β-pinene, myrcene, α-phellandrene, α-terpinene, *p*-cymene, limonene, γ-terpinene, and terpinolene). A forest database including the age, biomass, and species was constructed using data collected from several prefecture offices (Osaka, Kyoto, Shiga, Hyogo, Nara, Mie, Wakayama, Fukui, Tottori, Okayama, Kagawa, and Tokushima) to accurately estimate the BVOC emissions of the Kinki region. BVOC emissions potential maps were created using experimental BVOC emissions data at standard condition from plants and the forest database we constructed.

2. Target region

The estimated region size is 340 km × 220 km (latitude 32°55′N–36°00′N, longitude 134°00′E–136°22′E). The city of Osaka is located at the center of this region and it also includes other mega cities such as Kyoto and Kobe. It is a complex terrain that includes Osaka Bay and mountains (refer to Fig. 1). A wide range of land uses are found in this region. This area is mainly covered by broadleaf woods and Japanese coniferous forests which were forested a few decades ago. The distribution of the species of trees in the target region is shown in Fig. 2. The coniferous trees *C. japonica*, *C. obtusa*, and *P. densiflora* occupy 60.50% of the forest area. The deciduous broadleaf trees occupy 38.20% of the forest area, and the six deciduous broadleaf trees used in this study (*Q. serrata*, *Q. crispula*, *F. crenata*, *Q. acutissima Carruthers*, and *Q. glauca*) occupy 47.68% of the deciduous broadleaf trees. Extensive paddy fields are found in the plains near the Lake Biwa and Awaji Island. The paddy fields occupy

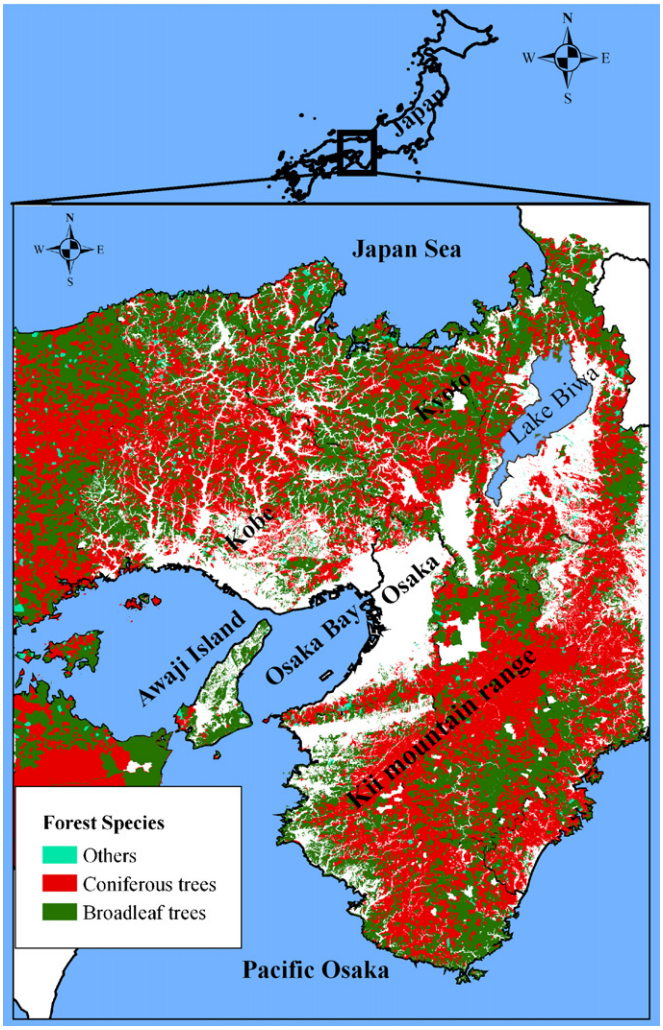

Fig. 1. Estimated domain.

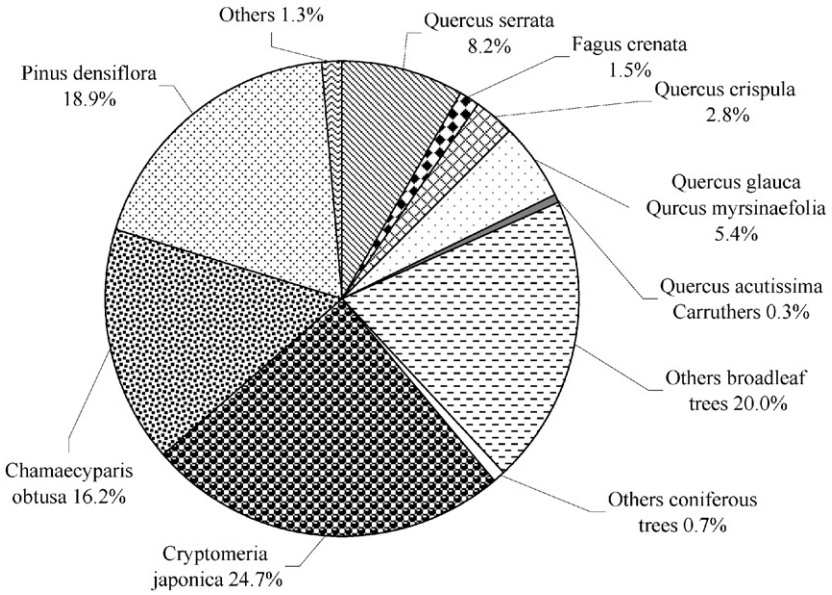

Fig. 2. The distribution percentage of the species of trees.

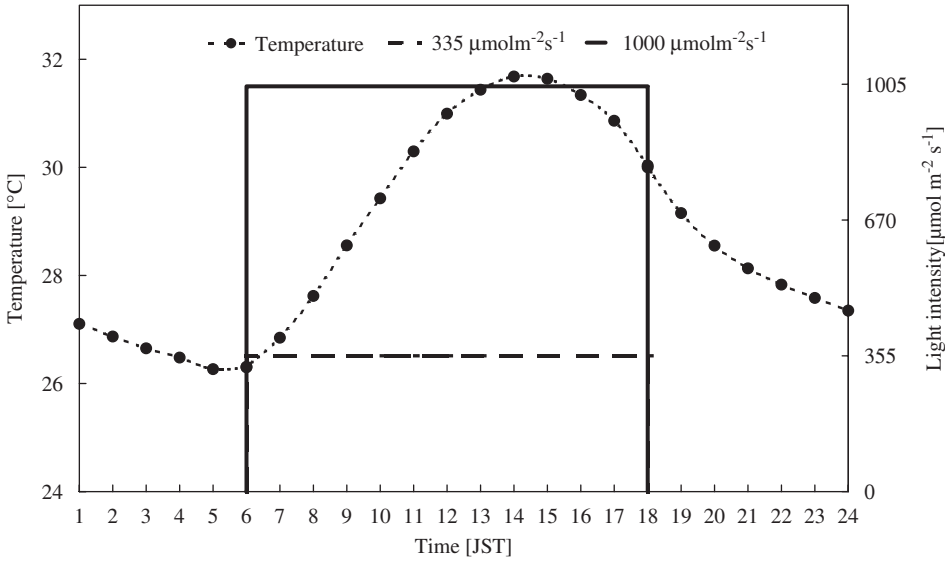

Fig. 3. Diurnal variation of temperature, light was turned on from 6 a.m. to 6 p.m.

12.02% of the target region area. Also, vegetation occupies about 70% of the land considered in the domain under study.

3. Experimental procedure

3.1. Sample preparation

C. japonica, *C. obtusa*, *P. densiflora*, *Q. serrata*, *Q. crispula*, *F. crenata*, *Q. acutissima Carruthers*, *Q. glauca*, and *Q. myrsinaefolia*, the nine most abundant plants in the area, were obtained from commercial nurseries. The plants under investigation were 3- to 5-year-old saplings that were planted in 10-L plastic pots. They were grown in open air and regularly watered and fertilized during the growing season to provide optimal growth conditions. Since a large portion of the area under research is covered by paddy fields, it is also important to measure the BVOC emissions of rice (*O. sativa*). Saplings of *O. sativa* were planted in 10-L plastic pots in spring and grown in open air until autumn.

3.2. Collection of BVOC

Emission measurements were performed by using a growth chamber that can manipulate temperature and light intensity. Ten plants of each species were grown outside and individually transferred 24 h before the experiments to an 8800-L closed growth chamber. Attention was focused on minimizing physical damage to the plants. Plants were then adapted to the following experimental conditions: average temperature of Osaka and PAR was set at 1000 $\mu mol\,m^{-2}\,s^{-1}$ from 6 a.m. to 6 p.m. (Fig. 3).

In order to collect air samples in a growth chamber, a 200 mg Tenax-TA adsorbent tube (Supelco, mesh 60/80) and a vacuum pump (GL Science SP208-1000Dual) with a flow rate of 100 mL min^{-1} were used. For measuring the BVOC emissions from *C. japonica*, *C. obtusa*, *P. densiflora*, and *O. sativa*, air samples of 6 L were collected at every 1 h since the concentration of BVOC from these species are lower than deciduous broadleaf trees (air samples of 1 L). The photon flux density in the photosynthetically active wavelength range was measured using a photometer (LI-1600 LI-COR).

3.3. Analysis of BVOC

The trapped compounds into adsorbent tubes were thermally desorbed at 280 °C by Thermal Desorber (Perkin-Elmer ATD-50) connected to GC/MS (Shimadzu GC/MS-QP2010). The separation of BVOC was performed by a capillary column (30 m × 250 μm × 0.25 μm, J&W Scientific). The carrier gas was helium. The temperature kept 35 °C during 2 min, raised 70 °C with the increase of 20 °C min^{-1}, kept 70 °C during 10 min and raised 280 °C with the increase of 20 min^{-1}. The identification of BVOC was based on the GC peak retention time of reference standards. Samples were analyzed using the selective ion mode (SIM). The calibration factor for BVOC used for calculation of concentrations was checked periodically throughout the analysis.

3.4. Decay experiment of concentrations

The temperature and PAR in a growth chamber were controlled to 30 °C and 335 μmol m^{-2} s^{-1}. The BVOC standard sample of 10 μL was evaporated in a growth chamber and was fully mixed during 10 min. The air samples in a growth chamber were collected at every 30 min during 6 h. The change of concentration is expressed by

$$\frac{dC}{dt} = -\alpha C, \tag{1}$$

where C is concentration, t is time, α is decay coefficient due to decomposition by photolysis, wall deposition and the leak from a growth chamber.

The experimental result of α-pinene is shown in Fig. 4. The decay coefficient of α-pinene can be obtained from the graph slope. The decay coefficients of 10 BVOC are shown in Table 1.

The decay coefficient due to only the leak was determined by the experiment of CO_2 with concentration of 6000 ppm. This experimental result is also shown in Fig. 4. The decay coefficient due to the leak was relatively small and its influence can be ignored. The measured BVOC emissions were corrected by using the decay coefficients.

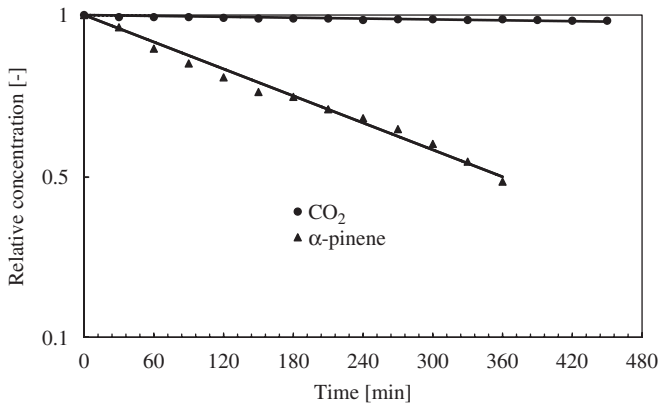

Fig. 4. Decay experiment CO_2 and α-pinene.

Table 1
Decay coefficient of BVOC [s^{-1}]

Isoprene	1.83E−05	α-Terpinene	1.35E−04
α-Pinene	4.97E−05	Limonene	5.83E−05
β-Pinene	3.67E−05	*p*-Cymene	2.17E−05
Myrcene	5.50E−05	γ-Terpinene	1.34E−04
α-Phellandrene	3.15E−04	Terpinolene	1.22E−04

Temperature at 30 ± 1 °C. BVOC initial concentration at 1.14 nL L^{-1}.

Table 2
Dried weight of each plant species

Plant name	Dried weight (g)
Quercus serrata	67.8
Quercus crispula	80.7
Fagus crenata	21.2
Quercus acutissima Carruthers	34.7
Quercus glauca	48.2
Quercus myrsinaefolia	50.5
Cryptomeria japonica	536.7
Chamaecyparis obtusa	178.3
Pinus densiflora	179.2
Oryza sativa	834.6

The leaves were dried for 48 h at 105 °C.

3.5. Leaf biomass of plants

In order to assess the biomass of the enclosed plants, the dry weight of individual leaves was determined after drying the plant materials for 48 h at 105 °C. Table 2 shows the dried weight of the plants used in the experiment. Using the mass of the dry leaves and the experimental data, BVOC emissions rates at standard condition were scaled per gram biomass (μg g_{dw}^{-1} h^{-1}).

4. Treatment of data

4.1. Isoprene emission algorithm

Guenther et al. (1993, 1995) have developed algorithmic expressions allowing a quantification of BVOC emissions from foliar biomass of forest ecosystems and other types of vegetation. E_{iso} (hourly isoprene emission) were estimated by

$$E_{iso} = EF_{iso} \times C_T \times C_L \times FBD \times V, \tag{2}$$

where EF_{iso} is the isoprene emission rate at standard conditions (temperature: 303 K, PAR: 1000 μmol m^{-2} s^{-1}). C_T is the correction factor due to temperature and C_L is the correction factor due to PAR. FBD is the foliar biomass density (g m^{-2}) and V is the seasonal ratio of leaves compared with the maximum value in summer. C_T, C_L are defined by

$$C_T = \frac{\exp(C_{T1}(T - T_s)/RTT_s)}{1 + \exp(C_{T2}(T - T_m)/RT_sT)}, \tag{3}$$

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{(1 + \alpha^2)L^2}}, \tag{4}$$

where α (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 empirical coefficients, L is the PAR flux (μmol m^{-2} s^{-1}), T_s is the standard reference temperature (303 K), R (8.314 J K^{-1} mol^{-1}) is the ideal gas constant, and T (K) is the foliar biomass temperature.

4.2. Monoterpene emission algorithm

While isoprene emissions are coupled to the rate of biosynthesis which is dependent upon temperature and PAR, monoterpenes emissions from coniferous plants are mainly reported to increase exponentially with temperature (Tingey et al., 1980; Juuti et al., 1990; Guenther et al., 1991). The primary monoterpenes identified as emission products from the 10 experimental plants are α-pinene, β-pinene, myrcene, α-phellandrene, α-terpinene, *p*-cymene, limonene, γ-terpinene, and terpinolene.

E_{mono} (hourly monoterpene emissions) are generally described by the following equation as an exponential function of temperature

$$E_{mono} = EF_{mono} \exp(\beta(T - T_s))\mathrm{FBD} \times V, \quad (5)$$

where EF_{mono} is the standard monoterpene emission factor (μg g$_{dw}^{-1}$ h^{-1}) at standard temperature $T_s = 303$ K. β is an empirical coefficient ranging between 0.057 and 0.144 K^{-1}. β can vary according to chemical species and environmental conditions (Owen et al., 1997; Street et al., 1997). 0.09^{-1} is a reasonable estimate for monoterpene emissions of most plants.

Table 3
Density of tree

	ρ_o (g cm^{-3})	BD (kg m^{-3})
Broadleaf trees	0.6	514
Cryptomeria japonica	0.35	319
Chamaecyparis obtusa	0.4	360
Pinus densiflora	0.47	415

ρ_o is oven-dry density (dried at 103 °C). BD is basic density.

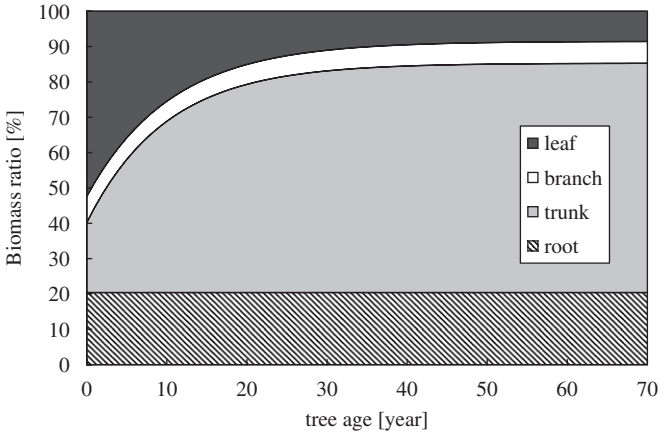

Fig. 5. Ratio of biomass.

5. Calculation of forest leaf biomass

5.1. Forest databases

In order to estimate BVOC emissions, it is needed to determine species distributions and leaf biomass densities. However, previously available land use data from the Environmental Ministry that were used to predict biogenic emission contain inaccurate information about the distribution of vegetation because that data only shows one representative plant species in a mesh (1-km^2 squared cells). Therefore, it has been an aim of this study to create a more accurate forest database for the purpose of estimating reasonable BVOC emissions. With this objective in mind, a new forest database was created. The forest database owned by prefecture offices has more accurate forest data. For example, it has the amount of trees of several species and tree age. But these prefectures do not use the same format, so it is necessary to collect and consolidate these data. The information for all areas within the region

Table 4
Experimental conditions for 10 plants

	Average temperature (1000 μmol m^{-2} s^{-1})	Temperature elevated at 5 °C (1000 μmol m^{-2} s^{-1})	Average temperature (335 μmol m^{-2} s^{-1})	Temperature elevated at 5 °C (335 μmol m^{-2} s^{-1})
Quercus serrata	○	○	○	○
Quercus crispula	–	–	○	–
Fagus crenata	–	–	○	–
Quercus acutissima Carruthers	–	–	○	–
Quercus glauca	–	–	○	–
Quercus myrsinaefolia	–	–	○	–
Cryptomeria japonica	○	○	○	○
Chamaecyparis obtusa	○	○	○	○
Pinus densiflora	○	○	○	○
Oryza sativa	○	○	–	–

'○' Symbol means the experiment was conducted. '–' Symbol means the experiment was not conducted.

was normalized and joined with the use of geographic information systems (GIS) to create one comprehensive map and database.

Table 5
BVOC emissions from coniferous trees at standard condition [30 °C, PAR: 1000 μ mol m^{-2} s^{-1}]

Compound	BVOC emissions (μg g_{dw}^{-1} h^{-1})			
	Cryptomeria japonica	*Chamaecyparis obtusa*	*Pinus densiflora*	*Oryza sativa*
α-Pinene	1.30	1.89	5.33	0.24
β-Pinene	0.06	0.22	0.84	0.02
Myrcene	0.32	0.35	1.79	0.03
α-Phellandrene	0.20	0.13	0.87	ND
α-Terpinene	0.15	0.13	0.23	ND
p-Cymene	0.10	0.28	0.14	0.03
Limonene	0.40	ND	0.82	0.08
γ-Terpinene	0.21	0.49	ND	ND
Terpinolene	0.08	ND	0.27	ND
Total monoterpenes	2.81	3.48	10.28	0.40

All emissions have been normalized at 30 °C using the algorithm by Guenther et al. (1993). ND means not detected.

Table 6
Isoprene emissions from Broadleaf trees at standard condition [30 °C, PAR: 1000 μ mol m^{-2} s^{-1}]

Plants name	Isoprene emission (μg g_{dw}^{-1} h^{-1})
Quercus serrata	224.21
Quercus crispula	26.04
Fagus crenata	0.79
Quercus acutissima Carruthers	0.18
Quercus glauca	0.04
Quercus myrsinaefolia	0.03

All emissions have been normalized at 30 °C using the algorithm by Guenther et al. (1993).

5.2. Forest leaf biomass

By using the forest database, the amount of leaf biomass was calculated. At first, the volume of biomass per unit area (m^3 m^{-2}) taken from the forest database was converted to the weight of biomass per unit area (kg m^{-2}). The density of trees depends on tree species. Table 3 was used for conversion from volume to weight. A basic density (BD (kg m^{-3})) is expressed by

$$\mathrm{BD} = \frac{\rho_o \times 100}{(100 + 28 \times \rho_o) \times 10^3}, \quad (6)$$

where ρ_o (g cm^{-3}) is an oven-dry density (dried at 103 °C).

After getting the data of tree weight, the weight of leaf was calculated. The ratio of leaves to the whole tree is dependent on the species and age. Fig. 5 shows the ratio of leaf, branch, trunk, and root of *C. japonica*. When the tree is young, the ratio of leaves is high, whereas when it is old the ratio becomes significantly lower to around 8%. In contrast, the ratio of trunk is low at a young age and high

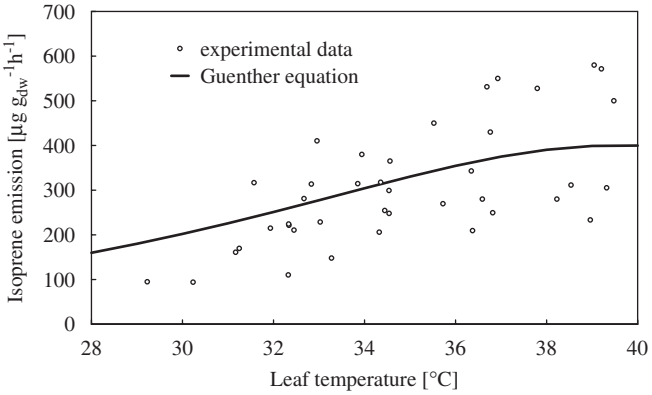

Fig. 7. BVOC emissions and leaf temperature (*Quercus serrata*).

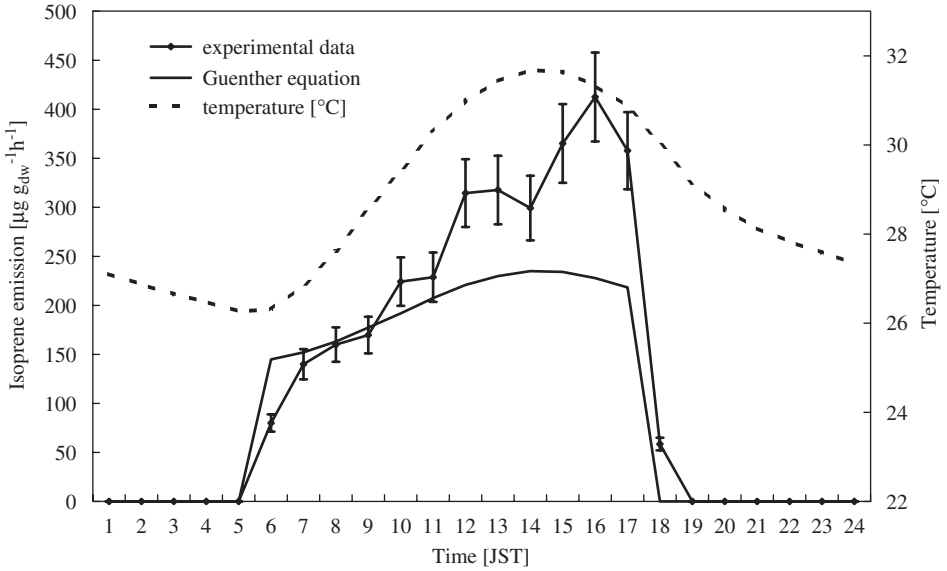

Fig. 6. Diurnal variation of isoprene emission.

when aged. Meanwhile, the ratios of branch and root remain relatively constant during the trees lifespan.

In order to calculate the biomass of *O. sativa*, land use database edited by the Environmental Ministry was used since rice is not categorized as a tree so the forest database does not show the biomass of *O. sativa*. From the land use database, the area of paddy field is provided. The average amount of rice harvest data in the Kinki district ($505\,g\,m^{-2}$) was used for estimating the biomass of rice. Using these data and the rate of rice production (24%; rice production/biomass), its biomass in the Kinki district was estimated. These data were used in the later section to estimate BVOC emissions from the Kinki district.

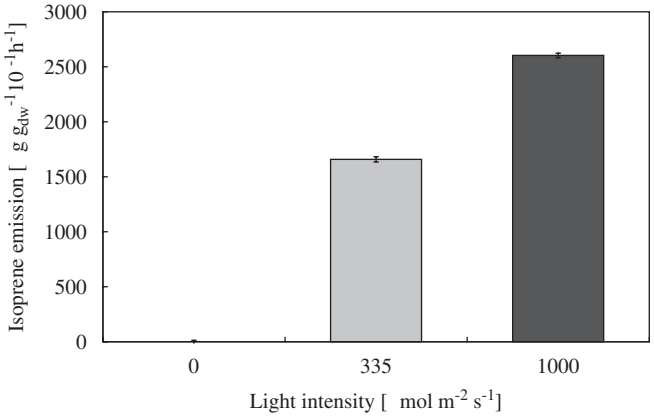

Fig. 8. Isoprene emission from *Quercus serrata* at the light intensity of 0, 335, and $1000\,\mu mol\,m^{-2}\,s^{-1}$.

6. Results and discussion

6.1. Standard BVOC emissions

The experiments conducted at several conditions for 10 plant species are shown in Table 4. As shown in later sections, experiments at different levels of temperatures and light intensities were conducted.

The BVOC emission from 10 plant species at several conditions were converted to the standard condition (30 °C, PAR: $1000\,\mu mol\,m^{-2}\,s^{-1}$) by using the Guenther equation. Table 5 shows the monoterpenes emission at standard conditions. Table 6 shows isoprene emission at standard conditions from six deciduous broadleaf trees, which are commonly found in Japan. A large amount of α-pinene and β-pinene was detected from *C. japonica*, *C. obtusa*, and *P. densiflora*. Previously, *O. sativa* has not been reported to emit BVOC, but five kinds of monoterpenes were detected. This detection could be very significant even though the amount is small because a large part of Japan is covered by paddy fields. In fact, the entire Asian region is also largely covered by paddy fields. A large amount of isoprene was detected from *Q. serrata*.

Table 7
Comparison of monoterpene emissions at the base condition and at the elevated temperature

Components	BVOC emissions [$\mu g\,g_{dw}^{-1}\,h^{-1}$]							
	Cryptomeria japonica		*Chamaecyparis obtusa*		*Pinus densiflora*		*Oryza sativa*	
	Base*	+5 °C	Base*	+5 °C	Base*	+5 °C	Base*	+5 °C
α-Pinene	1.29	2.68	2.15	1.34	2.71	5.69	0.23	0.39
Rate [–]		2.07		0.62		2.10		1.72
β-Pinene	0.08	0.19	0.21	ND	0.41	0.71	0.02	0.02
Rate [–]		2.37				1.76		1.27
Myrcene	0.34	1.09	0.17	1.01	0.70	2.54	0.05	ND
Rate [–]		3.19		5.98		3.63		
α-Phellandrene	0.07	0.24	0.04	0.29	0.06	0.34	ND	ND
Rate [–]		3.69		7.96		5.81		
α-Terpinene	0.06	0.20	0.05	0.46	ND	0.12	ND	ND
Rate [–]		3.31		8.89				
p-Cymene	0.12	0.28	0.12	0.94	0.07	0.24	0.03	0.05
Rate [–]		2.33		7.95		3.51		1.96
Limonene	0.40	1.44	ND	ND	ND	1.12	0.07	0.14
Rate [–]		3.61						2.01
γ-Terpinene	0.08	0.27	0.10	1.07	ND	ND	ND	ND
Rate [–]		3.51		10.53				
Terpinolene	0.02	0.12	ND	0.29	0.03	0.17	ND	ND
Rate [–]		5.50				5.00		

*Base is the condition of the diurnal variation temperature in Summer (July, August 2003 and 2004) at Osaka. ND means not detected.

6.2. Effect of temperature and light intensity on BVOC emissions from isoprene emitting plants

Since *Q. serrata* emits a large amount of isoprene and occupies 21.46% of the whole of deciduous broadleaf trees in the study region, the effect of temperature and light intensity on BVOC emissions from *Q. serrata* only is discussed here. It is basically understood that light and temperature exert primary control over isoprene production and emission (Schuh et al., 1997; Guenther et al., 1993). Fig. 6 shows the diurnal variation of isoprene emission at the average temperature in Osaka. Even though the temperature increased, there was no emission until 6 a.m. when the light was turned on. Therefore, it can be inferred that isoprene emission is dependent on light and temperature. During daytime however, the rate of emission was elevated by the increase in the temperature. In the afternoon, isoprene emissions started to decrease due to the falling temperature. The Guenther equation is also plotted in the figure. The resulting curve is similar to the Guenther equation, although the maximum emission is higher than that of Guenther equation.

In order to find the temperature dependency of the BVOC emissions, we conducted experiments at two different temperatures. First, the average summer temperature in Osaka was used and then in the second experiment the temperature was increased by five degrees during daytime. The results of isoprene emission at different levels of temperatures are shown in Fig. 7. The emission of isoprene from *Q. serrata* could be reasonably represented by the algorithm developed by Guenther et al. (1993).

In the case of finding light intensity dependency, light intensity was set at $0\,\mu mol\,m^{-2}\,s^{-1}$ (night condition), 335 and $1000\,\mu mol\,m^{-2}\,s^{-1}$. Temperatures were set at the average in Osaka. No isoprene was emitted at $0\,\mu mol\,m^{-2}\,s^{-1}$. More than twice the amount of isoprene was emitted at $1000\,\mu mol\,m^{-2}\,s^{-1}$ than at $335\,\mu mol\,m^{-2}\,s^{-1}$ (refer to Fig. 8). These results show that isoprene emission responds strongly to temperature and light intensity.

6.3. Effect of temperature and light intensity on BVOC emissions from monoterpenes emitting plants

Monoterpene emissions are basically dependent on light intensity not on temperature (Guenther et al., 1995). In this experiment, monoterpenes are emitted by *C. japonica*, *C. obtusa*, *P. densiflora*, and *O. sativa*, whereas isoprene is only emitted by deciduous broadleaf trees. In order to see

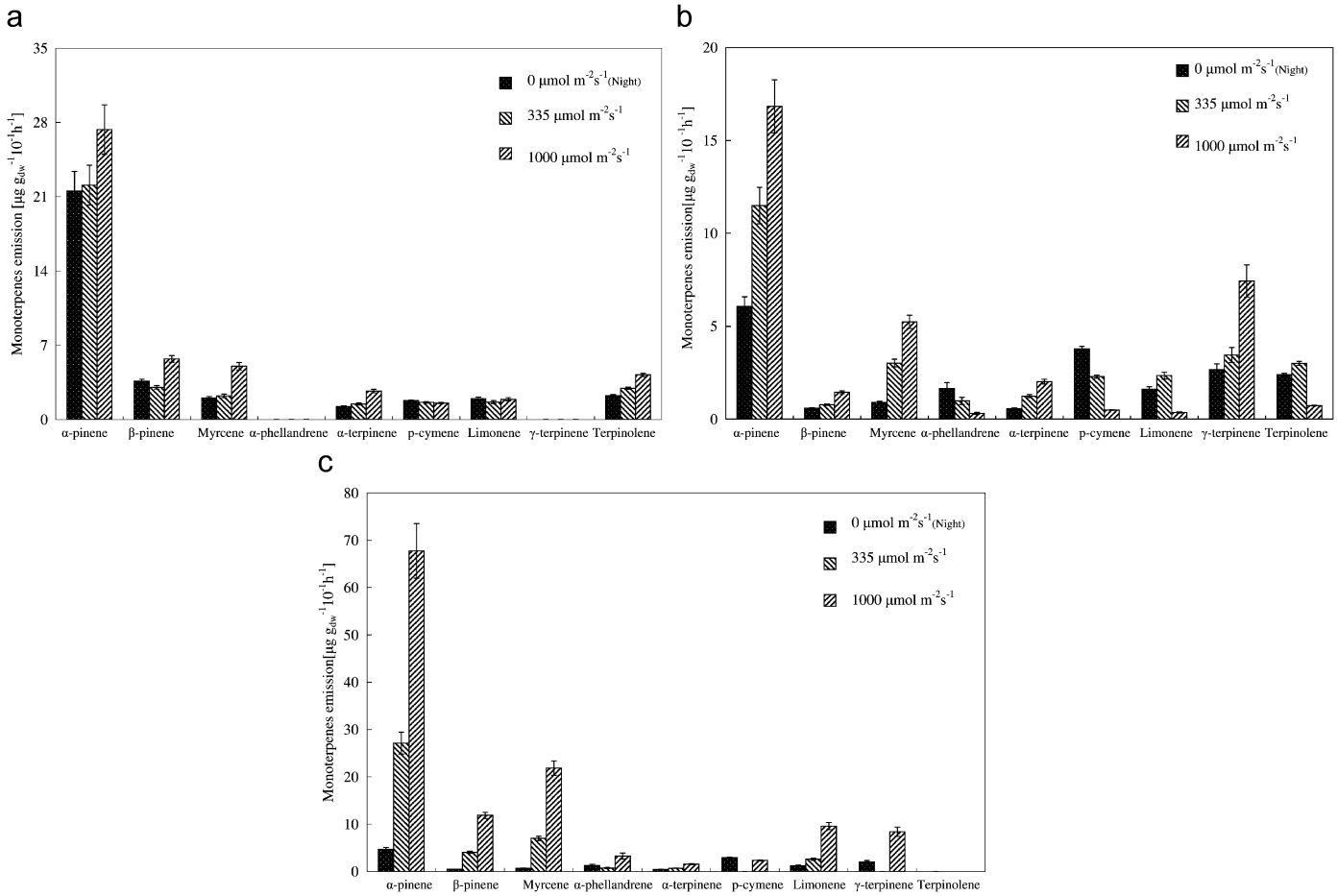

Fig. 9. Dependency of monoterpene emissions on light intensity (a) *Chamaecyparis obtusa*, (b) *Cryptomeria japonica*, and (c) *Pinus densiflora*.

the dependency of light intensity and temperature, the same experiment as *Q. serrata* was conducted for *C. japonica*, *C. obtusa*, *P. densiflora*, and *O. sativa*. Table 7 shows the comparison of monoterpenes emissions at the base temperature (average temperature in Osaka) and at 5 °C above base temperature. For most of the monoterpene emission amount from *C. japonica* and *P. densiflora* at 5 °C above base temperature was around two or three times more than at the base temperature. However, the amount of monoterpenes from *C. obtusa* increased much more. In particular, the emission of γ-terpinene increased by more than 10 times than at the base temperature. Therefore, monoterpene emissions from *C. obtusa* are sensitive to temperature as shown in Table 7.

In order to see the BVOC emissions at different levels of light intensity, the same experiment as *Q. serrata* was conducted. Fig. 9 shows the monoterpene emissions at 0, 335, and 1000 μmol $m^{-2} s^{-1}$. *C. obtusa* (Fig. 9a) shows no clear relation between monoterpene emissions and light intensity as predicted by Eq. (4). However, there was a clear relation for *C. japonica* (Fig. 9b) and *P. densiflora* (Fig. 9c). In the case of *C. japonica*, the increase in monoterpene emissions with light intensity can be clearly seen for α-pinene, β-pinene, myrcene, α-terpinene, and γ-terpinene; these comprise majority of the monoterpene emitted. In the case of *P. densiflora*, all major monoterpenes emitted showed dependence on light intensity. Yokouchi and Ambe (1984) also reported that monoterpene emissions from this tree depends on light intensify. Some other plant species that showed monoterpene emission dependence on light intensity have been reported by Steinbrecher et al. (1991), Simon et al. (1994), Staudt and Seufert (1995), Kesselmeier et al. (1997), Sabillon and Cremades (2001), and Shao (2001).

6.4. BVOC emissions potential distribution

Using the forest database created from this study, BVOC emissions potential maps were created. All the leaves were expected to receive the same amount of light (1000 μmol $m^{-2} s^{-1}$). However, isoprene emissions may be over estimated because isoprene emission is dependent on light intensity and therefore our results do not consider the fact that there are leaves that are in the shade. Fig. 10 shows the isoprene emission potential at standard condition. 596 ton h^{-1} of isoprene were emitted from the calculated region (47,000 km^2). The emission rate is high where *Q. serrata* is dominant in the region since *Q. serrata*

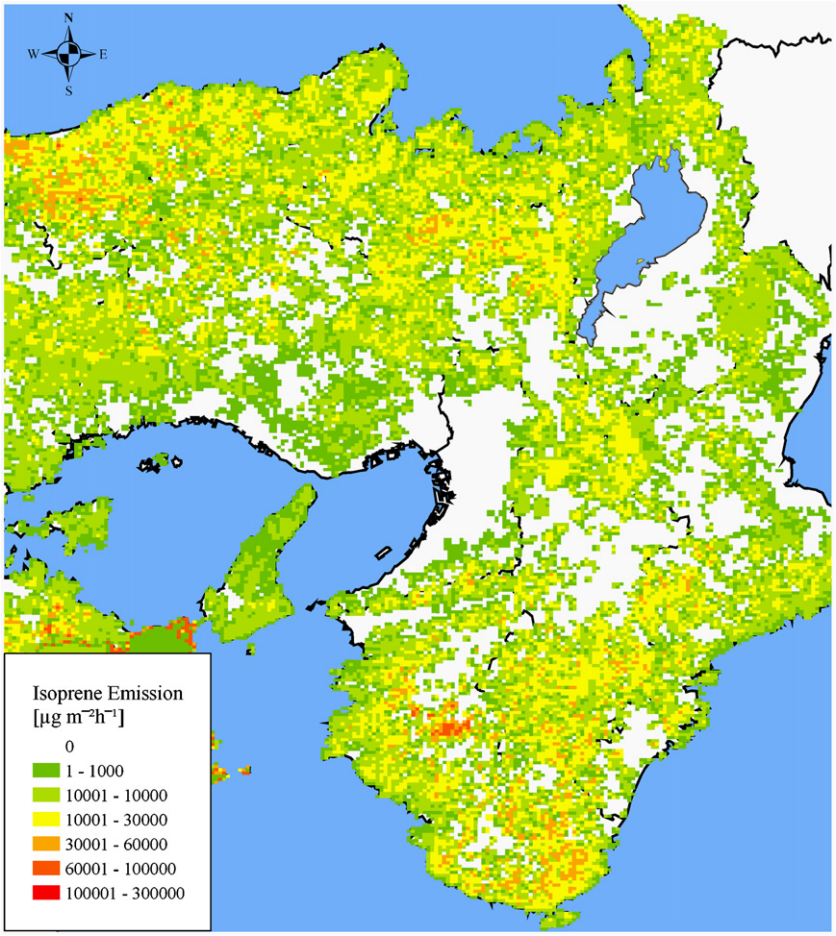

Fig. 10. Isoprene emission potential.

emits much isoprene. 54.08 ton h^{-1} of monoterpenes were emitted in the region (Fig. 11). The emission rate is high where there are lots of coniferous trees, such as *C. japonica*, *C. obtusa*, and *P. densiflora*. Fig. 12 shows the monoterpene emissions from *O. sativa*. The monoterpene emission from *O. sativa* is low; however the area of paddy fields is large in the region around the Lake Biwa and Awaji Island. Therefore, 5% of monoterpenes emission is contributed by *O. sativa*.

6.5. Diurnal variation of BVOC emissions

The standard BVOC emissions obtained by experiment and Eqs. (2) and (5) were used to estimate the diurnal variation of BVOC emissions. In order to accurately estimate the BVOC emissions, the temperature data in each place in summer were used. Hourly emissions of isoprene in the region in August are shown in Fig. 13(a). The result indicates that the total amount of BVOC reaches its maximum in the daytime due to the rapid increase of isoprene emission. On the other hand, monoterpenes are emitted constantly during night time as well because it is only dependent on temperature and not on light intensity. Fig. 13(b) shows the BVOC emissions potential in February. The amount is less than one tenth of August and the ratio of monoterpene emission to the total BVOC is higher than August due to the weakness of light intensity in winter and isoprene emission is dependent on light intensity. In addition, to estimate the isoprene emission more accurately, leaves in the shade can be taken into account by using LAI (leaf area index).

6.6. Seasonal variation of BVOC emissions

Seasonal variation of BVOC emissions has been measured before (Boissard et al., 2001; Hakola et al., 2003; Kim et al., 2005) and predicted that the amount of BVOC emissions tend to increase in summer. In this study, to estimate the seasonal variation of BVOC emission amount, not only temperature and light intensity but the amount of leaves in each season was taken into account. Fig. 14 shows the seasonal ratio of leaves compared with the maximum value in summer. Deciduous trees shed nearly 30% of their leaves in the winter, which is comparatively less than the deciduous trees that shed all the leaves exponentially by winter time. By using the seasonal ratio of tree leaves and the standard BVOC emissions of 10 plant species, the annual variation of

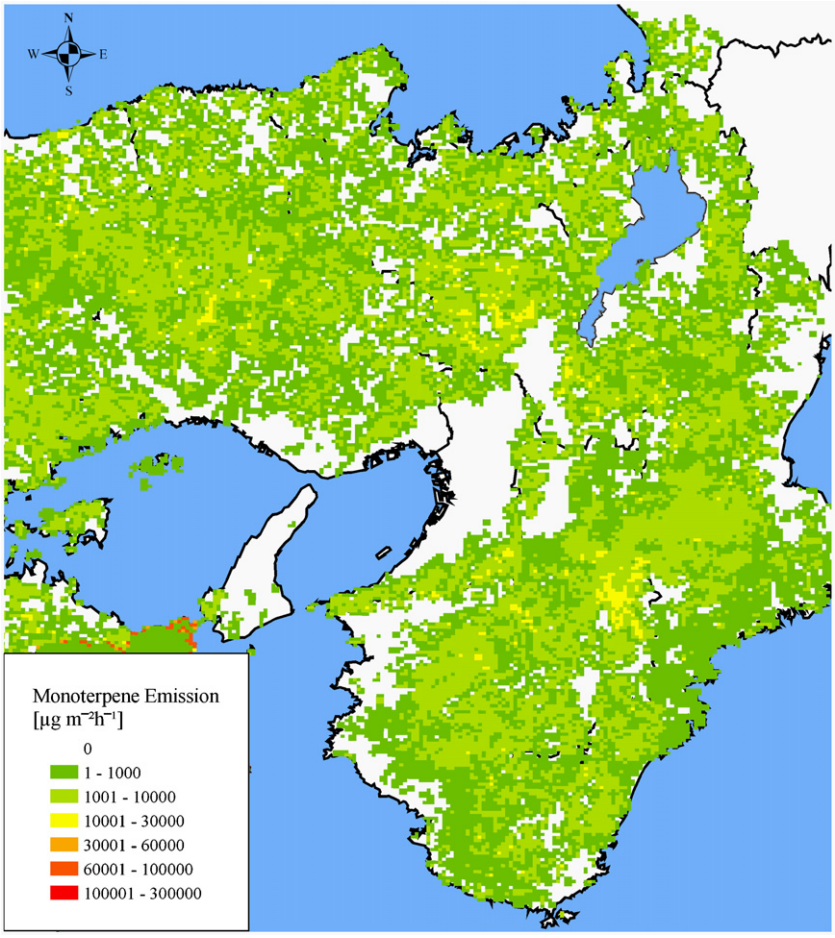

Fig. 11. Monoterpene emission potential.

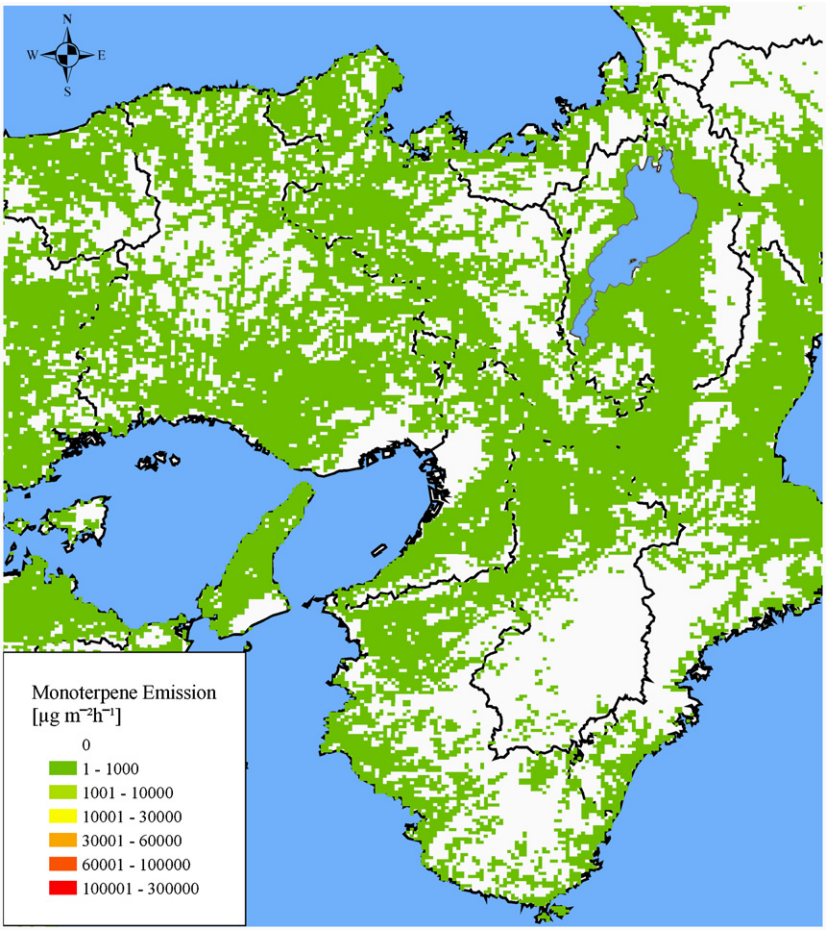

Fig. 12. Monoterpene emission potential *Oryza sativa*.

BVOC emissions were shown in Fig. 15. The BVOC emission in summer is more than 10 times as winter. However, Hakola et al. (1998) reported that significant monoterpene emissions emitted from *Salix phylicifolia* and *Populus tremula* soon after bud-break therefore there is a possibility BVOC emission might be high in spring season.

7. Conclusion

In this study, BVOC emissions from 10 different plants in Japan were measured in a growth chamber. Deciduous broadleaf trees, especially *Q. serrata* ($224\,\mu g\,g_{dw}^{-1}\,h^{-1}$), emitted isoprene. It was shown that α-pinene (1.3, 1.89, 5.33, and $0.24\,\mu g\,g_{dw}^{-1}\,h^{-1}$, respectively) and β-pinene (0.06, 0.22, 0.84, and $0.02\,\mu g\,g_{dw}^{-1}\,h^{-1}$, respectively) are main monoterpenes emitted by *C. japonica*, *C. obtusa*, *P. densiflora*, and *O. sativa*. Monoterpene emission from *O. sativa* was found in our experiment. Though the amount of monoterpenes from *O. sativa* ($0.4\,\mu g\,g_{dw}^{-1}\,h^{-1}$) was not very large, it could be quite significant for estimating BVOC emissions especially in regions like Asia where paddy fields are abundant.

Isoprene emission amount from *Q. serrata* increased about 2 times due to temperature rise from 30 to 35 °C and increased about 1.6 times due to light intensity from 335 to $1000\,\mu mol\,m^{-2}\,s^{-1}$. As for the effect of temperature on monoterpene emission amount, most of the monoterpene emission amount from *C. japonica*, *C. obtusa*, and *P. densiflora* increased about two times due to temperature rise from 30 to 35 °C. Especially the emission amount from *C. obtusa* increased much more; especially 10 times in γ-terpinene and 9 times in α-terpinene. Therefore, monoterpene emissions from *C. obtusa* are more sensitive to temperature than other plants. As for the effect of light intensity on monoterpene emission amount, *C. obtusa* showed no clear relation between monoterpene emissions and light intensity. However, there was a clear relation for *C. japonica* and *P. densiflora*. In the case of *C. japonica*, the increase in monoterpene emissions with light intensity from 0 to $1000\,\mu mol\,m^{-2}\,s^{-1}$ can be clearly seen for α-pinene (2.8 times), β-pinene (2.5 times), myrcene (5.8 times), α-terpinene (3.6 times), and γ-terpinene (2.8 times); these comprise majority of the monoterpene emitted. In the case of *P. densiflora*, all major monoterpenes (α-pinene (14 times), β-pinene (26 times), myrcene (31 times)) emitted showed dependence on light intensity, though the algorithm by Guenther cannot express the dependency of light intensity.

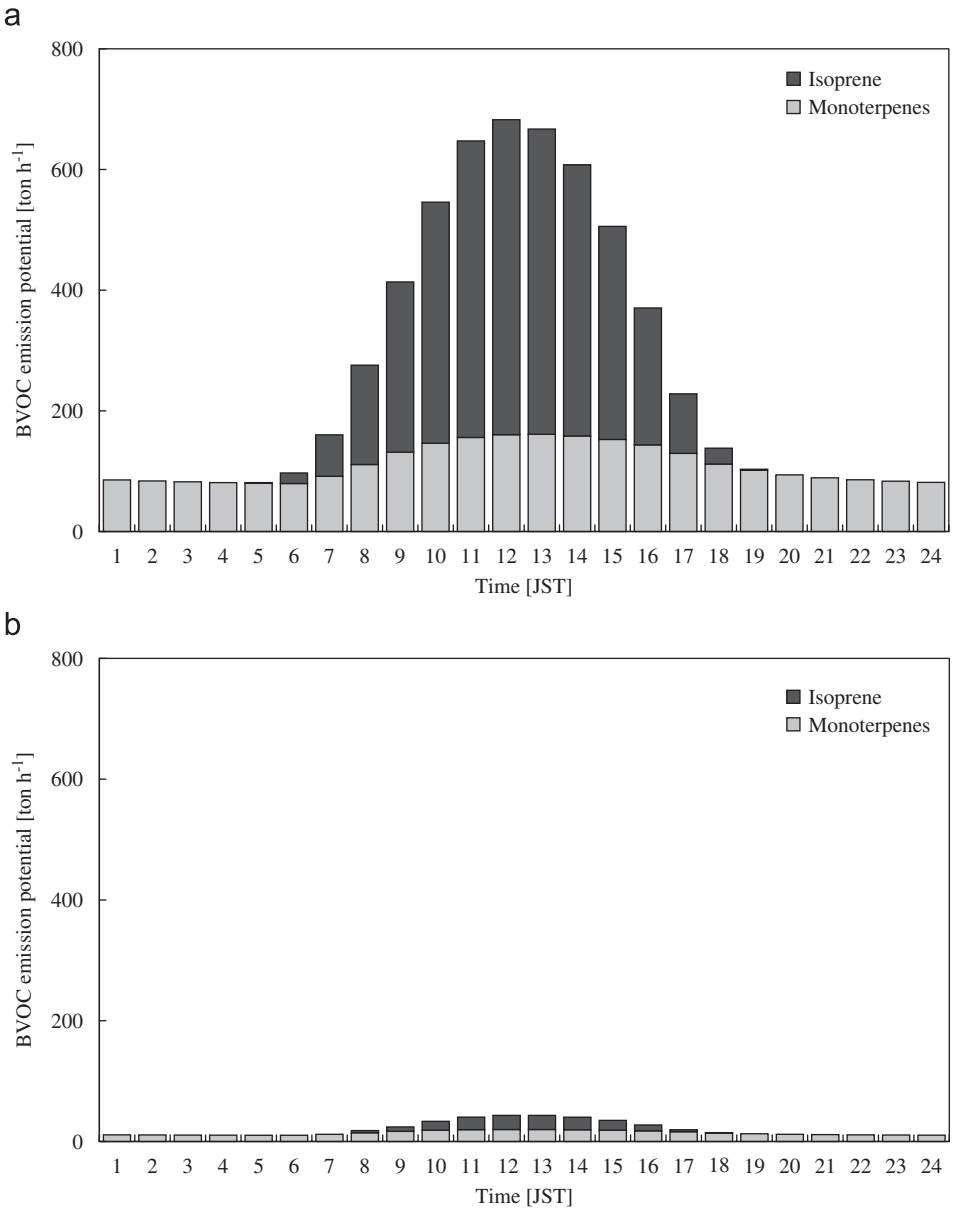

Fig. 13. Hourly emissions of isoprene and monoterpenes potential (a) in August and (b) in February.

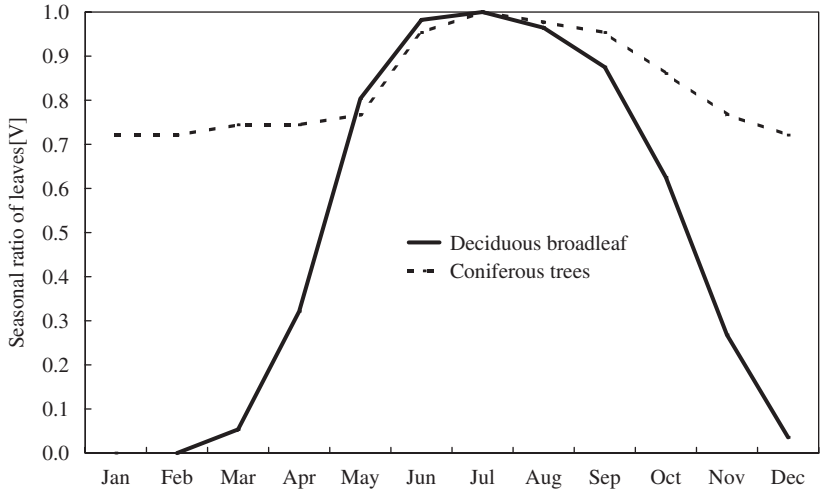

Fig. 14. Seasonal ratio of leaves calculated as, V [quantity of leaves]/[maximum quantity of leaves in summer].

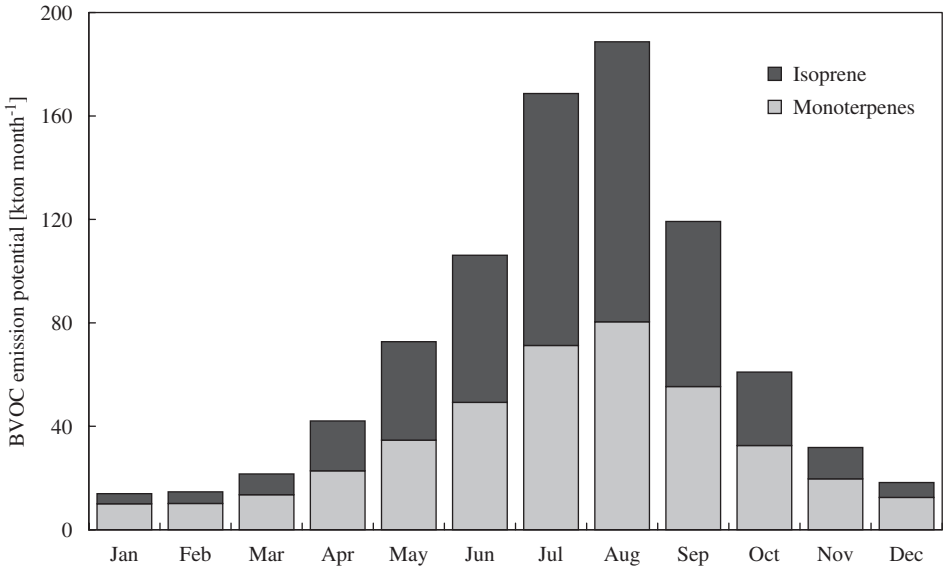

Fig. 15. Annual variation of BVOC emission potential in the estimated area.

Using the new forest database collected from several prefecture offices including the age, we made a more accurate BVOC emissions potential map. It was found that the emissions of isoprene and of monoterpene were 596 and 54 ton h^{-1} in the Kinki region, respectively. Moreover by considering the dependency of temperature and of light intensity and the variation of leaf biomass, diurnal and seasonal variations of BVOC emission potential were estimated. The BVOC emission was 14 times higher in summer than in winter; therefore oxidant concentration can be expected to be high in daytime due to the increase of BVOC emission.

Our experiments showed that BVOC emission of all plants we used in this study strongly depended on temperature and light intensity. The climate change due to global warming may induce the increases of BVOC emission and may raise photochemical oxidant concentration. In order to assess atmospheric environment in the future, the accumulation of BVOC emission in the various regions should be continued.

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