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Volatile diterpene emission from dominant conifers in Japan

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Abstract

Reactive volatile organic compounds (VOCs) are known to affect atmospheric chemistry, especially biogenic VOCs (BVOCs) which have a significant impact on regional air quality due to their large emission rates and high reactivities. Diterpenes (Kaur-16-ene and a diterpene likely to be Hibaene) were detected in all of the 205 enclosure air samples collected over multiple seasons at two different sites from *Cryptomeria japonica* and *Chamaecyparis obtusa* trees, the dominant coniferous trees in Japan. The emission rate of Kaur-16-ene, was determined to be from 0.01 to 7.1 µg dwg^{-1} h^{-1} (average: 0.61 µg dwg^{-1} h^{-1}) by branch enclosure measurements and solid phase – liquid extraction techniques. The emission rate was an order of magnitude higher than that of monoterpenes which are known to comprise a major portion of total BVOC emissions. In addition, total emission of Kaur-16-ene at 30 °C was estimated to be comparable to that of total anthropogenic VOC emissions. To our knowledge, this is the first report of volatile diterpene emissions from trees.

1 Introduction

Reactive volatile organic compounds (VOCs) have multiple important impacts on atmospheric chemistry and physics (Guenther et al., 2006). For example, VOCs are a precursor to tropospheric ozone, an effective greenhouse gas known to be toxic at sufficiently high concentrations (Mustafa, 1990). Reactive VOCs at high concentrations may also decrease atmospheric concentrations of the hydroxyl radical (OH), a strong oxidant and major sink of less reactive greenhouse gases such as methane in the atmosphere (Kulumala et al., 2004). VOCs also form secondary organic aerosols which may produce direct and indirect effects on the earth's radiation budget (Kavouras et al., 1998).

VOCs are known to have both anthropogenic and biogenic sources. Biogenic VOCs (BVOCs) are mainly emitted from terrestrial higher plants such as trees, and are

estimated to contribute approximately 90 % of total VOC emission on a global scale (Guenther et al., 2006). BVOCs often consist of unsaturated hydrocarbons, such as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) and oxygenated species such as methanol, 2-methy-3-butene-2-ol (methylbutenol) and others. However, it is suggested that there are still unmeasured constituents in the atmosphere (Di Carlo et al., 2004).

Coupled measurements of OH radical reactivity and VOC concentrations revealed that there is still a significant quantity of unmeasured reactant (most probably BVOCs) which cannot be detected by present analytical techniques (Di Carlo et al., 2004; Sinha et al., 2010). Studies revealed that there is a significant deviation between the observationally based and the atmospheric model based aerosol budgets, and is most likely caused by the existence of unmeasured compounds (Hallquist et al., 2009; Beerling et al., 2011). These findings suggest the existence of unknown source(s) of reactive VOCs. On the other hand, a study based on enclosure sampling showed good agreement between OH reactivity and VOC concentration measurements (Kim et al., 2011). This suggests that emissions of unknown compounds may depend on the tree species which is a common feature of biogenic emissions.

Diterpenes, a group of unsaturated biogenic hydrocarbons containing 20 carbon and 32 hydrogen atoms, have previously been identified in leaf oils and resins, however thought to not be emitted from the vegetation due to their low volatility (Nakatsuka et al., 1957; Appleton et al., 1968, 1970; von Rudloff, 1975; Yasue et al., 1987; Cool et al., 1998; Kato, 2005; Keeling and Bohlmann, 2006; Lee et al., 2009). Thermo-desorption is one of the techniques most commonly used for BVOC measurements, however, it is unsuitable for the detection of high molecular weight compounds such as diterpenes because less volatile compounds cannot be efficiently be desorbed. Thus, these compounds have been overlooked in previous studies.

We applied a new analytical technique which is based on solid adsorption – liquid extraction (Matsunaga et al., 2011). The technique can elute heavy compounds such as diterpenes effectively from the adsorbent, enabling the determination of emission rates of the heavier BVOCs. Kaur-16-ene and other compounds likely to be diterpenes were detected in all of the emission samples collected from *C. japonica* and *C. obtusa* over multiple seasons at two different sites. These two endemic tree species are the most dominant trees in Japan accounting for approximately 60 % of total leaf mass in Japanese forests (Matsunaga, 2011). Here, we present the first observations of biogenic emissions of diterpenes in remarkable concentrations.

Although the analytical technique cannot distinguish stereo-isomers compounds produced in leaves (Railton et al., 1984; Perry and Weavers, 1985; Cool et al., 1998), the Kaur-16-ene detected in this study is most likely to be ent-Kaurene. The emission rate of Kaur-16-ene was generally more than an order of magnitude higher than that of total monoterpene emissions. Assuming a temperature dependence of Kaur-16-ene emission used in the G93 model (Guenther et al., 1993), the emission was estimated to be comparable to total monoterpene emission, a group of commonly emitted BVOCs, and also to total anthropogenic VOC emission in Japan in summer.

2 Experiment

2.1 Site description and field campaign

Seven field campaigns have been conducted at two sites, Tanashi Experimental Station of the Tokyo University Forests (35°44′21″ N, 139°32′18″ E) in Tokyo and Miyazaki Research Forest of Kyushu University (32°21′23″ N, 131°6′2″ E) in Shiiba, Miyazaki, Japan. Both of the experimental forests have a planted area of mature *C. japonica* and *C. obtusa* trees. The campaigns were conducted in January, August, and November of 2009 and in April of 2010 at Tanashi and in May, August, and November of 2010 at Shiiba. Each sampling period was 5 days.

2.2 Branch enclosure system

Leaves were sampled at branch ends about 5–15 nodes from the trunk and were located at the top of the canopy approximately 10–15 m above the ground level. Tree ages of *C. japonica* at Tanashi and Shiiba were 54 and 56 yr, respectively and for *C. obtusa*, at Tanashi and Shiiba were 33 and 56 yr, respectively.

The branches were enclosed with a 15 l Teflon® bag (transparent to more than 95 % of PAR). The enclosure samples were collected from the branch of *C. japonica* at canopy top and 5 m (3 m for *C. obtusa*) below the top within same individual. The bags were installed at least 24 h prior to the first sample collection to avoid disturbance due to the installation of the bag. The air inside the bag was ventilated with a VOC free air at a flow rate of 4–5 l min^{-1} to avoid water condensation and excessive temperature increase in the bag (see Fig. 1 for an overview). The bags were installed onto the branches on the first day of the campaign and kept on the branches until the sampling period ended 5 days later. The air was supplied from a commercial compressed air cylinder and cleaned by an activated charcoal trap. The flow rate was controlled by a mass flow controller. Air entering the bag was supplied through a Teflon® tube ring roughly 1.5 mm in diameter with approximately 20 holes so that the inside air could be circulated and homogenized. The compressed air was taken from the atmosphere and, thus, the CO_2 concentrations are assumed to remain at average ambient level. The maximum relative humidity in the bag has been calculated to be 70–75 % in the daytime. Considering that water condensation was observed when the air flow rate was reduced to below 4 l min^{-1}, relative humidity in the bag was not too dry during sampling. Air temperature inside of the bag was recorded every 2 min by a data logger equipped with a Teflon® coated thermo sensor (RS-12, Especmic, Ohguchi, Niwa, Aichi, Japan). Branches were harvested after the completion of each field campaign and dried at 60 °C for 48 h to determine dry weight of the leaves, therefore, samples were collected from different branches of same individuals with other sampling periods in every season. For *C. japonica*, the dry weight was determined for whole branches harvested because stems also have green needle leaves. Therefore, the dry weight for *C. japonica* includes stem, bark and leaves.

2.3 Sample collection

Diterpene samples were collected from the enclosure bag described in Sect. 2.2. Monoterpenes and sesquiterpenes, which are C_{10} and C_{15} BVOCs, respectively, were also collected from the same bag and analyzed to confirm any disturbance (i.e., extraordinarily high concentrations from damage to storage reservoirs of the BVOCs).

The diterpene samples were collected into a 6.35 mm (1/4 inches) o.d. glass tube filled with approximately 60 mg of HayeSep Q (Hayes Separations, Inc., Bandera TX, USA). Sample flow rate was controlled at 200 $\mathrm{ml\,min^{-1}}$ by a mass flow controller connected to an electronic pump. The collection time ranged from 0.5 to 2 h. Diterpenes collected on the adsorbent were extracted with approximately 2 ml of hexane (Special grade, Wako chemical, Chuo-Ku, Osaka, Japan) at the site. The extracts were dropped into 2 ml glass vials (Supelco, Bellefonte PA, USA) directly from the sampling tube and stored in a freezer, which was kept at approximately −15 °C, at the site. The samples were transported to the laboratory by a commercial transport service, which kept the packages at −18 °C ("Cool Takkyu-bin", Yamato Transport Co., Ltd., Chuo-Ku, Tokyo, Japan) before further procedures were performed.

2.4 GC-MS analysis

A one micro liter of internal standard solution (20–100 $\mathrm{ng\,\mu l^{-1}}$ of cyclopentadecane in hexane) was added into the extracts prior to the concentration. Then, the extracts were evaporated to approximately 5–10 µl by a gentle argon flow at the laboratory. The internal standard solution was prepared for each field campaign. One µl of the concentrated extract containing the internal standard was injected into the split-splitless injector of the gas chromatograph (GC; Agilent 7890A GC, Agilent Technologies Inc., Santa Clara CA, USA) connected to a mass spectrometer (MS; Agilent 5975C MSD). Diterpenes

were separated using a fused silica capillary column (HP-5ms, 30 m × 0.25 mm i.d., film thickness of 0.25 µm; Agilent Technologies Inc.) and helium carrier gas. The injector (300 °C) was equipped with a deactivated quartz insert tube and operated in the pulsed splitless mode. GC oven temperatures were programmed to start at 60 °C and increase to 150 °C at 2.5 $\mathrm{^{\circ}C\,min^{-1}}$, then raised to 300 °C at 30 $\mathrm{^{\circ}C\,min^{-1}}$ and held for 10 min. The identification of Kaur-16-ene was made comparing its GC retention time and mass spectra with those of the authentic standard (Figs. 2 and 3). The authentic standard was purchased from OlChemIm Ltd., Olomouc, Czech Republic. Only Kaur-16-ene and an unknown diterpene, likely to be Hibaene, were detected as two abundant peaks of diterpenes (Fig. 2).

Kaur-16-ene was quantified using the MS in the selected ion monitoring mode. The amount of the Kaur-16-ene was determined by comparing response intensity (peak area on a chromatogram for the selected ions) between the internal standard and the target compounds. The response of the Kaur-16-ene was adjusted based on the ratio of the response for internal standard to Kaur-16-ene at the same amount because the selected ions are different between Kaur-16-ene and the standard. The ratio was determined by analyzing authentic standard for Kaur-16-ene and internal standard (cyclopentadecane) purchased from Wako and Sigma-Aldrich (Co., St. Louis MO, USA). The amount of the standard was gravimetrically determined. The precision of the whole analytical procedure was around 5 %. Detection limit was approximately 0.1 $\mathrm{ng\,g^{-1}\,h^{-1}}$ (depending on the leaf mass enclosed in the bag and the sampling time).

2.5 Calculation for the emission rate of Kaur-16-ene

The emission rate was determined based on the Eq. 1 below.

$$E = \frac{F_{\mathrm{air}} \times C - C_{\mathrm{blank}}}{f_{\mathrm{samp}} \times t_{\mathrm{samp}} \times W_{\mathrm{leaf}}} \tag{1}$$

where, E and C are the emission rate in $\mathrm{\mu g\,g^{-1}\,h^{-1}}$ and determined amount of Kaur-16-ene by the GC-MS analysis in µg, respectively. F_{air}, C_{blank}, F_{samp}, t_{samp} and W_{leaf} are flow rate of the purified air supplied to the bag in ml min^{-1}, amount of Kaur-16-ene in the blank sample in µg adjusted for the actual sampling time, sample flow rate, sampling time in hour and dry weight of the leaf in g, respectively. C_{blank} for Kaur-16-ene was below the detection limit through all field campaigns.

3 Results and discussion

3.1 Basal emission rate of Kaur-16-ene

Only Kaur-16-ene was identified and quantified in the diterpenes using an authentic standard. To estimate the regional emission rate, the basal emission rate of Kaur-16-ene was calculated. Basal emission rate is defined to be an emission rate of BVOC, which is emitted into the canopy, at the standard condition (30 °C for temperature dependence) (Guenther et al., 1993, Guenther et al., 2006). Therefore, it is regarded to be a constant in most BVOC emission models. Figure 4a and b presents observed relationships between the inside air temperature of the enclosure bag and measured emission rate of Kaur-16-ene from *C. japonica* and *C. obtusa* observed at Tanashi and Shiiba. Plot for *C. obtusa* was only for data obtained at Shiiba due to insufficient number of samples at Tanashi. Assuming temperature dependence of the emission of Kaur-16-ene, the emission rate can be estimated according to the G93 algorithm (Eq. 2).

$$E = E_s \exp\{\beta(T - T_s)\} \tag{2}$$

$$\ln E = \beta(T - T_s) + \ln E_s \tag{3}$$

where, E presents measured emission rate. T and T_s presents measured temperature and the standard temperature, respectively. An empirical coefficient β can be calculated as the slope of the liner regression for the plot and quantifies the intensity of temperature dependence (Eq. 3). Natural logarithm of the basal emission rate E_s is

the intercept at y-axis (Guenther et al., 1993). The calculated E_s and β over the seven campaigns are presented in Table 1. Although there may be another factor which controls the emission (e.g. light intensity), we concluded that temperature is the most effective controlling factor of the emission of Kaur-16-ene based on comparisons of the emission rate between branch at the canopy top and the light attenuated branch. The comparisons have been conducted for both *C. japonica* and *C. obtusa* trees. The basal emission rate did not show any significant difference with light intensity.

The basal emission rate of Kaur-16-ene did not show significant seasonal variation. As mentioned above, basal emission rate is regarded to be a constant in most emission models because it is a normalized emission rate at a set of standard conditions. However, recent studies report that the basal emission often has a seasonal variation (Geron and Arnts, 2010). Matsunaga et al. (2011) also reports that the basal emission rates of monoterpenes and sesquiterpenes emitted from *C. japonica* change with season. However, the basal emission rate of Kaur-16-ene emitted from *C. japonica* and *C. obtusa* did not clearly change with seasons. This may suggest that diterpenes are produced for other purposes or are produced through different processes than mono- and sesquiterpenes.

3.2 Estimate on the Kaur-16-ene emission over Japan

The total emission rate of Kaur-16-ene over Japan at 30 °C and 5 °C was based on leaf mass calculated from trunk volumes for *C. japonica* and *C. obtusa*. The trunk volumes are recorded in a statistical table of timber resources by each prefectural administration in Japan (Matsunaga, 2011). As shown in Fig. 5, the emission rate of Kaur-16-ene was estimated to be 630 and 3.3 ton h^{-1}, respectively, while the emission rate of total monoterpenes (molecular weight; MW: 136) in Japan were estimated to be 250 tons h^{-1} at 30 °C and 26 tons h^{-1} at 5 °C by the emission model MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006). On the other hand, the emission rate based on MEGAN employing observed basal emissions for Kaur-16-ene and the coefficient β was also estimated at 30 °C and 5 °C as 460 and

2.7 ton h^{-1}, respectively. It appears that the emission rate of Kaur-16-ene estimated at 30 °C exceeds the total emission rate of anthropogenic VOCs in Japan (220 ton h^{-1}) (Kannari et al., 2008). Considering the result, Kaur-16-ene can be regarded as a new and important atmospheric constituent that has a remarkable influence on the air quality in Japan.

4 Summary

4.1 Diterpene emission

A significant emission of diterpenes, which has not been recognized to be emitted into the atmosphere, has been determined employing both enclosure and ambient air measurements. Their reactivity is expected to be high due to their unsaturated structure and high molecular weight of molecules which contain many hydrogen atoms. In addition, the aerosol formation yield by the oxidation of diterpenes is also expected to be high due to their high molecular weight and reactivity. Considering the comparable emission rate to other classes of BVOCs such as monoterpenes and sesquiterpenes, which are known to be major BVOC constituents, impacts of the diterpene emissions can be important in atmospheric chemistry and physics.

4.2 Unknown diterpene and future study

Samples also contained other diterpene-like compounds, which have not been identified by the authentic standards. One abundant unknown compound in the samples seemed to be Hibaene which is a diterpene also known as a constituent of coniferous leaves (Yatagai et al., 1985; Nagahama and Tajima, 1996). The mass spectrum was similar to that in NIST library. The Hibaene like compound was detected in the samples at similar intensities with Kaur-16-ene. Therefore, total diterpene emission can be larger than presented in this study. Also, to confirm the importance of diterpene

emissions at larger scales, other conifers such as *Abies, Larix, Picea* and *Pinus* spp., which are common at the global scale, should be investigated for the diterpene emissions in the near future.

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Table 1. Calculated basal emission E_s of Kaurene and total monoterpenes in $\mu g\, dwg^{-1}\, h^{-1}$, coefficient β and correlation coefficient obtained from seven field measurements conducted at two sites.

	Tree species	Number of individuals	Number of samples	E_s	β	r^2
Tanashi, Tokyo, 2009–2010[1]						
Kaur-16-ene	*C. japonica*	3	72	1.05	0.15	0.61
	C. japonica[2]			2.79	0.21	
	C. obtusa	1	17	2.20	0.21	0.50
Total monoterpenes	*C. japonica*	2	90	0.27	0.10	0.64
Shiiba, Miyazaki, 2010[3]						
Kaur-16-ene	*C. japonica*	2	57	8.74	0.22	0.49
	C. obtusa	2	59	0.99	0.20	0.53
Total monoterpenes[4]	*C. japonica*	2	14	0.48	0.10	
	C. obtusa	2	12	0.26	0.10	

[1] The measurements were conducted on January, August, November of 2009 and April 2010.

[2] Averaged E_s calculated assuming β of 0.21 by the equation of $E_s = E/\exp(\beta(T - T_s))$.

[3] The measurements were conducted on May, August and November of 2010.

[4] Averaged E_s calculated assuming β of 0.10 by the equation of $E_s = E/\exp(\beta(T - T_s))$ measured on May 2010.

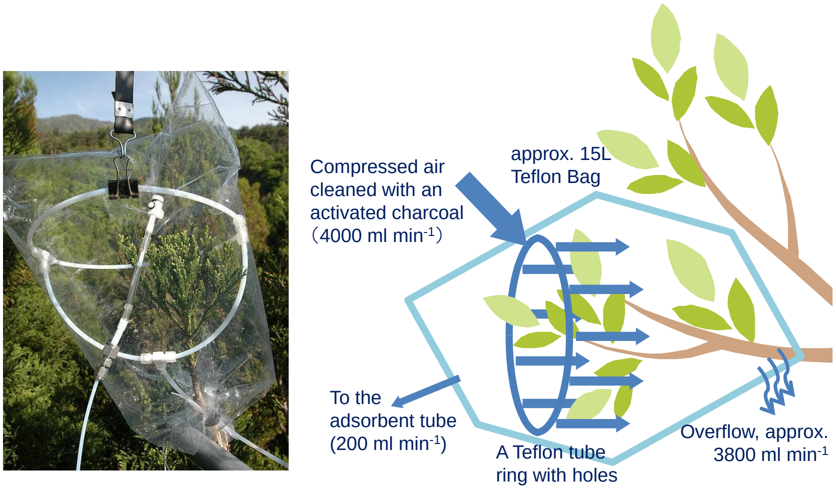

Fig. 1. An overview for the branch enclosure sampling system.

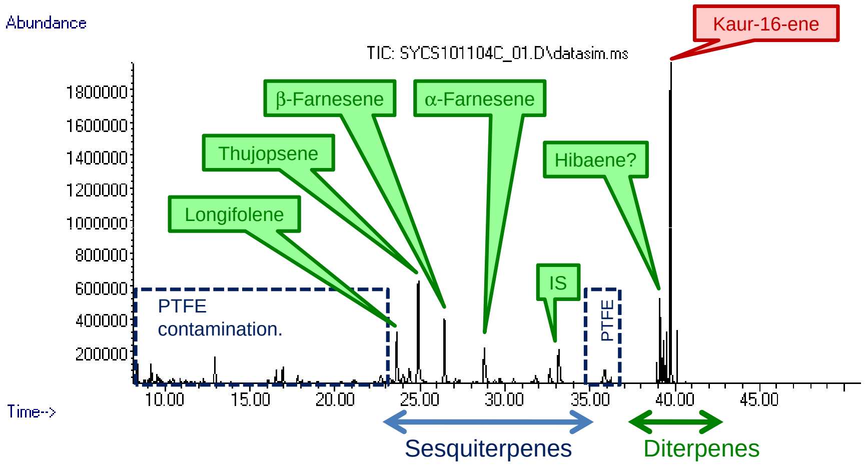

Fig. 2. Typical gas chromatogram of samples collected from *C. japonica*.

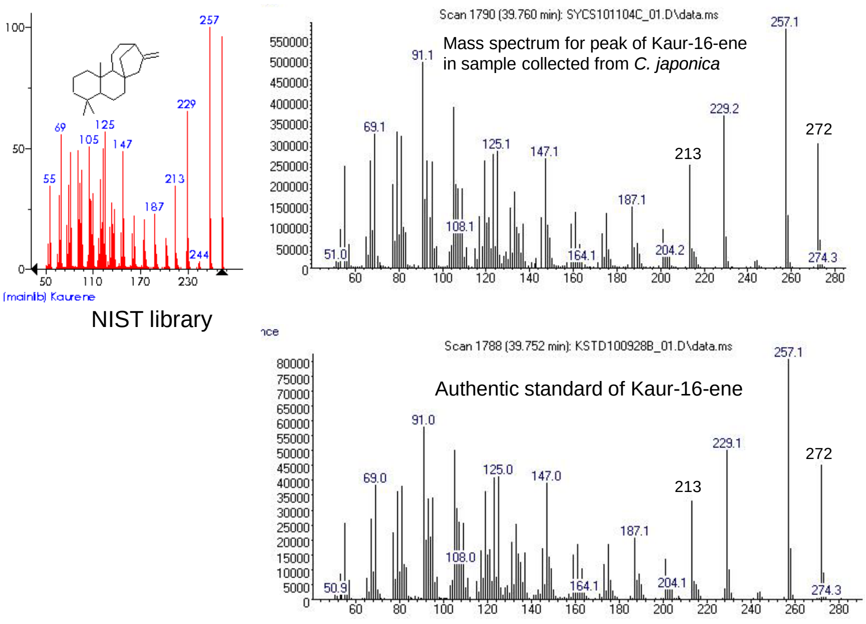

Fig. 3. Structure and typical sample mass spectrum of Kaur-16-ene, analysis of the authentic standard, and NIST library.

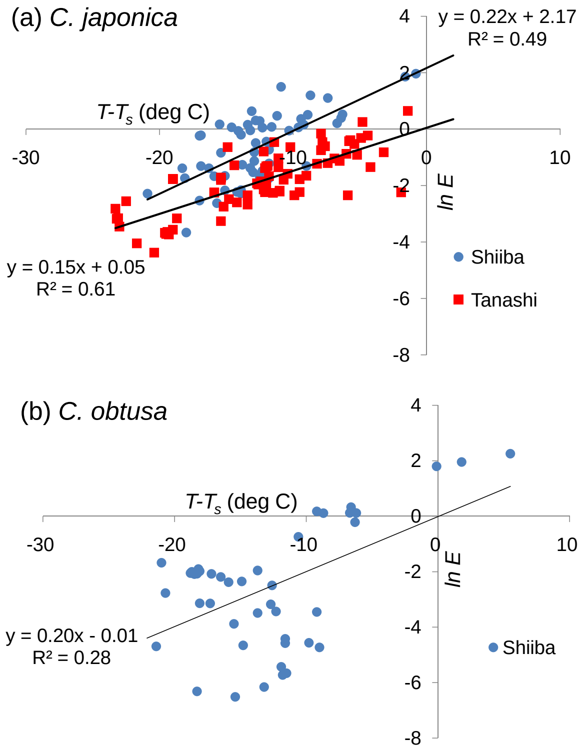

Fig. 4. A liner relationship between the temperature and natural logarithm for the measured emission rate of Kaur-16-ene collected from **(a)** *C. japonica* and **(b)** *C. obtusa* (only for Shiiba).

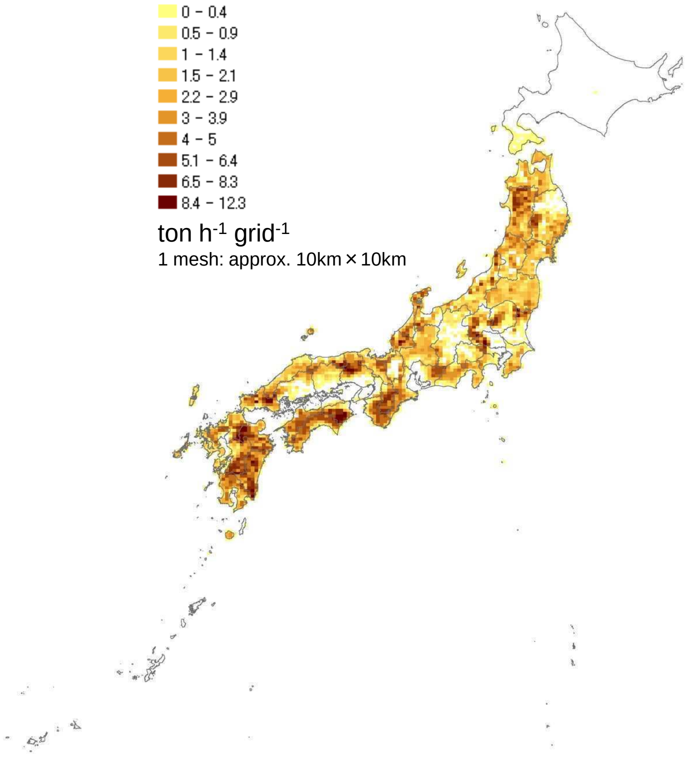

Fig. 5. Estimated emission rate of Kaur-16-ene at 30 °C over Japan.