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Interactive comment on “Volatile diterpene emission from dominant conifers in Japan” by S. N. Matsunaga et al.

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Response to referee #1

p.4 line 1 Reference Hallquist et al.2009 is not listed in “References”.

→ The reference has been added into the list.

p.4 line 7. Although molecular formulas of volatile diterpenes are C₂₀H₃₂, there are many diterpenes which contain oxygen. Therefore, correct the definition of diterpens.

→ According to referee's comment, a sentence “Oxygenated diterpenes, which contains one or more oxygen atoms besides carbon and hydrogen atoms, are also known.” has been added into L10p4.

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p.4. line 16. The aouthor says “ a new analytical technique”. But solid-adsorption ?liquid extraction method is very popular method. It is not newly developed method. Should describe what is new .

→ As the referee mentioned, an analytical technique solid adsorption and liquid extraction itself has been commonly applied for sediment analysis or other environmental samples. However, it has never been applied for an analysis of atmospheric samples, including enclosure samples. One of the reasons is probably majority of the atmospheric scientists have not been interested in high molecular weight compounds which are not likely to evaporate effectively.

“Consequently heavier BVOC may have been neglected by atmospheric scientists. In this study, we focused on heavier BVOC (diterpenes) and applied the solid adsorption - liquid extraction analytical technique (Matsunaga et al., 2011).” have been added at L16p4 to provide background information.

p.7. line 11. Some of monoterpenes such as α -pinene which is quantitatively major compound of volatile plant terpenes are unstable. Also those monoterpenes easily stick to an enclosure bag. The author should confirm if monoterpenes stick to a bag or not.

→ (Stability of the BVOCs) As mentioned by the referee, monoterpenes are generally very reactive in the atmosphere, therefore unstable, in the presence of oxidants such as OH radical, ozone and others. However, the air in the enclosure bag is purified by an activated charcoal trap which also removes the oxidants. Therefore, BVOCs emitted into the inside of the bag was not degraded by oxidants during the sampling.

An additional comment has been added to explain this issue at L12p6: The air inside the bag was ventilated with the air, which does not contain VOCs or oxidants at significant concentrations, at a flow rate of 4-5 liter min⁻¹ to avoid water condensation and excessive temperature increase in the bag (see Figure 1 for an overview). Therefore, contamination and degradation of the target BVOCs can be avoided during the

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sampling."

→ ("Memory effect" of the BVOC on the bag) As the referee pointed out, BVOC may be adsorbed onto the surface of the bag. Especially, heavier BVOCs such as diterpenes may be adsorbed more readily onto the inside of the bag, even if the bag and tubes in the bag are made with inert material such as Teflon. Therefore, we conducted analysis for the "memory effect" and found that the effect is negligible (below the detection limit) in the sampling time of around 1 hour.

Sentences have been added into L18p6: "The adsorption of the diterpene onto the surface inside of the enclosure has been examined by the analysis of air inside the bag immediately after removal of the branch. The amount of diterpene adsorbed onto the surface was found to be around 0.1% of the amount of target compound collected within one hour of sampling time."

Many reports say that usually most major terpenes emitted from tree leaves are α -pinene. However on Figure 2 in the report, α -pinene is missing. It is unusual.

→ As mentioned by the referee, α -Pinene is one of the most common BVOC emissions. However, there are also trees which do not emit α -Pinene. The trees sampled in this study (*C. japonica* and *C. obtusa*) did emit α -Pinene in most samples. The most abundant monoterpene emitted from these trees was Sabinene (please refer Matsunaga et al., 2011 and Mochizuki et al., 2011). Because these two references have already reported on mono- and sesquiterpenes from these species, the authors avoided discussion of these BVOC in this paper. The emission rate of total monoterpene is shown in Table 1.

The chromatogram presented in Figure 2 is obtained by the analysis of the heavier fraction of the emission employing the liquid extraction technique which is not quantitative for monoterpenes (monoterpenes and the heavier BVOCs were collected and prepared separately before the GC analysis). Monoterpenes are also actually visible

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in the chromatogram, however, because those are not quantitative in this fraction due to the loss during concentration process, authors did not mention about monoterpenes in this paper.

Detailed discussions for monoterpenes and sesquiterpenes from *C. japonica* and monoterpenes from *C. obtusa* are described in Matsunaga et al. (2011) and Mochizuki et al. (2011), respectively. *C. obtusa* did not emit sesquiterpenes. Monoterpenes are sampled from the same enclosure technique used in this study and analyzed employing a cryo-focus thermo-desorption technique (different from the technique described in this study).

The authors added typical values of sesquiterpene emission rates to compare with those of Kaur-16-ene into the text in L18p10 for an easy comparison (monoterpene emission rates had been presented in Table 1 in the former form of the manuscript). Sentences have been added at L18p10: "As shown in table 1, the basal emission rate E_s of Kaur-16-ene was significantly higher than those of monoterpenes, a more common BVOC emission, measured from same branches. Sesquiterpenes were detected only from *C. japonica*. The averaged basal emission rate of total sesquiterpenes from *C. japonica* was 2.9 and 7.1 micro g g⁻¹ h⁻¹ at Tanashi and Shiiba, respectively, while that of Kaur-16-ene was determined to be 2.8 and 8.7 micro g g⁻¹ h⁻¹. Therefore, emission of Kaur-16-ene is significant compared to those of mono- and sesquiterpenes which are commonly known BVOC emissions."

p.10. line 16. "did not show any significant difference with light intensity". Should show the data. It is known that emission amounts of volatile terpenes from plants depend on light, temperature.

→ As mentioned by the referee, emission of some terpenoids such as monoterpene may have a light dependence. Terpenoids emission, which have a light dependence, is limited to some species. Mochizuki et al. (2011) reported that monoterpene emission from *C. obtusa* did not show light dependence.

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According to the referee's comment, authors added the basal emission rates of Kaur-16-ene determined at light exposed and shaded branch of *C. japonica* in L14p11.

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The paragraph has been changed to be "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 basal emissions of Kaur-16-ene from *C. japonica* were 2.9 and 2.0 $\mu\text{g g}^{-1} \text{h}^{-1}$ at sun exposed and shaded branches, respectively. Therefore, the light intensity may not be an important factor to control the emission of Kaur-16-ene from *C. japonica*."

And seasonal variation of emission are recognized. As the author says, the production mechanism and process of emission of deiterpenes will be different from mono- and sesquiterpenes.

→ As pointed by the referee, there is an obvious seasonal variation in "raw" emission rate of the Kaur-16-ene. It is driven by variation of temperature over the seasons. Authors mentioned that seasonal variation in basal emission rate, which is a normalized emission rate at a set of standard condition, was not significantly recognized. As shown in Figure 4, the scatter plot of \ln (emission) and T -Ts generated single linear relationship for each of the sites. It suggests that there is only a single basal emission rate, which is the normalized emission rate at the standard temperature of 30°C , for each site. Multiple lines will appear on the plot if there would be multiple basal emission rate, implying that the basal emission rate has a seasonal variation. Please refer Figure 3 in Matsunaga et al., (2011) for example).

Terms "is the normalized emission rate" were added into L10p11 to emphasize definition of the basal emission rate. Because BVOC emission generally depends on temperature, a normalized emission rate for temperature is useful to examine its seasonal variation, which may be caused by physiology of trees, by cancelling effect of temperature on the "raw" emission rate.

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This report is unnatural and insufficient, because only kaur-16-ene was picked up. Although GC spectrum shows sesquiterpenes, and also other diterpenes, the author neglect them. It is also unnatural that monoterpenes were not recognized on GC. It can be presumed that experimental procedure was insufficient. Further detailed experiment is needed to say that emission amount diterpens from tree leaves is larger than mono-and sesquiterpenes.

→ There are three reasons why the authors focused only on Kaur-16-ene:

1. Volatile emission of diterpene has been recognized here for the first time, and its emission rate was found to exceed monoterpenes (more common foliar BVOC emissions).
2. Only Kaur-16-ene was available for its authentic standard and is essential for identification and determination.
3. As well as mono- and sesquiterpenes, Kaur-16-ene can be assumed to be very reactive in the atmosphere and has not been known as atmospheric constituent. Authors wanted to focus on the high emission rate of Kaur-16-ene.

The authors did not neglect mono- and sesquiterpenes. The authors already described about those classes of BVOC and wanted to focus on significant diterpene emission because it is the first discovery.

Please find supplement pdf file for the revised text.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/8/C3063/2011/bgd-8-C3063-2011-supplement.pdf>

Interactive comment on Biogeosciences Discuss., 8, 6681, 2011.

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